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Photocatalytic degradation of phenols in aqueous solution under irradiation of 254 and 185 nm UV light

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Abstract

The photocatalytic decomposition and mineralization of 4-chlorophenol (4-CP), hydroquinone and 4-nitrophenol (4-NP) in aqueous solution were investigated using two kinds of low-pressure mercury lamps: one was UV (ultraviolet) lamp emitting at 254 nm and the other was VUV (vacuum ultraviolet) lamp emitting at both 254 and 185 nm. VUV irradiation led to the most efficient degradation of the organics. Different mechanisms of photocatalysis and photolysis under VUV irradiation were observed. The degradation rate was subjected to the molecular structures of the substrates. 4-CP was easy to be decomposed, while hydroquinone was easy to be mineralized. However 4-NP was difficult to be decomposed or mineralized. VUV was efficient for decomposition of refractory compounds, such as nitrophenols, and the catalyst was efficient for TOC removal.

Keywords: Phenols; Photolysis; Photocatalysis; VUV; TiO_2

1. Introduction

Heterogeneous photocatalysis, an advanced oxidation process, had been widely studied to degrade or remove a wide range of pollutants in water and air [1]. The basic mechanism of heterogeneous photocatalysis had been well established [2]. The main oxidant, hydroxyl radical, was strong enough to degrade most pollutants effectively. However, the photocatalytic oxidation process actually was of low efficiency, and it took long time to purify the water or air, which resulted in high cost and no competitiveness. To improve the efficiency of photocatalytic oxidation process, many modification methods had been adopted [3]. In addition, strong oxidants [4,5] such as ozone, hydrogen peroxide, persulfate ion and periodate were added in the reaction system, which significantly increased the overall oxidation rate.

Photolysis of water using vacuum ultraviolet light (VUV, $\lambda < 200$ nm) was another means to generate hydroxyl radical. Under irradiation with VUV light, water itself was photolyzed into hydrogen atom and hydroxyl radical, and other oxidative species such as hydrogen peroxide would probably be formed simultaneously [6]. This process had recently received much attention since the excimer light sources became available. For example, Gonzalez et al. [7] found that nitrogen-containing organic compound (3-amino-5-methylisoxazole) could be more efficiently mineralized at reductive conditions (argon saturated solutions) under 172 nm irradiation. Shirayama et al. [8] investigated the effect of dissolved oxygen (DO) on the photodegradation of chlorinated hydrocarbons under irradiation of 254 and 185 nm, confirming that the degradation rates of all chlorinated hydrocarbons were elevated in the absence of DO. An indirect comparison between VUV (172 nm) and TiO_2/UV for phenol decomposition was also conducted, phenol degraded much faster in the former process [9]. Actually due to its capability of TOC reduction, 185 nm UV illumination accompanied with membrane technology had been widely applied in the electronic industry to decrease trace TOC in ultrapure water [10].

In aerated solutions, H atoms obtained from photolysis of water under VUV irradiation were scavenged by oxygen to form $HO_2^{\bullet}$ radicals, which finally converted to $^{\bullet}OH$ radicals. Therefore, the principal reaction leading to organics decomposition would be the one with $^{\bullet}OH$ radicals. Oxygen was considered to be important in the steps to form $^{\bullet}OH$ radicals

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[11]. Oxygen itself would hardly absorbed 185 nm light directly to form hydroxyl radical or ozone due to its weak absorption coefficient at 185 nm (about 0.1 cm^{-1} atm^{-1} in the gas phase [12]) and low concentration in water. However, the path that 185 nm light penetrated the water was very short due to its high absorption coefficient (1.8 cm^{-1} at 25 °C [13]). The intensity of 185 nm UV light decreases nearly 90% in 5 mm thick water. Actually in the experimental photoreactor, no more than 0.2% of 185 nm UV light arrived at the photocatalyst when the water thickness was up to 15 mm between photocatalyst and quartz tube. Therefore, no matter what oxidant was produced by VUV photolysis, it would not be consumed by photocatalyst due to the long distance. Thus in TiO_2/VUV process, probably VUV photolysis (including UV photolysis) and TiO_2/UV functioned independently, and no significant synergism occurred. The difference between photolysis and photocatalysis under VUV irradiation possibly was due to the intermediate degradation on the surface of the photocatalyst.

Although there were reports [14] on the effect of different wavelengths on photocatalysis quantum yield, to our knowledge, the photocatalysis under VUV (185 nm) had rarely been investigated in aqueous solution. We had been asking the questions: was there any relationship between the degradation rates and the structures of the substrates; was TiO_2 catalyst necessary for degradation under VUV irradiation.

Phenols were common while refractory compounds in industrial wastewater. Several researchers had studied the photocatalytic decomposition of phenols in aqueous solution [15,16]. In photocatalysis of low concentration phenols, reactions between aromatic compounds and $^\bullet OH$ radicals corresponded to processes of hydrogen substitution. The first step was complexation of $^\bullet OH$ with the π-system of the aromatic ring, thus forming a π-complex in which the $^\bullet OH$ group did not have a specific position in the molecule. The second step corresponded to the formation of a σ-complex between the carbon atom of the aromatic ring and the radical $^\bullet OH$. The formation of the σ-complex was usually the rate-determining step of the reaction.

In this paper, phenols were chosen as model compounds to investigate photocatalytic decomposition and mineralization efficiency under irradiation of UV and VUV.

2. Experimental

2.1. Preparation of TiO_2 film

The photocatalyst used in the present study was TiO_2 thin film coated on the aluminum sheet by the following method. Tetrabutylorthotitanate ($Ti(OC_4H_9)_4$, C.P.), acetyl acetone (C_5H_8O, A.R.), deionized water and *n*-propanol (C_3H_8O, A.R.) were mixed with a volumetric ratio of 1:0.3:0.4:7 at room temperature. Afterwards, the nanometer black carbon powder (Degussa Printex L6, with primary particle size of 18 nm and BET surface of 265 m^2/g) was added and mixed uniformly in the above solution at the ratio of 1 ml $Ti(OC_4H_9)_4$:2.35 mg black carbon. The polished aluminum sheet (300 mm × 180 mm × 0.18 mm) was dipped in the mixture. After being taken out of the mixture, the aluminum sheet was dried at room temperature and then heated at 500 m for 2 h. After seven times of dip coating on the aluminum sheet, an optimized thin TiO_2 photocatalyst film was formed. The loaded quantity of TiO_2 film on the aluminum sheet was 2.6 g (TiO_2)/m^2, the surface area was 82.3 m^2/m^2 and the mean particle size of TiO_2 was 24 nm.

2.2. Chemicals and analysis

Phenols were analytical grade. In all the decomposition experiments, deionized water was used, while in the mineralization experiments, ultrapure water made by Millipore purifier (Milli-Q) was applied.

The concentrations of phenols in aqueous solution were analyzed by HPLC (Shimadzu, LC-10AD) with an ODS C8 column (250 mm × 4.6 mm). The eluent was methanol and 1% acetic acid at volume ratio of 50:50. The flow rate was 1 ml/min. The detective wavelength was 270 nm. Total organic carbon (TOC) was measured with a Shimadzu TOC 5000.

2.3. Experimental procedure

A glass tubular photoreactor shown in Fig. 1 was 330 mm high, with an inner diameter of 55 mm and available volume of 0.6 l. The TiO_2-coated aluminum sheet (300 mm high, 180 mm wide and 0.18 mm thick) was attached to the interior surface of the photoreactor. For photolysis experiment, no catalyst or aluminum sheet was used. Two types of low-pressure mercury lamps were used to provide UV illumination: a UV lamp emitting at 254 nm (15 W) and a VUV lamp emitting at both 254 and 185 nm (15 W). The two lamps had approximate illumination intensity at 254 nm, and their photon numbers were $(1.2 \pm 0.1) \times 10^{-5}$ mol/s. The VUV lamp had additional photons of 185 nm, which had higher energy than photons of 254 nm, and its photon number was $(1.5 \pm 0.2) \times 10^{-6}$ mol/s. The lamp was placed in the center of the photoreactor with quartz tube protection (with external diameter of 25 mm), the distance from

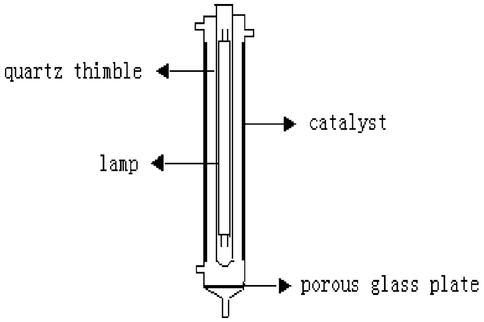


Fig. 1. Schematic diagram of the photochemical reactor.

the inner wall of the photoreactor to the external wall of quartz tube was 15 mm. Air was continuously bubbled into the reactor through a porous glass plate with a flow rate of 300 ml/min.

The photodegradation experiments were conducted in a semi-batch mode. The sample volume was 3.0 l, which was circulated between the photoreactor and a storage tank with a diaphragm pump at a flow rate of 1.2 l/min. The mineralization experiments were operated in a static mode.

3. Results and discussion

Decomposition and mineralization of 4-chlorophenol (4-CP), hydroquinone and 4-nitrophenol (4-NP) in aqueous solution had been studied under four different conditions: UV irradiation in the presence and absence of TiO_2 (hereafter referred as UVPCD and UVPD respectively); VUV irradiation in the presence and absence of TiO_2 (hereafter referred as VUVPCD and VUVPD respectively). The initial concentrations of phenols in each solution were listed in Table 1. The results were plotted in Fig. 2.

According to the control experiment without any irradiation, the concentration of phenols decreased less than 2% possibly due to air stripping or TiO_2 adsorption after being aerated in the dark and in presence of TiO_2 for 20 min.

In all cases, VUV irradiation led to the most efficient degradation of the organics, which was contributed to the abundant powerful oxidant, hydroxyl radical.

No significant difference of degradation rate was observed due to TiO_2 catalyst under UV or VUV irradiation except the UV-irradiated 4-chlorophenol solutions. Detail reasons would be demonstrated in later paragraph.

The variations of the total organic carbon of 4-chlorophenol versus time in different cases were shown in Fig. 3. TOC removal rates of various phenols in four different conditions were depicted in Table 2. The TOC removal rate of each phenols followed in the order of VUVPCD > VUVPD > UVPCD > UVPD, except 4-NP under VUV irradiation, which had no significant difference due to TiO_2 catalyst.

The orders of decomposition and mineralization of phenols in different process were due to two possible reasons. One was the additional photons of 185 nm and its higher energy of illumination in VUV lamp than UV lamp. The other should be ascribed to the photocatalytic degradation of intermediates on the surface of the catalyst.

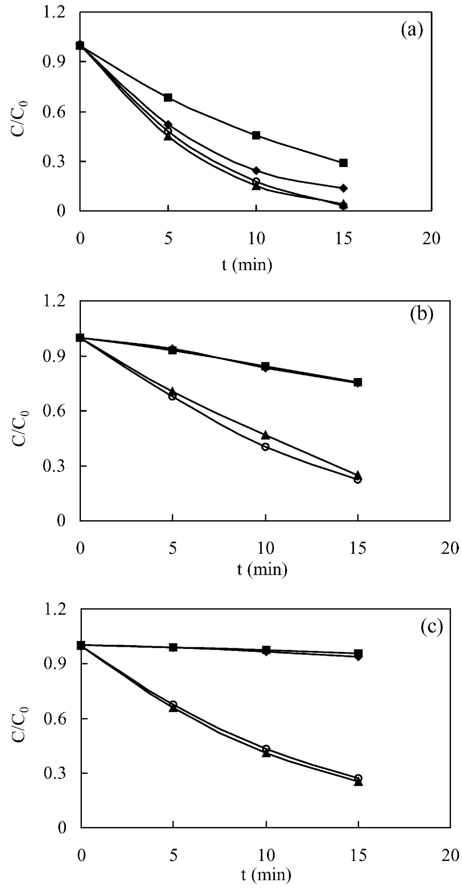


Fig. 2. (a) 4-CP; (b) hydroquinone; (c) 4-NP. The time courses of the concentration of phenols in different processes: (■) UVPD; (◆) UVPCD; (▲) VUVPD; (○) VUVPCD.

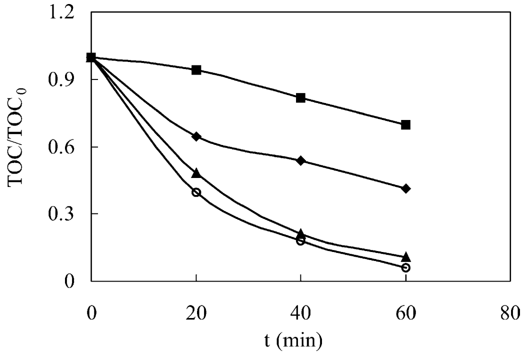


Fig. 3. The time courses of the TOC of 4-CP: (■) UVPD; (◆) UVPCD; (▲) VUVPD; (○) VUVPCD.

Table 1
Initial concentrations in various processes

Processes	4-CP		Hydroquinone		4-NP	
	C_0 (mg/l)	TOC_0 (mg/l)	C_0 (mg/l)	TOC_0 (mg/l)	C_0 (mg/l)	TOC_0 (mg/l)
UVPD	2.08	0.967	1.94	1.073	2.02	1.026
UVPCD	2.13	0.996	2.13	1.080	1.94	0.866
VUVPD	2.19	1.109	1.95	1.181	2.02	0.978
VUVPCD	2.10	1.092	1.97	1.177	2.00	0.867

Table 2
TOC removal rates of various phenols

	t (min)	4-CP (%)	Hydroquinone (%)	4-NP(%)
UVPD	20	5.7	3.1	−1.2[a]
	60	30.4	32.8	9.1
UVPCD	20	35.5	44.9	8.1
	60	58.6	86.5	43.9
VUVPD	20	51.9	48.9	46.1
	60	89.4	87	81.4
VUVPCD	20	60.7	66.2	45.1
	60	94	96	80.9

[a] Negative may be ascribed to error in detection.

The initial mineralization rates of 4-CP and hydroquinone were very small in UVPD process, which should be ascribed to the accumulated intermediates, especially quinone [17].

TiO_2 catalyst was more effective for TOC removal than phenols' decomposition under VUV irradiation, which indicated that the main reaction on the catalyst surface was degradation of the intermediates.

3.1. Photocatalytic degradation of 4-CP

The experimental results showed that 4-CP under UV and VUV irradiation were easy to be photolyzed and to react with hydroxyl radicals on the catalyst's surface as well.

Fig. 4 showed the time course of intermediates under all different experimental conditions. Under whatever irradiation, the concentrations of intermediates in photocatalysis were much lower than those in photolysis. So an important reaction on the catalyst surface could be removing of the intermediates. This viewpoint could be further proved by TOC removal rates in Table 2, in which the TOC removal rates were much larger in photocatalytic mineralization than those in photolytic mineralization. Hugul et al. [16] pointed that the main intermediates of 4-CP in photolytic and photocatalytic degradation were quinone, hydroquinone, catechol, etc. The color of effluents in all cases were brown, especially those under UV irradiation, which indicated that the intermediate I in Fig. 4 was quinone, and the intermediate II was hydroquinone or catechol.

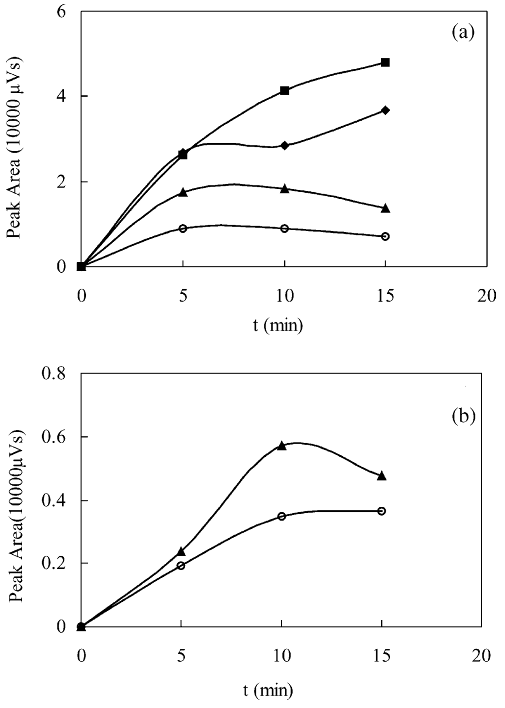


Fig. 4. (a) Intermediate I; (b) Intermediate II. The time courses of intermediates of 4-CP: (■) UVPD; (◆) UVPCD; (▲) VUVPD; (○) VUVPCD.

In addition, under VUV irradiation, other different intermediates were found in photocatalytic and photolytic degradation, which implicated that besides the principle mechanism of VUVPD and VUVPCD, hydroxyl reaction, the direct photolysis of substrate by VUV, could be also an important reaction. Exact mechanisms of photocatalysis and photolysis under VUV illumination need further investigation.

3.2. Photocatalytic degradation of hydroquinone

The decomposition rates of hydroquinone were very similar between photolysis and photocatalysis under whatever irradiation. Compared to 4-CP, hydroquinone was more difficult to be photolyzed under UV irradiation. The catalyst was not efficient to decompose hydroquinone under UV or VUV irradiation. The reason should be ascribed to the competing reaction of intermediates with hydroquinone on the surface of the catalyst.

Fig. 5 showed the time course of the intermediate under different conditions. The orders of the intermediate's concentration and TOC removal rate were consistent with those of 4-CP degradation. The color of effluents under different experimental conditions were all brown, especially those under UV irradiation, which indicated that the intermediate in Fig. 5 was quinone.

3.3. Photocatalytic degradation of 4-NP

Compared to 4-CP and hydroquinone, 4-NP was more difficult either to be photolyzed or to react with hydroxyl

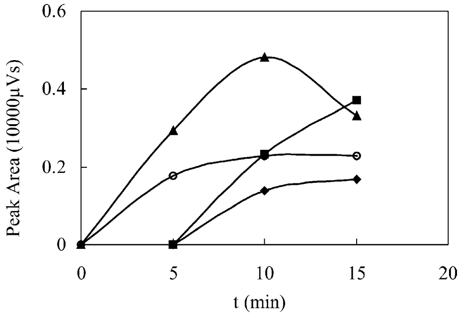


Fig. 5. The time courses of the intermediate of hydroquinone: (■) UVPD; (◆) UVPCD; (▲) VUVPD; (○) VUVPCD.

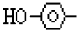
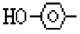
radicals on the catalyst's surface under UV irradiation. However the TOC removal rate in UVPCD process was much greater than that without catalyst, which indicated that decomposition of 4-NP could be the rate-determining step in UVPCD process. However, the catalyst under VUV irradiation was not efficient to decompose or mineralize 4-NP, which implied different reaction mechanisms under UV and VUV irradiation.

No intermediate was detected by HPLC under UV and VUV irradiation. The reason should be ascribed to direct photolysis under VUV illumination or the complex decomposition mechanisms of 4-NP reacting with hydroxyl radical and electrons [15].

3.4. Comparison among three phenols

The results indicated that there was relationship between the degradation rates and the molecular structures of substrates.

The decomposition rate followed the order as 4-CP > hydroquinone > 4-NP.

By direct illumination of the aqueous solutions, organic radicals were generated from photolysis of the substrates. These radical intermediates were subsequently trapped by dissolved molecular oxygen, via the charge transfer complex (CTC), peroxyl radicals ($ROO^{\bullet}$), and thus induced to an enhancement of the overall degradation process [18]. The larger the negativity of substitute groups on the aromatic ring, the lower the decomposition rate obtained. Nitryl had larger negativity than hydroxyl, thus the decomposition rate of hydroquinone by photolysis under UV irradiation was much larger than 4-NP. When the substitute group was halogen on the aromatic ring, the main photolysis mechanism was homolysis of X–C, forming  and $X^{\bullet}$ radical, and the  radical would be further oxidized. The intro-heavy-atom-effect promoted the homolysis of X–C bond. Therefore, the decomposition rate of photolysis under UV irradiation decreased in the order of 4-CP > hydroquinone > 4-NP, which was consistent with the experimental results.

Compared to UVPD process, UVPCD process did not elevate decomposition of the substrates except 4-CP. TiO_2 photocatalyst under UV irradiation was efficient to decompose 4-CP and the intermediates from hydroquinone photolysis, but not hydroquinone or 4-NP. The neglectable effect of TiO_2 photocatalyst for hydroquinone was ascribed to the competing reaction by its intermediate, quinone. The neglectable effect of TiO_2 photocatalyst for 4-NP were ascribed to large negativity of nitryl and big π-system between the nitryl and aromatic ring. The reaction rates of 4-CP, hydroquinone and 4-NP with hydroxyl were 7.6×10^9, 5.2×10^9 and $3.8 \times 10^9\,m^{-1}\,s^{-1}$, respectively. Therefore, the decomposition rate of photocatalysis (including photolysis) under UV irradiation decreased in the order of 4-CP > hydroquinone > 4-NP, which was consistent with the experimental results.

As being mentioned above, the principal decomposition mechanism of VUVPD and VUVPCD was the reaction of substrate with $^{\bullet}OH$ radicals. The decomposition rates of photocatalysis and photolysis under VUV irradiation decreased in the order of 4-CP > hydroquinone > 4-NP, which was consistent with the experiment results.

The TOC removal rates of UVPD were similar between hydroquinone and 4-CP, and the initial rates were very small. It was because their intermediate, quinone, was not easy to be further oxidized in UVPD process. 4-NP had very slow TOC removal rate in UVPD process, which should be ascribed to the difficult photolysis of itself and its intermediate as well.

The TOC removal rates of UVPCD were much greater than those of UVPD, which indicated that the intermediates could be adsorbed and oxidized on the surface of the TiO_2 catalyst. The mineralization rates of UVPCD decreased in the order of hydroquinone > 4-CP > 4-NP, which was different with that of the decomposition rates. 4-CP had various intermediates including hydroquinone, thus needed more steps to be mineralized than hydroquinone. Consequently, the mineralization rate of hydroquinone was greater than that of 4-CP. 4-NP was difficult to be oxidized by hydroxyl radical, and the mineralization mechanism was very complex, so that its TOC removal rate was the smallest.

TOC removal rates of VUVPD decreased in the order: 4-CP > hydroquinone > 4-NP, while TOC removal rates of VUVPCD decreased in the order of hydroquinone > 4-CP > 4-NP. Although additional mechanism of VUVPD and VUVPCD was the direct photolysis of the substrate by VUV, the orders of TOC removal rates were the same as UV processes.

After 15 min decomposition, the photocatalytic and photolytic decomposition rates of 4-CP, hydroquinone and 4-NP under VUV irradiation were 1.13, 3.12, 11.95 times and 1.35, 3.10, 16.6 times of those under UV irradiation respectively. After 60 min mineralization, the values were 1.6, 1.11, 1.84 times and 2.94, 2.65, 8.95 times respectively.

The results indicated that VUV was efficient for decomposition of refractory oxides compounds, such as nitrophenols, while the catalyst was efficient for TOC removal. It was important to choose appropriate process according to different organic compounds.

4. Conclusion

VUV irradiation led to the most efficient degradation of the organics. No significant difference of degradation rate was observed due to TiO_2 catalyst under UV or VUV irradiation except the UV irradiated 4-chlorophenol solutions, which indicated that the main reaction on the catalyst surface was degradation of the intermediates. TOC removal rate followed in the order: VUVPCD > VUVPD > UVPCD > UVPD. There was relationship between the degradation rate and the molecular structures of substrates. The decomposition rates in whichever process decreased in the order: 4-CP > hydroquinone > 4-NP. Photocatalytic mineralization rate decreased in the order: hydroquinone > 4-CP > 4-NP under both UV and VUV irradiation, while photolytic mineralization rate decreased in the order: 4-CP > hydroquinone > 4-NP under VUV irradiation. VUV was efficient for decomposition of refractory compounds, such as nitrophenols, while the catalyst was considerably efficient for TOC removal.

Acknowledgements

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