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# THE INFLUENCE OF pH AND CADMIUM SULFIDE ON THE PHOTOCATALYTIC DEGRADATION OF 2-CHLOROPHENOL IN TITANIUM DIOXIDE SUSPENSIONS

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**Abstract**—The influence of pH and cadmium sulfide on the photocatalytic degradation of 2-chlorophenol (2-CP) in titanium dioxide suspensions was investigated to evaluate the feasibility of mixed semiconductors on the photodegradation of chlorinated organics in aqueous solution. Apparent first-order rate constants ($k_{obs}$) and initial rate constants were used to evaluate the degradation efficiency of 2-CP. Higher degradation efficiency of 2-CP was observed at higher pH values. The apparent pseudo-first-order rate constant was $0.036\,min^{-1}$ at pH 12.5 in $TiO_2$/UV system, while a 2- to 9-fold decrease in $k_{obs}$ was observed over the pH range of 2.5–9.5. The addition of phosphate buffer solutions at different pH values have different effects on the degradation of 2-CP. $H_2PO_4^-$ has little effect on the photodegradation of 2-CP, while $HPO_4^{2-}$ could inhibit the photodegradation efficiency of 2-CP. Chlorocatechol, hydroquinone, benzoquinone and phenol were identified as the predominant aromatic intermediates for the photocatalytic degradation of 2-CP. Moreover, less aromatic intermediates at higher pH were observed. Direct oxidation contributed significantly to the photodegradation of 2-CP. An addition of a semiconductor decreased the initial and apparent first-order rate constants of 2-CP. The cutoff of wavelength of 320 nm could diminish the contribution of direct photolysis of 2-CP. The combination of cadmium sulfide and titanium dioxide can lead to an enhanced rate of disappearance of 2-CP compared to those in single semiconductor system. A 1.2 to 2.5-fold increase in rate constant in coupled semiconductor system relative to the single semiconductor system was obtained. © 2001 Elsevier Science Ltd. All rights reserved

*Key words*—photodegradation, 2-chlorophenol, coupled semiconductor system, apparent first-order rate constant

## INTRODUCTION

The presence of chlorinated compounds in aquatic environments has caused severe environmental pollution problems. Monochlorophenols, such as 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP), constitute an important category of water pollution. Their toxicity to mammalian and aquatic life is classified as moderate, but they have strong organoleptic effects and their taste threshold is 0.1 ppb. Their presence in water is principally from industries, which produce as chemical intermediates or generate during the chlorination of effluents containing phenolic compounds.

Photocatalytic degradation has proven to be a promising technology for degrading refractory chlorinated aromatics (Calza *et al.*, 1997; Schmelling *et al.*, 1997; Chu, 1999; Davis and Green, 1999; Topalov *et al.*, 1999). The primary mechanism of photodegradation is the generation of hydroxyl radicals obtained by the reaction of holes with surface hydroxyls or water and their attachment to organic compounds. The semiconductor which has attracted most attention for sensitizing the photodegradation of organic compounds is titanium dioxide ($TiO_2$). Research has demonstrated that $TiO_2$ can form electron–hole pairs under the illumination of near-UV light, which encompasses energies higher than the corresponding band gap (Fox and Dulay, 1993; Hoffmann *et al.*, 1995). However, the recombination of electrons and holes hampers the photocatalytic reaction process. Recently, researches have demonstrated that the addition of heavy metals, such as platinum (Pt), palladium (Pd), gold (Au) and other semiconductors can enhance the degradation efficiency of photocatalytic reactions (Mills *et al.*, 1993a, b; Hirano *et al.*, 1997; Chen *et al.*, 1999; Wilke and Breuer, 1999). The enhancement of

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photodegradation efficiency by the addition of metal powders may be attributed to the rapid transfer of the photogenerated electrons from the semiconductors to the metal particles, resulting in the effective separation of the electrons and holes. Hoffmann et al. (1995) depicted that doping with $Fe^{3+}$, $Mo^{5+}$, $Ru^{3+}$, $Os^{3+}$, $Re^{5+}$ and $Rh^{3+}$ at 0.1–0.5% significantly increased the photoreactivity for both oxidation and reduction reactions, while $Co^{3+}$ and $Al^{3+}$ doping decreased the photoreactivity.

Moreover, coupled semiconductor systems, in which illumination of one of the semiconductors produces a response in the other semiconductor, have shown to be an effective technology for promoting the degradation of organic compounds (Linsebigler et al., 1995; Serpone et al., 1995; Mills and Le Hunte, 1997). Serpone et al. (1995) showed that combinations of semiconductors, such as $CdS/TiO_2$, $ZnO/TiO_2$ and $ZnO/Fe_2O_3$, had good efficiency and then proposed interparticle electron transfer (IPET) pathway to explain the behavior of electron transfer. This coupling of two semiconductors possessing different redox energy levels for their corresponding conduction and valence bands provides an attractive approach to achieve more efficient charge separation. This will increase the lifetime of the charge carrier and enhance the efficiency of the interfacial charge transfer to adsorbed substrate. However, the photocatalytic characteristics of coupled systems have received less attention. Since the efficiency of photocatalytic degradation is dependent on the environmental parameters, the comparison of the effect of the environmental conditions between the single and coupled systems still remains in demand.

The pH of the aqueous solution is one of the important environmental parameters significantly influences the physicochemical properties of semiconductors, including the charge on particle, the aggregation numbers of particles, and the position of the conduction and valence bands. Schmelling et al. (1997) depicted that a change in pH causes a shift in Fermi level of the semiconductor so that the photocatalyst becomes a better oxidant with decreasing pH. However, the surface of titanium dioxide carries a net negative charge under alkali condition, and then increases the degradation rates of some pollutants. Mills et al. (1993a,b) showed that the rate of photocatalysis is not usually found to be strongly dependent upon pH value. Higher reaction rates for various $TiO_2$-sensitized photomineralizations have been reported at both low and high pH values. Therefore, the effect of pH value should be considered when assessing the photocatalytic degradation reaction.

The objective of this study is to investigate the effect of pH and cadmium sulfide on the photocatalytic degradation of chlorophenols in $TiO_2$ systems. 2-CP was selected as the target compound because it is one of the most frequent found priority pollutants in wastewater. Cadmium sulfide (CdS) was selected due to that the band gap of cadmium is 2.5 eV and the potential levels of valence and conduction bands of CdS are higher than those of $TiO_2$. Therefore, it is easy to undergo IPET pathway with the illumination of UV–visible light. An apparent first-order rate constant and an initial rate constant were used to describe the degradation behavior of 2-CP under different conditions. In addition, the effects of type and dose of semiconductors and wavelength were evaluated to elucidate the enhanced effect of coupled system on the photodegradation of 2-CP. Moreover, intermediates produced from the photodegradation of 2-CP were also identified.

## METHODS AND MATERIALS

### Chemicals and reagents

2-CP (99.0%) was obtained from Riedel-de Haen Co. (Sleeze, Germany). Titanium dioxide ($TiO_2$) was purchased from High Purity Chemicals (Japan). Cadmium sulfide (CdS) (99.9%, 325 mesh) was obtained from Prochem Inc. (Rockford, IL, USA). Chlorocatechol and hydroquinone were obtained from TCI Co. (Tokyo, Japan). Acetonitrile (99.97%, HPLC/Spectro grade) was obtained from Tedia Co., Inc. (Fairfield, OH, USA). Deionized distilled water (Millipore Co., Bedford, MA, USA) was used throughout the experiment unless otherwise mentioned. All other reagents were analytical grade and were used without further treatment.

### Photodegradation procedure

The experiments were carried out in a 1.2-L hollow cylindrical photoreactor equipped with a water jacket. The inner wall of the water jacket is made of fused silica and the outer wall is made of Pyrex. A 100 W medium pressure mercury lamp (ACE glass Inc., NJ, USA) was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the lamp. At a distance of 0.5 m, the light intensity yielded 230 $\mu$W/cm$^2$ in the wavelength of 222–1367 nm. From these values, the light intensity close to the surface of the lamp was calculated as 575 mW/cm$^2$ using the equation $\ln E_{e,0} = 2 \ln r + \ln E_{e,r}$, where $E_{e,0}$ and $E_{e,r}$ represent the light intensity at distance 0 and $rm$, respectively (Haarstrick et al., 1996).

Batch experiments were conducted at $25 \pm 1°C$. A standard experiment involved the addition of 100 mg of 2-CP (dissolved in acetonitrile) to deionized distilled water. After $TiO_2$ and/or CdS were added to the suspension, the sample was sonicated for 20 min to obtain a good dispersion. Immediately after the addition of the stock solution of chlorophenol, the light was turned on. Aliquots (10 mL) were withdrawn from the solution at various time intervals for analysis after removal of semiconductors by centrifugation at 14,000 rev/min for 10 min. Also, phosphate buffer solutions consisting of 10 mM $Na_2HPO_4$ and 10 mM $NaH_2PO_4$ were used throughout the experiment to yield a pH value of $7.0 \pm 0.1$ unless otherwise mentioned.

Two control experiments were conducted under the same experimental conditions in thermostatic baths at the temperature indicated. The first set of experiment involved the presence of a catalyst and stirring in dark to determine the reaction in darkness. The second experiment involved the irradiation of the dispersion without the addition of a catalyst to account for any direct photolysis.

*Analytical methods*

The samples were determined by high-performance liquid chromatography (HPLC) equipped with a variable wavelength UV detector. A Supelcosil LC-18 column (15 cm × 0.46 mm × 5.0 μm) was employed for determining the 2-CP and the intermediates. The mobile phase was a mixture of 40 : 60 : 0.1 acetonitrile:water:acetic acid. The elute was delivered at a rate of 1.0 mL/min and the wavelength for detection was 254 nm. The detection limit of 2-CP was 0.075 mg/L.

Oxygen concentration was measured during irradiation using an oxygen-sensitive membrane electrode, which is capable of accurately detecting oxygen levels up to 0.5 mg/L. The crystal structure of the TiO$_2$ particles determined by an X-ray powder diffractometer (MAC, MXP10) showed that anatase is the primarily form, with greater than 99.9% purity. The average particle diameters of TiO$_2$ and CdS in aqueous solution, determined by laser particle analyzer (Photal, LPA-300) were 0.37 and 31.4 μm, respectively. The average-specific BET surface area of TiO$_2$ and CdS, determined by Micromertics ASAR 2000 apparatus, were $7.35 \pm 0.14$ and $6.04 \pm 0.01$ m$^2$/g, respectively.

## RESULTS AND DISCUSSION

### Effect of pH value on photocatalytic degradation of 2-CP

Figure 1 illustrates the degradation of 2-CP in TiO$_2$/UV and direct photolysis systems under various pH values with the illumination of a 100 W medium-pressure mercury lamp. No obvious degradation of 2-CP was observed after 24 h in darkness. However, obvious degradation of 2-CP was observed in TiO$_2$-amended system with the illumination of UV–visible light, indicating that the decomposition of 2-CP is mainly from photoassisted degradation. Nearly complete degradation of 2-CP was observed within 120 min at pH 12.5. Decreasing the pH values could decrease the degradation efficiency of 2-CP. Removal of 94% of the original 2-CP within 490 min was observed when pH decreased to 4.5. Also, the degradation behavior followed apparent first-order rate equation. The apparent first-order rate constants ($k_{obs}$) of 2-CP in TiO$_2$/UV system, calculated by a least-squares regression of ln ($C/C_0$) vs. time, ranged

from 0.036 min$^{-1}$ at pH 12.5 to 0.004 min$^{-1}$ at pH 4.5 (Table 1).

Similar degradation pattern of 2-CP in direct photolysis system was observed. Removal of 99.9% of 2-CP was obtained within 60 min at pH 12.5. Decreasing the pH values also decreased the degradation efficiency of 2-CP, and illumination time of 360 min was needed for the complete decomposition of 2-CP under acidic conditions. The $k_{obs}$ ranged from 0.013 to 0.015 min$^{-1}$ under acidic condition, while a 2- to 10-fold increase in $k_{obs}$ was observed under alkali environments (Table 1). It also highlights the fact that the degradation rate of 2-CP at pH 4.5 in both TiO$_2$/UV and direct photolysis systems was lower than that at pH 2.5, implying that phosphate buffer solution may inhibit the photodegradation of 2-CP. Several researches have reported that anionic ions such as phosphate, chloride and sulfate can lower the photodegradation efficiency of pollutants to 20–70% in the presence of titanium dioxide (Abdullah *et al.*, 1990; Hua *et al.*, 1995). However, Kormann *et al.* (1991) proposed that the degree to which anions inhibited degradation was correlated strongly with the extent to which they sorbed to the catalyst surface. Our previous results also showed that there was no significant difference between phosphate buffer-amended and -unamended systems in the photodegradation of parathion in UV/TiO$_2$/H$_2$O$_2$ system (Doong and Chang, 1997).

To further evaluate the effect of buffer solution on the photodegradation of 2-CP, experiments without the addition of phosphate buffer solution were performed. The pH values were adjusted with 0.1 N NaOH or 0.1 N HCl to reach the desired pH values. Figure 2 illustrates the photodegradation of 2-CP under different pH values without the amendment of buffer solutions by direct photolysis. Although the degradation patterns of 2-CP without the amendment of buffer solution were similar with those with the amendment of buffer solution, the degradation of 2-CP at pH 2.5 in buffer-unamended system was slower than that at pH 4.5. This means that
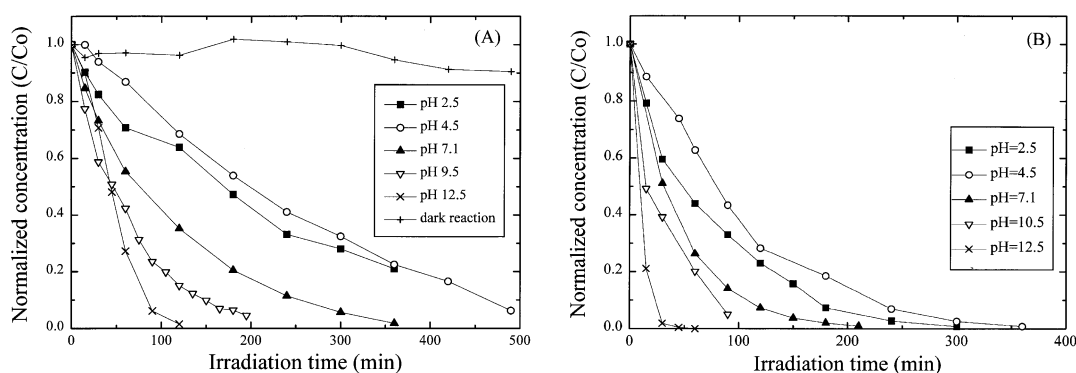


Fig. 1. The photodegradation of 2-chlorophenol in TiO$_2$/UV and direct photolysis system under different pH values with the amendment of phosphate buffer systems. (A) TiO$_2$/UV system. (b) Direct photolysis system.

Table 1. The apparent first-order rate constant ($k_{obs}$) of 2-CP and predominant phosphate ions in TiO$_2$/UV and direct photolysis systems in the pH range of 2.5–12.5

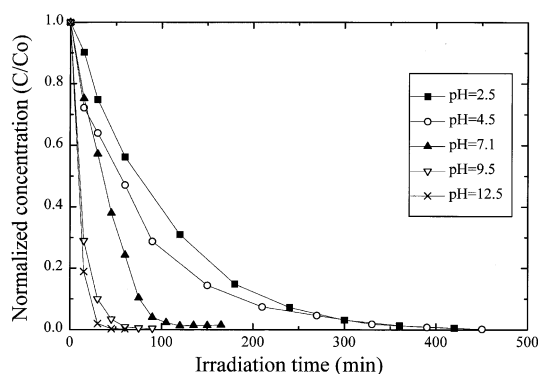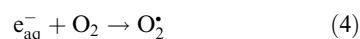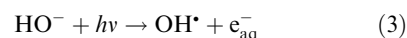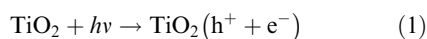| pH | Apparent first-order rate constants ($k_{obs}$) (min$^{-1}$) | | | Phosphate species |
| | TiO$_2$/UV system | Direct photolysis system | | |
| | Buffered | Buffered | Unbuffered | |
| --- | --- | --- | --- | --- |
| 2.5 | 0.005 | 0.015 | 0.012 | H$_3$PO$_4$, H$_2$PO$_4^-$ |
| 4.5 | 0.0042 | 0.013 | 0.013 | H$_2$PO$_4^-$ |
| 7.0 | 0.013 | 0.022 | 0.038 | H$_2$PO$_4^-$, HPO$_4^{2-}$ |
| 9.5 | 0.016 | 0.031 | 0.064 | HPO$_4^{2-}$ |
| 12.5 | 0.036 | 0.126 | 0.129 | HPO$_4^{2-}$, PO$_4^{3-}$ |



Fig. 2. The photodegradation of 2-chlorophenol in direct photolysis system under different pH values without the amendment of phosphate buffer systems.

phosphate buffer solution may inhibit the photodegradation efficiency of 2-CP under acidic condition. Moreover, the initial rate constants and pseudo-first order rate constants of 2-CP between buffer-amended and -unamended systems were pH-dependent. As illustrated in Table 1, the initial and pseudo-first-order rate constants of 2-CP in the buffer-amended system at pH 2.5 was 1.3 times higher than those in the unbuffered system. However, no significant difference in $k_{obs}$ was observed between these two systems at pH 4.5, implying that the H$_2$PO$_4^-$ has little effect on the photodegradation of 2-CP. Moreover, the $k_{obs}$ in unbuffered system was higher than those in buffer-amended systems under neutral and alkali conditions. A 1.7- to 2.1-fold increase in $k_{obs}$ relative to buffer-amending system was observed in the system without the addition of phosphate buffer solutions, showing that HPO$_4^{2-}$ could inhibit the photodegradation efficiency of 2-CP.

The pH value has a great effect on the photodegradation efficiency of 2-CP in the presence of TiO$_2$. Several researches showed that the removal efficiency of chlorophenols decreased with increasing pH values (Kormann *et al.*, 1991; Ku *et al.*, 1996; Leyva *et al.*, 1998). It is suggested that TiO$_2$ surface carries a net positive charge (pH$_{zpc}$ = 6.25) at low pH value, while the chlorophenols and intermediates are primarily negatively and neutrally charged. Therefore, low pH values can facilitate the adsorption of the organic molecule and promote better photocatalytic degradation. However, previous studies showed

that very small amounts of chlorophenols are sorbed by titanium dioxide from aqueous because it has to compete with water for adsorption sites (Mills *et al.*, 1993a,b; Stafford *et al.*, 1994). Therefore, better removal efficiency of chlorophenols in TiO$_2$/UV system under alkali condition was also reported (Stafford *et al.*, 1994; Serpone *et al.*, 1995; Schmelling *et al.*, 1997), which is consistent with our results. One possible explanation is that the photocatalytic transformation of chlorophenols does not involve hydroxyl radical oxidation exclusively. Direct electron transfer and surface sorption reactions also contribute significantly to the disappearance of chlorophenols in TiO$_2$ suspensions (Stafford *et al.*, 1994; Schmelling *et al.*, 1997). Although there is no semiconductor existed in the solution of direct photolysis system, hydroxyl radicals (OH$^\bullet$) and hydrated electrons (e$_{aq}^-$) can be formed when water is irradiated with high energy UV light. Therefore, higher pH value can provide higher concentration of hydroxyl ions to react with holes to form hydroxyl radicals, subsequently enhancing the photodegradation rate of 2-CP:

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \qquad (1)$$

$$OH^- + h^+ \rightarrow OH^\bullet \qquad (2)$$

$$HO^- + h\nu \rightarrow OH^\bullet + e_{aq}^- \qquad (3)$$

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \qquad (4)$$

Although the concentration of 2-CP can be completely decomposed in the presence of TiO$_2$ and/or CdS, the mineralization ratio of 2-CP was low. Figure 3 illustrates the concentration profile of TOC and chloride formation in the liquid phase of UV/TiO$_2$ system with the amendment of 100 mg/L 2-CP under neutral condition. The TOC concentration slowly decreased from 56 mg/L in the initial to 44.2 mg/L after the irradiation of 24 h. The decrease of TOC also followed the first-order rate reaction and the mineralization rate constant was $1.07 \times 10^{-4}$ min$^{-1}$. This value is far less than that of photodegradation of 2-CP. This may be mainly attributed to the formation of organic intermediates in the photocatalytic reaction. Various organic intermediates were reported to be produced from the decomposition of chlorophenols by
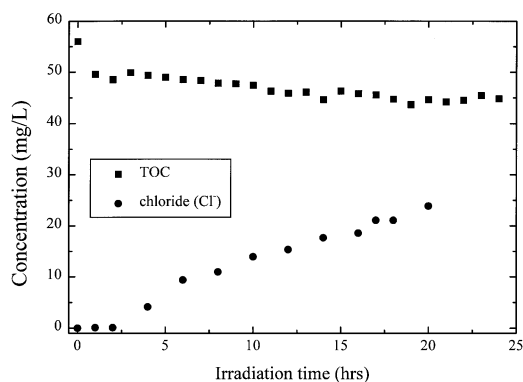
Fig. 3. The concentration profiles of TOC and chloride in TiO₂/UV system under neutral condition when 100 mg/L 2-chlorophoenol was photocatalytically degraded by a 100 W mercury lamp.

Table 2. The concentration profile of chlorocatechol produced from the photocatalytic decomposition of 100 mg/L 2-CP in TiO₂/UV system

| Reaction time (h) | Concentration of chlorocatechol (mg/L) | | |
|---|---|---|---|
| | pH 5 | pH 7 | pH 9 |
| 0 | 0 | 0 | 0 |
| 1 | 0.23 | 0.34 | 0.04 |
| 2 | 0.54 | 0.66 | 0.04 |
| 3 | 0.74 | 0.78 | 0.1 |
| 4 | 0.63 | 0.85 | 0.1 |
| 5 | 1.08 | 0.97 | 0.12 |
| 6 | 1.28 | 1.05 | 0.11 |
| 7 | 1.26 | 1.29 | 0.18 |
| 8 | 1.31 | 1.31 | 0.2 |
| 9 | 1.55 | 1.44 | 0.22 |
| 10 | 1.67 | 1.56 | 0.26 |

photocatalytic reactions in aqueous solution (Kormann *et al.*, 1991; Mills *et al.*, 1993a,b; Martin *et al.*, 1995). Research has confirmed that the hydroxymediated 4-CP oxidation followed at least three separated degradation pathways (Mills *et al.*, 1993a,b; Stafford *et al.*, 1994). One reaction pathway leads to an unstable intermediate that undergoes ring cleavage and subsequently rapid decarboxylation and dechlorination. The other two reaction pathways results in stable intermediates, including 4-chlorocatechol, hydroquinone, benzoquinone and 4-chlororesorcinol. Stafford *et al.* (1994) showed that the distribution of intermediates of 4-CP was pH-dependent. 4-Chlorocatechol and hydroquinone were the major intermediates when 4-CP was oxidized by $\gamma$-radiolysis at pH 3 and 6, while no aromatic intermediates were detected at pH 9. In this study, consistent result of the formation of the observed reaction intermediates, including chlorocatechol, hydroquinone, benzoquinone and phenol, were identified during the photocatalytic reaction. Chlorocatechol was the predominant intermediate detected in this study. Table 2 illustrates the concentration changes of chlorocatechol from the photocatalytic degradation of 2-CP in TiO₂/UV system. The

concentration of chlorocatechol at pH 9 was lower than that at pH 5 and pH 7, which is consistent with the reported data. This suggests that photocatalytic degradation of 2-CP at higher pH favor direct ring cleavage (Stafford *et al.*, 1994). However, the concentration of chlorocatechol was low in the range of 5–9, implying that large amounts of non-aromatic intermediates may be produced when 2-CP was photocatalytically degraded by a 100 W medium-pressure mercury lamp.

## Effect of dose of semiconductors

Figure 4 illustrates the photodegradation of 100 mg/L 2-CP with the illumination of a 100 W lamp in the presence of different dosages of TiO₂ and CdS. Increasing TiO₂ dosage decreased the photodegradation efficiency of 2-CP. Removal of 71% of 2-CP was observed with the illumination time of 150 min when 0.1 g/L TiO₂ was amended into the system. However, only 50% of 2-CP were decomposed when the dosage of TiO₂ increased to 1 g/L. Similar photodegradation pattern of 2-CP was also demonstrated in the CdS-amended system. Removal efficiency of 2-CP decreased from 87 to 78% as the CdS loading increased from 0.1 to 1 g/L. Figure 5 illustrates the apparent first-order and initial rate constants of 2-CP with the amendment of different doses of semiconductors. Highest degradation rate with apparent first-order rate constant of 0.021 min⁻¹ was obtained in direct photolysis system. The $k_{obs}$ of 2-CP decreased from 0.0081 to 0.0039 min⁻¹ in TiO₂-amended system and from 0.014 to 0.01 min⁻¹ in CdS-amended system when the loading of semiconductors increased from 0.1 to 1 g/L. Similar distribution pattern of the initial rate was observed. The rate constants decreased from 6.2 to 2.8 μM/min in TiO₂-amended system, while rate constants of 7.68–4.88 μM/min was obtained when CdS was added into the photo-system. The addition of the semiconductor decreased the photodegradation efficiency of 2-CP, suggesting that a shielding effect
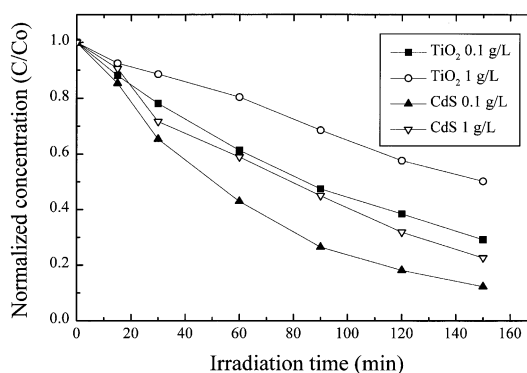


Fig. 4. The photodegradation of 2-chlorophenol in the presence of different dosages of titanium dioxide (TiO₂) and cadmium sulfide (CdS) under neutral condition.
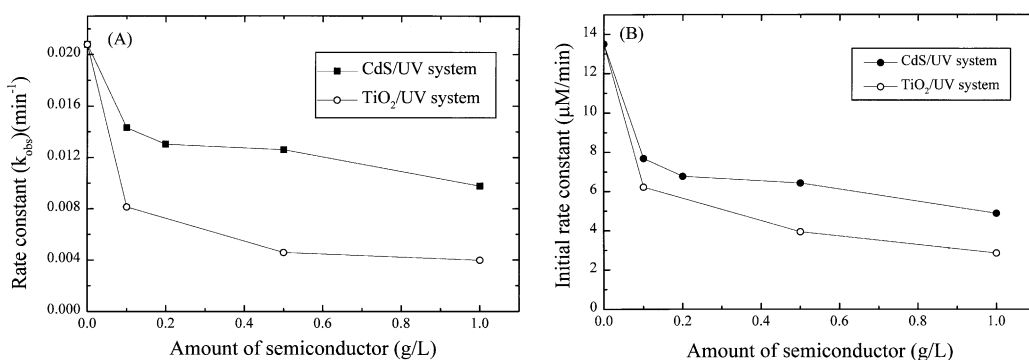
Fig. 5. The relationship between the apparent first-order rate constants and initial rate constants of 2-chlorophenol and dosage of semiconductor. (A) Apparent first-order rate constant. (B) Initial rate constant. The apparent first-order rate constant was calculated by a least-square regression of ln $(C/C_0)$ vs. time. The initial rate constant was determined using the equation of $k_{ini} = (C_0 - C_{20})/20$.

occurred in the semiconductor-amended system. Cadmium sulfide had a higher rate constant than titanium dioxide for the photodegradation of 2-CP. This may be attributed to that the average particle size of cadmium sulfide is larger than that of titanium dioxide. The turbidity measurement showed that the fraction of light absorbed by 0.1 g/L of $TiO_2$ were between 91.9 and 98.1% when the wavelength increased from 243 to 600 nm. Whereas only 9.7–11.1% of the incident light was absorbed by 0.1 g/L of CdS. Therefore, the shielding effect of titanium dioxide is obviously larger than that of cadmium sulfide, and then decreases the degradation efficiency more significantly.

Several researches have demonstrated that the photodecomposition rates of pollutants are influenced by the active site and the photo-absorption of the catalyst used (Doong and Chang, 1998; Martin et al., 1995; Al-Sayyed et al., 1991; Ku et al., 1996). Adequate loading of the semiconductor increases the generation rate of electron/hole pairs for promoting the degradation of pollutants. However, the addition of a high dose of semiconductor decreases the light penetration by the photocatalyst suspension (Doong and Chang, 1998). Al-Sayyed et al. (1991) showed that the decomposition rate of 4-CP increased linearly with the amount of $TiO_2$ added. However, Ku et al. (1996) reported that the rate constant of 2-CP decreased with the increasing $TiO_2$ amount for loading above 0.1 g/L under alkali conditions. Recently, Doong and Chang (1998) depicted that the addition of $TiO_2$ has little effect on the enhancement of photodegradation rate of readily degradable pesticides. Stafford et al. (1994) also depicted that direct oxidation contributed significantly to the photodecomposition of 4-CP in $TiO_2$ slurry system. It can be speculated that the degradation of 2-CP was mainly due to the direct photolysis. The bond energy of aryl-Cl is 97 kcal/mol, which cleavages readily with the illumination having a wavelength less than 294 nm. The wavelength from the lamp used in this study ranged from 222 to 1367 nm. Therefore, the addition of semiconductor could hamper the penetration of the high intensity wavelength that is less than 275 nm, thereby decreasing the photodegradation rate of 2-CP.

*Effect of the coupled semiconductor*

Figure 6 illustrates the photodegradation of 2-CP with the illumination of a 100 W lamp in the presence of 0.5 g/L $TiO_2$ and/or CdS under neutral condition. Removal of 50% of 2-CP was observed within 150 min in the $TiO_2$-amended system, while 87% of the initial 2-CP was removed in the CdS-amended system. The pseudo-first-order rate constants of 2-CP in $UV/TiO_2$ and $UV/CdS$ systems were 0.0045 and 0.0098 $min^{-1}$, respectively. The combination of 0.5 g $TiO_2$ and 0.5 g CdS showed a higher degradation efficiency of 2-CP than that in the single semiconductor system. The pseudo-first-order rate constant of 2-CP in the coupled system was 0.011 $min^{-1}$, which is 1.2–2.5 times higher than that in CdS- and $TiO_2$-amended system. The enhancement of photodegradation efficiency of 2-CP in $TiO_2/CdS/UV$ system may be attributed to the rapid transfer of
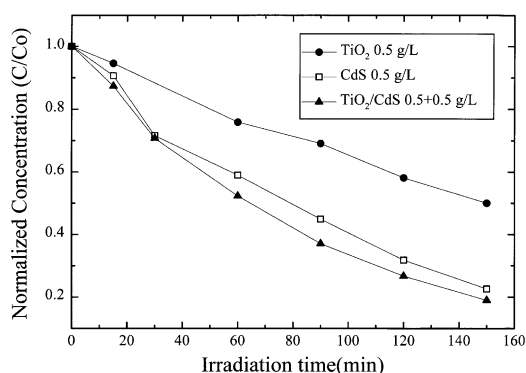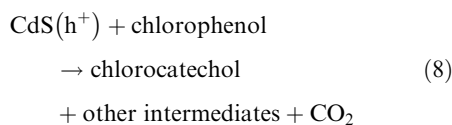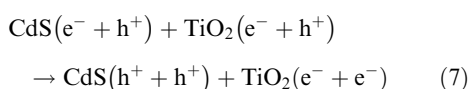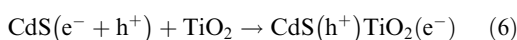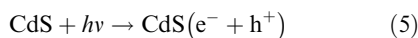


Fig. 6. The photocatalytic degradation of 2-chlorophenol using quartz reactor in the coupled titanium dioxide and cadmium sulfide under neutral condition.

the photo-generated electrons from the cadmium sulfide to the titanium dioxide conduction band, resulting in the effective separation of the electrons and holes (Serpone *et al.*, 1995).

The photocatalytic expectations from coupled systems can be predicted and described from the knowledge of the flat band potentials of the system components. In the presence of titanium dioxide in a coupled CdS/TiO$_2$ system, it can be sensitized by interparticle electron transfer process from the irradiated CdS particle to the conduction band of TiO$_2$, thereby leaving an excess of surface-trapped holes on the CdS:

$$CdS + hv \rightarrow CdS(e^- + h^+) \quad (5)$$

$$CdS(e^- + h^+) + TiO_2 \rightarrow CdS(h^+)TiO_2(e^-) \quad (6)$$

$$CdS(e^- + h^+) + TiO_2(e^- + h^+)$$
$$\rightarrow CdS(h^+ + h^+) + TiO_2(e^- + e^-) \quad (7)$$

$$CdS(h^+) + chlorophenol$$
$$\rightarrow chlorocatechol \quad (8)$$
$$+ other\ intermediates + CO_2$$

When both TiO$_2$ and CdS are simultaneously activated by the UV–visible light, electron transfer may occur from the conduction band of CdS to the TiO$_2$, whereas hole transfer may occur from the valence band of TiO$_2$ to the CdS. This will retards the electron–hole recombination rate in the respective semiconductor. Moreover, the excess electron on TiO$_2$ can be scavenged by chemisorbed molecular oxygen to produce superoxide radical and hydrogen peroxide. We observed that the oxygen concentration of the semiconductor-amended system decreased from 7.5 to 3.4 mg/L. However, no hydrogen peroxide was quantified.

In this study, cadmium sulfide is shown to be more effective on the photodegradation of 2-CP. Serpone *et al.* (1995) showed that cadmium sulfide is a poorer photooxidation catalyst than titanium dioxide for decomposing chlorophenols when the semiconductor was illuminated with a UV–visible lamp under alkali conditions. This discrepancy may be due to the wavelength used in the study. Serpone *et al.* (1995) used a 1000 W Hg/Xe lamp and cutoff filters (355 and 406 nm) to photocatalyze the decomposition of chlorophenols in a Pyrex reactor under alkali condition, whereas a 100 W medium-pressure mercury lamp and fused silica reactor under neutral conditions were used in this study. To evaluate the effect of wavelength on the photodegradation of 2-CP, a Pyrex reactor was used instead of a fused silica reactor to cut off the wavelength below 320 nm. Figure 7 illustrates the photo-assisted degradation of 2-CP using Pyrex reactor ($\lambda > 320$ nm) under alkali conditions (pH 12.5). Nearly complete degradation of 2-CP within 420 min was observed in the presence
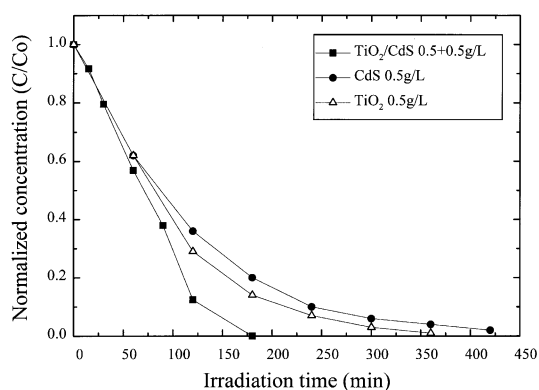


Fig. 7. The photocatalytic degradation of 2-chlorophenol using Pyrex reactor in the coupled titanium dioxide and cadmium sulfide system under alkali condition.

of semiconductors. Also, the disappearance rate of 2-CP in CdS-amended system was smaller than the system amended with TiO$_2$. The apparent first-order rate constants were 0.009 and 0.013 min$^{-1}$ in CdS- and TiO$_2$-amended systems, respectively, which is consistent with the reported data. Moreover, more than 99.9% of original 2-CP was removed in the coupled CdS/TiO$_2$ system within 180 min. The apparent first-order rate constant of 0.016 min$^{-1}$ was observed, which is 1.2–1.8 times higher than those in CdS- and TiO$_2$-amended systems. This result proves again that the combination of semiconductors can lead to an enhanced rate of disappearance of 2-CP than those in single semiconductor systems.

## CONCLUSIONS

The results obtained in this study demonstrate that the pH and cadmium sulfide has a great effect on the photocatalytic degradation of 2-CP in TiO$_2$ suspensions. Higher pH value was conducive to the degradation of 2-CP. The degradation follows apparent first-order degradation behavior. The apparent first order rate constants ranged from 0.004 to 0.005 min$^{-1}$ under acidic conditions in TiO$_2$/UV system. A 3- to 9-fold increase in $k_{obs}$ relative to acidic conditions was observed under alkali environments. Also, the addition of a phosphate buffer solution has different effects on the photodegradation of 2-CP at different pH values. H$_2$PO$_4^-$ has little effect on the photodegradation of 2-CP, whereas HPO$_4^{2-}$ could inhibit the photo-degradation efficiency of 2-CP. Chlorocatechol, hydroquinone, benzoquinone and phenol were identified as the predominant aromatic intermediates for the photocatalytic degradation of 2-CP. Less aromatic intermediates at higher pH were observed, suggesting that the photodegradation at high pH favors direct ring cleavage.

The photocatalytic transformation of 2-CP does not involve hydroxyl radical oxidation exclusively. Direct electron transfer also contributes significantly

to the disappearance of chlorophenols in $TiO_2$ suspensions. In the present study, the addition of cadmium sulfide is shown to be more effective than titanium dioxide on the photo-degradation of 2-CP under neutral condition due to that cadmium sulfide absorbed less incident light than that of titanium dioxide. The apparent first-order and initial rate constants ranged from 0.014 to 0.01 $min^{-1}$ and from 7.68 to 4.88 $\mu M/min$, respectively, in CdS-amended system. A 1.7- to 2.5-fold decrease in rate constant was observed when $TiO_2$ was amended to the system. The combination of $TiO_2$ and CdS can lead to an enhanced rate of disappearance of 2-CP than those in single semiconductor systems. Moreover, the photocatalytic capability of titanium dioxide used in this study showed higher photocatalytic capability on the degradation of 2-CP than that of cadmium sulfide under alkali condition when using Pyrex reactor to cut off the wavelength lower than 320 nm.

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