



Enhanced photodegradation of pentachlorophenol by single and mixed cationic and nonionic surfactants

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ABSTRACT

The photocatalytic degradation of pentachlorophenol (PCP) using a TiO₂ catalyst in a surfactant-containing system was investigated. PCP abatement by photocatalysis was significantly enhanced by the addition of cationic and nonionic surfactants, both single and mixed, at appropriate concentrations. The enhanced photodegradation can be mainly attributed to the formation of admicelles on the TiO₂ surface. This phenomenon can lead to the incorporation of more PCP, thereby providing TiO₂ with remarkably higher capture rates for target pollutants. Hence, PCP was rendered easily available to photo-yielded oxidative radicals on the catalyst surface. Notably, mixed cationic–nonionic surfactants yielded much higher photodegradation efficiencies than the corresponding single surfactants, indicating the existence of a synergistic effect in the complex system. The adsorption behavior of PCP on TiO₂ in the surfactant solutions was investigated to elucidate this synergism. Fourier-transform infrared (FTIR) spectroscopy was adopted to gain insight into the structural changes induced by the surfactants and a better understanding of the surfactant-assisted photocatalytic degradation mechanism was obtained.

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1. Introduction

Soil and groundwater contamination by hydrophobic organic pollutants is a widespread environmental problem. Surfactant-enhanced remediation has been suggested as a promising technology for abating such contaminants [1]. The application of appropriate amphiphilic molecules can render the washing system more feasible. Nonionic surfactants have often been employed based on their high solubilization capabilities and comparatively low critical micelle concentrations (CMCs) [2]. Ionic (anionic or cationic) surfactants generally exhibit higher CMCs or adsorption onto soil, thus causing lower washing efficiencies [3].

However, a major problem arises after soil washing because the collected surfactant-containing wastes must be properly disposed or treated. In recent decades, heterogeneous photocatalysis, especially photodegradation using TiO₂ as a catalyst, has been proposed as one of the most promising treatments for a wide variety of waste washing processes [4–6]. Heterogeneous photocatalysis can enable both the prior washing and effective degradation of washed pollutants for the remediation of soil and groundwater contamination. The possible application of surfactants coupled with the photodegradation process in complex systems needs to be thoroughly investigated.

The existence of surfactants in a complex system has multiple impacts on the photocatalytic degradation process because many processes can be involved in the system. In a complex system, the surfactants themselves are degraded [7] and may compete with the target pollutants for the active sites in the semiconductor [8], thus inhibiting the degradation of contaminants. On the other hand, the incorporation of hydrophobic solutes into surfactant admicelles on the catalyst surface may provide beneficial kinetic effects [9,10] and enhance the photodegradation of target pollutants. Fabbri et al. [8,11–13] have investigated the effects of surfactants in a soil washing–photodegradation coupled system. Their findings indicate that different surfactants exert various effects on the photodegradation process. The effects can be related to the pollutant hydrophobicity, pH, and surfactant concentration. Generally, the existence of a surfactant can inhibit the photodegradation efficiency mainly because of its competition for an active site on the catalyst. On the other hand, the degradation of some hydrophobic substances can be slightly enhanced with the appropriate type of ions and amount of surfactants. However, the specific mechanism of the complex system remains largely unknown.

The use of mixed surfactants has gained increasing attention in recent years. They exhibit different synergistic/antagonistic effects than the corresponding single surfactants [14] and have potential practical industrial applications [15]. Generally, mixed surfactants show higher cloud points than nonionic surfactants, and lower Krafft points than ionic surfactants. Mixed surfactants also exhibit

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a number of synergistic advantages due to the formation of mixed micelles [16]. The synergistic effect of mixed surfactants with different ionic types show significant impact on the adsorption, surrounding acidity, and surface structure of adsorbents mainly through electrostatic force and hydrogen bonding [17]. However, to the best of our knowledge, the effect of mixed surfactants on photocatalysis for the disposal of complex washing waste systems has been accorded little attention.

The current work investigated the specific mechanism of the effect of surfactants (single or mixed) on the photocatalytic degradation of hydrophobic organic pollutants in a simulated system containing the targeted pollutant and different type of surfactants. The purpose was to enhance the efficiency of photocatalytic decomposition for soil washing waste using the appropriate type and quantity of surfactants. Pentachlorophenol (PCP), a typical hazardous pollutant listed as a priority contaminant, was selected as the model hydrophobic pollutant in our simulated complex system. The investigation focused not only on PCP removal but also on the interactional mechanisms of the catalyst/PCP/surfactant complex system. Fourier-transform infrared (FTIR) spectroscopy was adopted to gain insight into the microstructure of surfactants adsorbed on TiO₂.

2. Materials and methods

2.1. Materials

4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol (TX100), a nonionic surfactant with a CMC of about 120 mg L⁻¹ (0.20 mM) [18], was supplied by Pharmacia. 1-Hexadecylpyridinium bromide (HDPB), a cationic surfactant with a CMC value of about 273.6 mg L⁻¹ (0.68 mM), was purchased from Alfa Aesar. PCP was purchased from Dima (USA). Commercial P25 TiO₂ (80% anatase and 20% rutile) supplied by Degussa Corporation (Germany) was employed in all photodegradation experiments. The Brunauer–Emmett–Teller specific surface area of P25 TiO₂ was 54.77 m² g⁻¹, as calculated from its nitrogen adsorption–desorption isotherm obtained using a Quantachrome gas adsorption instrument (Autosorb AS-1 N2). The samples were degassed for 4 h at 300 °C before measurements. The two surfactants, PCP and P25, were used as received.

2.2. Photocatalytic degradation

An aqueous PCP stock solution (7.50 mM) was prepared with methanol and stored below 5 °C. In all photodegradation experiments, the same initial PCP concentration (0.075 mM) was adopted, and the methanol concentration was strictly maintained at 1% because it is a hydroxyl radical scavenger [19]. Methanol is believed to affect the pattern of PCP degradation to similar extents in all experiments, but not the pattern of PCP degradation kinetics or the adsorption of PCP onto TiO₂ at methanol contents less than 2% [20].

The degradation experiments were carried out in a vigorously stirred batch reactor containing 500 mL of PCP solution and 100 mg of P25 catalyst. The reactor was equipped with a high-pressure mercury lamp (300 W), and the temperature was maintained at 25 °C. The photocatalytic degradation experiments were performed both in a simple target PCP aqueous system and in the presence of simple or mixed surfactants. The TX100 concentration varied between 0 and 0.40 mM, and the HDPB concentration varied between 0 and 0.025 mM. Before irradiation, the suspension was stirred in the dark for 30 min to obtain adsorption–desorption equilibrium. At definite time intervals, an appropriate aliquot of the suspension was collected, and the concentrations of PCP and surfactants were

determined. All data shown were the means of two replicates with a deviation of within ±5%.

2.3. Surface tension measurements

The CMC and effective CMC (CMC_{eff}) of the TX100-containing systems (pure TX100 and mixed HDPB/TX100 solutions) were measured according to the Wilhelmy plate method using an interfacial tensiometer (Tensiometer K14 Krüss, Germany). The measurements were performed in the absence and presence of P25 TiO₂ after 1.5 h of adsorption. The mean value of five measurements set at 25 °C was accepted as the result.

2.4. Adsorption experiments

Batch adsorption experiments were conducted to examine the adsorption kinetics and characteristics of the target pollutant, as well as the effect of single or mixed surfactants on the adsorption in the complex system. In the adsorption experiments, 100 mg of P25 TiO₂ was added to a 500 mL brown flask containing a complex solution with 0.075 mM PCP and surfactants (single or mixed) of different contents. The flasks were allowed to reach equilibrium at 25 ± 1 °C in a reciprocating shaker at 150 rpm for 1.5 h, which has been proven sufficient [21]. An appropriate aliquot of the suspension was manually sampled at definite time intervals for the PCP and surfactant tests. The adsorption amount of P25 for PCP and surfactants was calculated based on the analyte concentration difference before and after the adsorption process.

2.5. Analytical determination

To examine the degradation and adsorption process, about 3 mL of each mixture was collected at definite time intervals. To recover quantitatively the analytes adsorbed on P25, an equal volume of methanol was added to the suspension sample, which was then adequately shaken. The processed suspension was filtered through a 0.45 μm-pore size membrane filter. The PCP, TX100, and HDPB contents were determined using high-performance liquid chromatography (Agilent 1260) fitted with an ultraviolet (UV) detector and an Agilent TC-C18 column (4.5 mm × 250 mm; 5 μm). The UV wavelengths were set at 249 nm for PCP, 254 nm for HDPB, and 280 nm for TX100. Total organic carbon (TOC) was tested with samples of different time interval using a Shimadzu TOC-V_{CPH} device, data shown were the means of two replicates with a deviation of within ±5%.

2.6. FTIR spectroscopy analysis

The surfactant-modified P25 samples obtained from the adsorption experiments mentioned in Section 2.4 were filtered and dried at 60 °C in darkness for FTIR spectroscopy analysis to characterize the structural conformation of adsorbed surfactants (single and mixed) onto TiO₂. FTIR spectra were obtained using a spectrometer (Spectrum GX, PerkinElmer, USA) within the 4000–400 cm⁻¹ region at a 4 cm⁻¹ resolution. About 2 mg of the milled sample was ground with 200 mg of KBr (FTIR grade) and compressed into a pellet under a vacuum at a pressure of 75 kN cm⁻² for 3 min. A total of 32 scans were performed, averaged for each spectrum, and corrected against air as a background on each acquisition. To illustrate the emerging peaks, the spectra were subjected to a Savitsky–Golay second derivative (using a third-order polynomial and seven-point smoothing) [22].

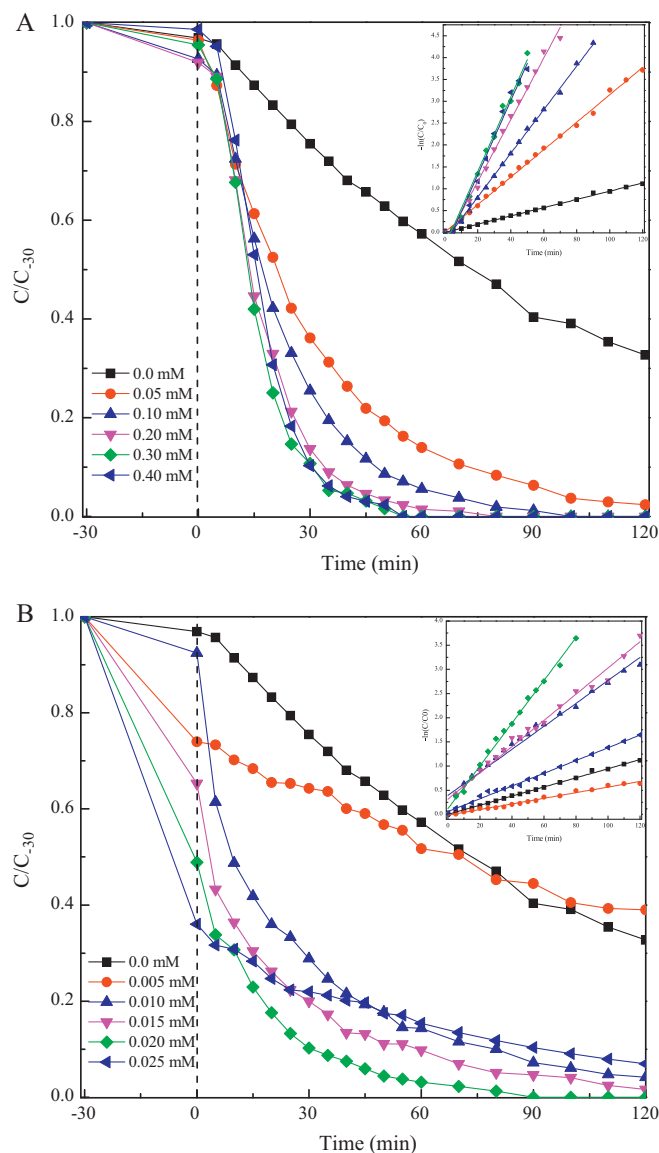


Fig. 1. Photodegradation of PCP with P25 TiO₂ catalyst under different TX100 (A) and HDPB (B) concentrations, and first-order fitting curves (inset).

3. Results and discussion

3.1. Effect of surfactants on the PCP photodegradation kinetics

3.1.1. Effect of single surfactants on PCP degradation

The photocatalytic degradation of PCP in aqueous TiO₂ dispersions containing single surfactants, TX100 or HDPB, was initially investigated. The concentrations of TX100 were set at higher and lower levels than its CMC, whereas the concentrations of HDPB were much lower as predetermined by previous trials. The photodegradation of PCP with P25 under different TX100 and HDPB concentrations are shown in Fig. 1(A) and (B), the portion –30 to 0 min referred to the 30 min of dark adsorption. Within 120 min of UV irradiation, 67.3% PCP was degraded using P25 alone. Fig. 1(A) shows that TX100 addition greatly enhanced PCP photodegradation. Within the region of 0–0.30 mM, the degradation efficiency increased with the increase of TX100 concentration, however, with TX100 higher than 0.30 mM, slight abatement of PCP degradation can be seen. Within 120 min of irradiation, complete degradation of PCP occurred in all tested batches with TX100 concentration higher than 0.05 mM.

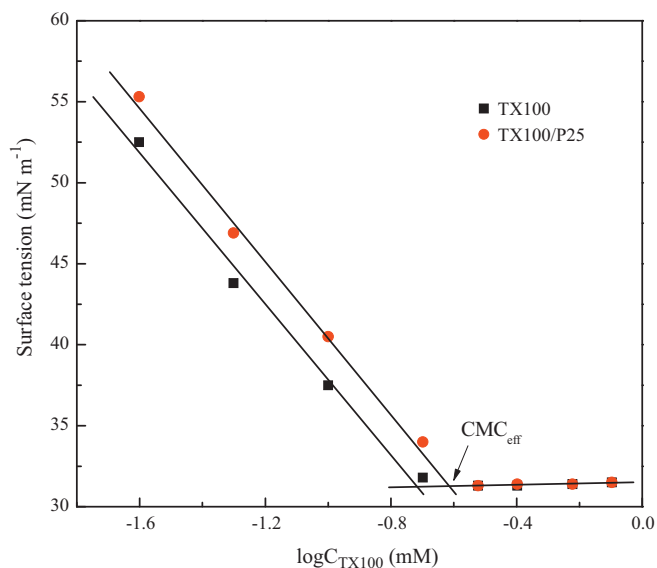


Fig. 2. Variations in the surface tension as a function of the logarithm of the TX100 concentration at 25 °C in the absence and presence of P25 TiO₂.

The degradation curves were fitted to the pseudo-first-order kinetic law described by the following equation:

$$-\ln\left(\frac{C}{C_0}\right) = kt \quad (1)$$

The first-order rate constants k_{TX100} for the initial reaction under UV irradiation with different TX100 concentrations are shown in Table 1. All degradation curves were well fitted by Eq. (1), with all R^2 values ≥ 0.979 . TX100 addition significantly increased k_{TX100} for PCP degradation. The decomposition rate of PCP in a complex system at 0.30 mM C_{TX100} was higher by a factor of 9.33 than that without TX100.

To explain the above mentioned effects on the investigated substrates, both processes occurring in the bulk solution and at the TiO₂–solution interface had to be carefully analyzed. The adsorption of surfactant molecules onto TiO₂ particles must be in particular considered because the surfactant-assisted photodegradation can be mainly attributed to the incorporation of solutes into admicelles formed on the TiO₂ surface [9]. In an aqueous solution, the minimum surfactant concentration at which surfactant monomers start aggregating to form micelles is the CMC. For a solid–aqueous solution, the surfactant dose required for micelle formation is greater due to surfactant partitioning onto solid particles. This higher surfactant dose is referred to as the CMC_{eff} . Fig. 2 shows the variations in the surface tension of TX100 containing systems with and without TiO₂. The CMC of the TX100 solution was 0.20 mM, and the CMC_{eff} of TX100/TiO₂ was 0.24 mM. The discrepancy between these two values can be attributed to the adsorption of surfactant molecules onto TiO₂. At sub-CMC concentration, TX100 in the bulk solution and solid–water interface existed in monomeric form. The monolayer or bilayer of adsorbed admicelles formed on the solid surface via ion–dipole interaction or hydrogen bonding. Adsorbed surfactants can be very effective for PCP partitioning [23]; hence, increased solute partitioning on the TiO₂ surface resulted in more opportunities for PCP to occupy the active sites of the semiconductor surface. Consequently, the degradation efficiency increased [24]. With increased TX100 concentration, the adsorbed amount of surfactant molecules increased and more PCP can be photodegraded. However, with further increased TX100 concentration to higher levels than its CMC_{eff} , self-assembled micelles can compete with adsorbed surfactants to solubilize PCP into a bulk solution, thereby decreasing the degradation efficiency.

Table 1Apparent first-order rate constant k (min^{-1}) values for the photocatalytic degradation of PCP in the presence of surfactants ($R^2 \geq 0.979$).

Sample	k_{TX100}	Sample	k_{HDPB}	Sample	k_{mixed}
P25	0.9×10^{-2}			TX100/HDPB (0.0 mM)	5.0×10^{-2}
TX100 (0.05 mM)	3.1×10^{-2}	HDPB (0.005 mM)	0.6×10^{-2}	TX100/HDPB (0.005 mM)	9.4×10^{-2}
TX100 (0.10 mM)	5.0×10^{-2}	HDPB (0.010 mM)	2.4×10^{-2}	TX100/HDPB (0.010 mM)	8.1×10^{-2}
TX100 (0.20 mM)	7.1×10^{-2}	HDPB (0.015 mM)	2.7×10^{-2}	TX100/HDPB (0.015 mM)	7.8×10^{-2}
TX100 (0.30 mM)	8.5×10^{-2}	HDPB (0.020 mM)	4.4×10^{-2}	TX100/HDPB (0.020 mM)	7.1×10^{-2}
TX100 (0.40 mM)	8.4×10^{-2}	HDPB (0.025 mM)	1.3×10^{-2}	TX100/HDPB (0.025 mM)	7.6×10^{-2}

Similar results were obtained for the HDPB group, as shown in Fig. 1 (B). HDPB significantly enhanced PCP photodegradation at very low HDPB concentrations (0.005 mM to 0.025 mM) compared with TX100. PCP decomposition increased with increased HDPB concentration, with the highest rate corresponding to 0.020 mM HDPB. k_{HDPB} obtained from the pseudo-first-order kinetic law was 4.89 times higher than that of P25 (Table 1). However, with the lowest HDPB concentration (0.005 mM), k_{HDPB} was slightly lower than k_{P25} . This finding can probably be ascribed to the competition of low-concentration surfactants with PCP for adsorption sites on the adsorbent surface.

The adsorption of HDPB molecules onto TiO_2 differed from that by TX100. Within the pH range of the degradation experiments (7.6 ± 0.3), the TiO_2 surface was negatively charged. The cationic surfactants were adsorbed onto TiO_2 due to electrostatic interactions. Electrostatic interactions are often stronger than hydrogen bonding, which was the main force of TX100 adsorption, hence, giving HDPB generally greater adsorption than TX100 [25]. Adsorption of PCP is mainly driven by its partitioning into surfactant layers on TiO_2 surface, giving PCP quite high adsorption at even very low HDPB concentrations.

3.1.2. Effect of mixed surfactants on PCP degradation

Mixtures of different ionic surfactants exhibit various properties compared with the corresponding single surfactants, and often cause synergistic/antagonistic effects in both liquid and solid–liquid systems [3,14,25]. For better understanding of the degradation pattern of hydrophobic organic pollutants in surfactant-containing systems, the effects of binary surfactant mixtures on PCP photodegradation were investigated. The TX100 concentration in the degradation experiments was fixed at 0.10 mM, with the C_{HDPB} range of 0.0–0.025 mM. Fig. 3 shows that the addition of a cationic surfactant significantly enhanced PCP photodegradation, the portion –30 to 0 min referred to the 30 min of dark adsorption. Complete PCP decomposition was observed in all HDPB groups within 60 min of irradiation.

The degradation curves were also fitted by the pseudo-first-order kinetic law using Eq. (1), and the first-order rate constants k_{mixed} for the initial reaction are recorded in Table 1. With the addition of HDPB, the corresponding k_{mixed} values were much higher than in the TX100-only group. The highest k_{mixed} was achieved with the TX100/HDPB 0.005 mM mixed solution, wherein the PCP decomposition rate was higher by a factor of 1.88 than that without HDPB. This phenomenon was notably different from the HDPB-only groups, wherein 0.005 mM cationic surfactant showed the lowest decomposition rate. However, further increased HDPB concentration slightly decreased k_{mixed} .

To gain a better understanding of the binary surfactant mixture-assisted PCP photodegradation, the adsorption patterns of the surfactants were examined via the variations in the surface tension of the mixed systems with and without TiO_2 . The concentration of HDPB was fixed at 0.005 mM. Fig. 4 reveals that the CMC for the HDPB/TX100 solution system was 0.19 mM, slightly lower than for the TX100-only solution (0.20 mM). This effect can be mainly ascribed to the non-ideal mixing effects in mixed surfactant aggregates, which are due to the insertion of head groups between

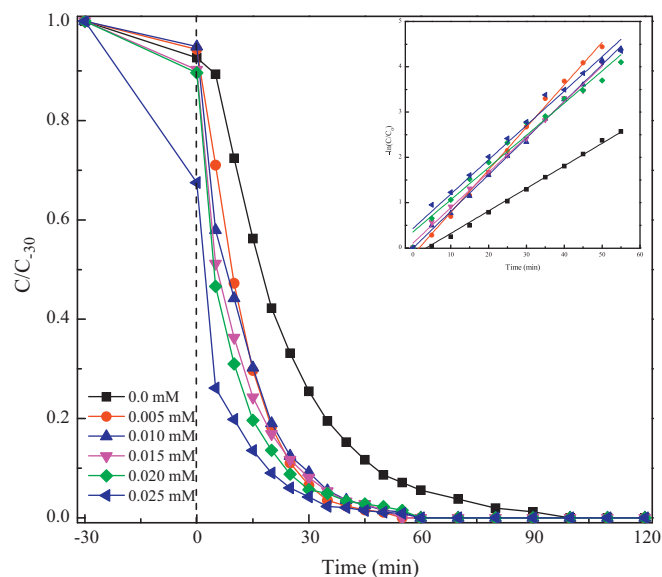


Fig. 3. Photodegradation of PCP with P25 TiO_2 catalyst under different mixed TX100/HDPB surfactant concentrations and first-order fitting curves (inset).

different surfactants [14]. These non-ideal mixing effects reduce the electrostatic repulsion between cationic surfactant head groups, resulting in a substantially lower CMC value than with individual surfactants [26]. In the presence of TiO_2 , CMC_{eff} in the solid–liquid system increased to 0.27 mM, which is much higher than that of TX100/ TiO_2 (0.24 mM). This finding showed that the addition of

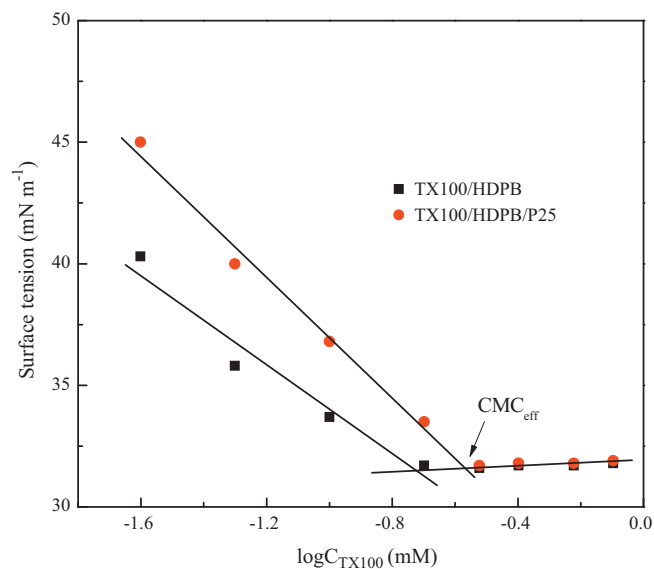


Fig. 4. Variations in the surface tension of mixed surfactants as a function of the logarithm of the TX100 concentration at 25 °C in the absence and presence of P25 TiO_2 .

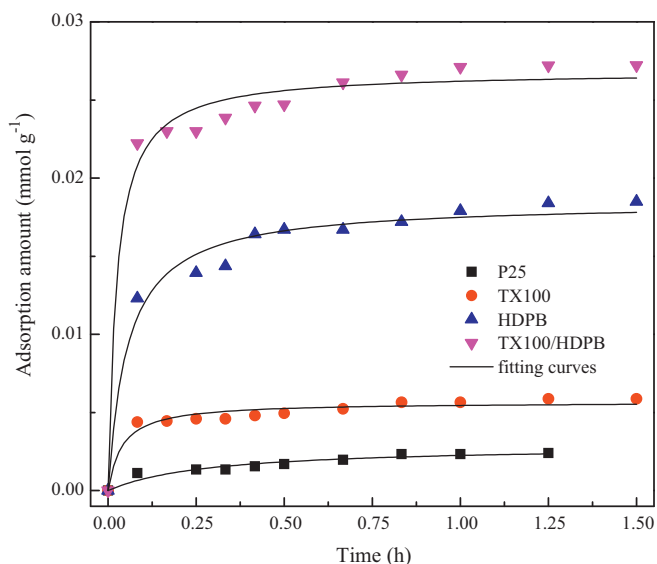


Fig. 5. Effects of surfactants (single or mixed) on the adsorption kinetics of PCP onto P25 TiO₂ catalyst by pseudo-second-order fitting.

HDPB increased the adsorption of the mixed surfactants onto the TiO₂ surface. However, with increased C_{HDPB} , the higher number of HDPB molecules in the bulk solution enabled the easier formation of mixed micelles that did not adsorb onto TiO₂, but competed with admicelles for PCP. Hence, PCP photodegradation decreased. Total organic carbon (TOC) of the P25-PCP samples were tested (data were shown in Supplementary material Fig. S-1). With 120 min of irradiation, 42.1% mineralization of PCP was achieved, lower than the decomposition of PCP (67.3%). The mineralization rate was slower than the degradation rate of PCP, suggesting that the dechlorination was stepwise, and the dechlorinated intermediates were subsequently oxidized to open up the aromatic ring [27]. However, after 2 h of irradiation, the decreasing tendency of TOC can clearly be seen. The continuous decrease of TOC was due to the decomposition of small molecule acid such as formic acid and acetic acid.

3.2. Effect of surfactants on PCP adsorption

The adsorption kinetics of PCP on the catalyst with different types of surfactants added (TX100, HDPB, are TX100/HDPB) is shown in Fig. 5. The initial concentrations of TX100 and HDPB were fixed at 0.10 and 0.005 mM, respectively. The pseudo-second-order model was adopted to fit the adsorption kinetics data. The model assumed that the adsorption rate was controlled by the chemical sorption, and that the sorption capacity was proportional to the number of active sites on the sorbent [28]. This model was expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k \times q_e^2} + \frac{t}{q_e} = \frac{t}{v_0} + \frac{t}{q_e} \quad (2)$$

where v_0 is the initial adsorption rate ($\text{mM g}^{-1} \text{h}^{-1}$), q_e and q_t are the amounts of PCP adsorbed on the catalyst at equilibrium and time t (mM g^{-1}), and k is the adsorption rate constant ($\text{g mM}^{-1} \text{h}^{-1}$).

Fig. 5 and Table 2 show that the adsorption data for PCP well fitted the pseudo-second-order model over the entire adsorption time, implying that chemical interactions were involved in the adsorption processes [29]. The adsorption equilibrium was quickly achieved within 0.5 h. As shown from the equilibrium adsorption amount of PCP (q_e) and initial sorption rate (v_0), the adsorption capacity of P25 TiO₂ for PCP was substantially elevated with the aid of a surfactant. The initial adsorption rates

Table 2
Kinetic parameters of the pseudo-second-order model of PCP adsorption.

Sample	Pseudo-second-order parameters			
	q_e (mM g^{-1})	v_0 ($\text{mM g}^{-1} \text{h}^{-1}$)	k ($\text{g mM}^{-1} \text{h}^{-1}$)	R^2
P25	0.0029	0.0102	1210.5	0.914
TX100	0.0057	0.1450	4508.4	0.951
HDPB	0.0195	0.2670	703.6	0.974
TX100/HDPB	0.0278	0.8754	1131.1	0.983

of PCP onto TiO₂ in TX100 and HDPB solutions were 0.1450 and 0.2670 $\text{mM g}^{-1} \text{h}^{-1}$, respectively, whereas this value for P25 was 0.0102 $\text{mM g}^{-1} \text{h}^{-1}$. This finding indicated that the surfactant molecules greatly enhanced the adsorption of PCP on the adsorbent surface. Noticeably, the mixture of TX100/HDPB in the solid-liquid system yielded a 0.8754 $\text{mM g}^{-1} \text{h}^{-1}$ initial adsorption rate of PCP onto TiO₂, which was much higher than those of the corresponding single surfactants. The equilibrium adsorption amount also reached 0.0278 mM g^{-1} . This phenomenon can only be ascribed to the synergistic effect of the binary mixed surfactant system.

Adsorbed surfactant molecules can be more effective adsorbents for hydrophobic organic compounds (HOCs) [30]. The distribution of HOCs in solid-liquid systems is mainly controlled by their partitioning into organic matter. A higher surfactant adsorption results in a higher TiO₂ organic content, and consequently, a higher distribution coefficient for PCP on its surface. In solid-liquid systems, factors such as electrostatic attractions, covalent bonding, hydrogen bonding, and non-polar interactions between the adsorbent and adsorbed species have been considered to contribute to the adsorption of surfactants [31]. HDPB has a positively charged head group, and a TiO₂ surface is negatively charged. HDPB can be adsorbed via electrostatic attraction; thus, pre-adsorbed HDPB molecules can serve as anchors for further TX100 adsorption via hydrophobic chain-chain reactions, forming mixed aggregates [32]. During this process, TX100 shields the electrostatic repulsion between HDPB head groups, forming a more stable admicelle on the TiO₂ surface. By this synergistic effect, the adsorption amount of surfactants can be increased, thus enhancing the partitioning of PCP into the formed admicelle and promoting its photodegradation.

3.3. FTIR spectra

The FTIR spectra and their second derivatives at the wavenumber range of 3500 cm^{-1} to 2000 cm^{-1} of the original P25 TiO₂, TX100-P25, HDPB-P25, and TX100/HDPB-P25 are shown in Fig. 6. The concentrations were fixed at 0.10 mM for TX100 and 0.005 mM for HDPB, as decided by the above described performance of surfactant-assisted photodegradation. The FTIR spectra in Fig. 6(A) reveal a peak at around 3406 cm^{-1} due to the stretching vibration of $\nu(\text{O-H})$ lattice water [33], and a band at 1631 cm^{-1} assigned to H-O-H bending $\delta(\text{H-O-H})$ [33]. The $\text{CH}_3\text{-N}^+$ vibration (1490 cm^{-1}) can be attributed to the replacement of metallic cations by HDPB [34]. The absorption peak at 1385 cm^{-1} was due to $\delta(\text{R-CH}_3)$ [35].

The bands at around 2920 and 2850 cm^{-1} corresponded to the asymmetric and symmetric stretching frequencies of the CH₂ of the hydrocarbon tails of the surfactants, respectively. The changes in these bands can be used to characterize the adsorption of surfactants. These bands were found to be a function of the micelle composition, namely, the *gauche/trans* conformer ratio [35]. The increased "ordering" of the alkyl chains was characterized by decreased frequencies of the CH₂ stretching bands. As shown in Fig. 6(A1) and (B), the TX100-P25 bands (2920 and 2850 cm^{-1}) shifted to lower frequencies in the TX100/HDPB-P25 case (2911

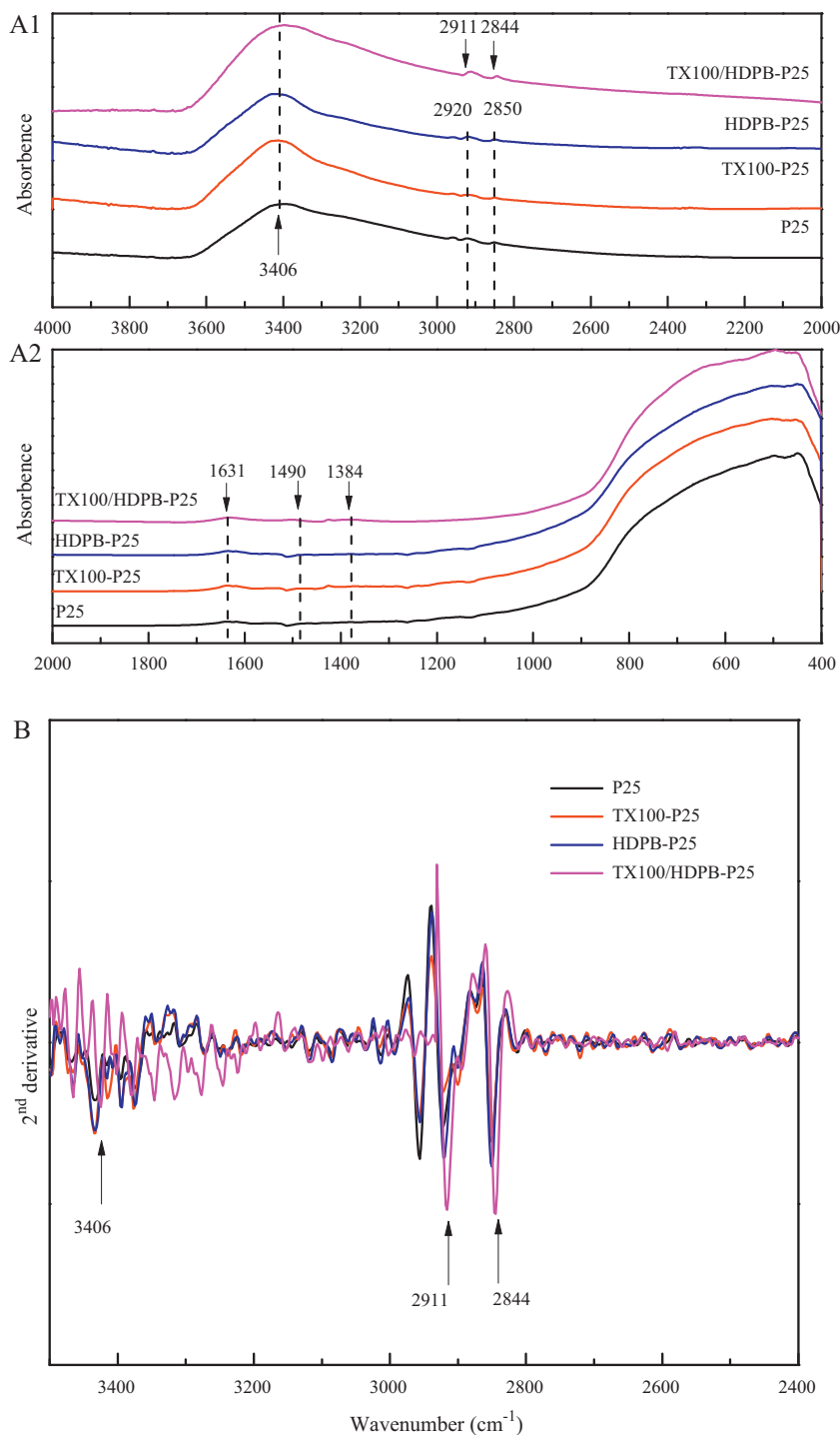


Fig. 6. FTIR spectra (A) and their second derivatives (B) of the surfactants adsorbed onto P25 TiO_2 .

and 2844 cm^{-1}). This finding showed that the mixed surfactant admicelle had a comparatively more “ordered” and compact structure. This structure corresponded to the fact that more surfactants can be adsorbed in the mixed system because the more compact structure endows TiO_2 with a higher surface adsorption capability than the loose structure in the single-surfactant systems. The lower frequencies revealed that the *trans* conformation of the admicelle aggregates can be ascribed to non-ideal mixing, with the shielding effect of TX100 between HDPB head groups inducing decreased electrostatic repulsive interactions on the TiO_2 surface.

3.4. Proposed mechanism of the surfactant-assisted PCP photodegradation

Based on the above results, a schematic diagram for the adsorption of PCP onto the TiO_2 surface in a single or mixed surfactant system is proposed in Fig. 7. In the TX100– TiO_2 system shown in Fig. 7(A), the TX100 molecules mainly adsorbed onto the TiO_2 surface via hydrogen bonding, which enhanced the adsorption of PCP. However, at a higher concentration than its CMC_{eff} in the system, TX100 tended to self-assemble into micelles that solubilized PCP

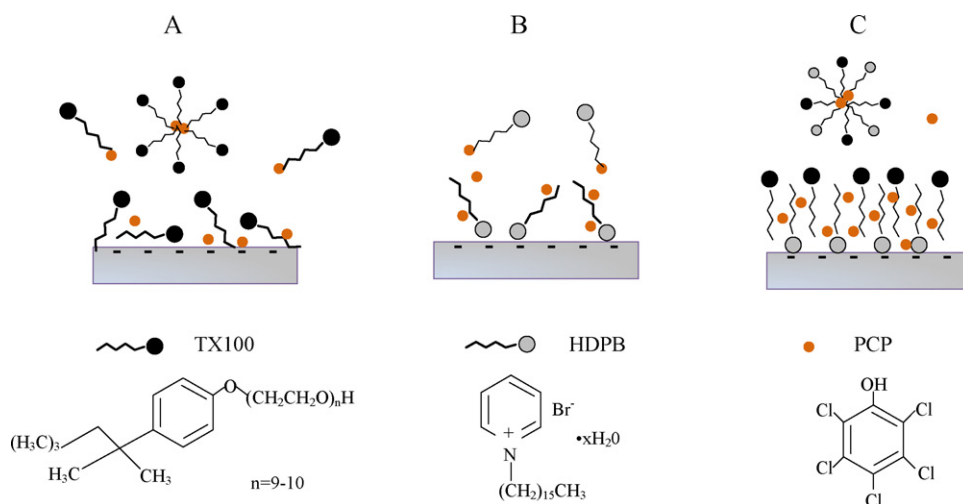


Fig. 7. Proposed mechanism of the enhanced adsorption of PCP onto TiO_2 surface in (A) TX100, (B) HDPB, and (C) mixed TX100/HDPB systems.

into its hydrophobic core, thus competing with the admicelles on the TiO_2 surface. Consequently, PCP adsorption on solid particles decreased. The diagram of the HDPB– TiO_2 system in Fig. 7(B) shows that cationic molecules adsorbed onto TiO_2 via electrostatic interactions, and greatly enhanced the adsorption of PCP even with a low HDPB concentration. In the mixed system shown in Fig. 7(C), a synergistic effect existed between HDPB and TX100, thus forming mixed admicelles on the TiO_2 surface and mixed micelles in the bulk solution. With a higher amount of adsorbed surfactants, more PCP molecules were incorporated into the mixed aggregates, thereby enhancing PCP photodegradation.

4. Conclusions

The effects of single and mixed surfactants on the efficiency of PCP photodegradation were investigated. The adsorption of PCP onto TiO_2 catalyst was also examined. The addition of surfactants (single and mixed) significantly enhanced the photodegradation process, but different surfactants showed various degradation-assisting patterns. The enhancement of PCP degradation by TiO_2 can be mainly attributed to the increased adsorption of solutes in the surfactant admicelle onto the solid surface. A higher amount of adsorbed surfactants and a higher stability of surfactant admicelles resulted in a higher organic content on the adsorbent. Consequently, more PCP molecules were incorporated into the admicelle via partitioning, providing more opportunities to occupy the active sites on the TiO_2 surface.

Overall, the results of this study can contribute to the further utilization of TiO_2 catalyst in the photodegradation of a complex system containing hydrophobic organic pollutants and surfactants (single or mixed).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.04.005>.

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