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ULTRASONIC EFFECT ON THE PHOTODEGRADATION OF 2,4-DICHLOROPHENOL WASTEWATER

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ABSTRACT

Chlorophenols (CPs) is one of the organic pollutants and are most widespread in aqueous environment. Advanced oxidation processes (AOPs) have been extensively utilized for the decomposition of hazardous or recalcitrant pollutants in the environment. The study combined UV/TiO₂ with ultrasonic procedure to degrade 2,4-dichlorophenol (2,4-DCP) wastewater. The effects of factors including pH value, initial concentration of 2,4-DCP and quantities of TiO₂, Fe (II), and Fe (III) added on the removal efficiency of 2,4-DCP wastewater were investigated. Experimental results revealed significant additive effect attributed to the combination of two procedures, 13-watt UV irradiation and 10-watt ultrasound, under the pH 10 and 1g L⁻¹ TiO₂. In additional, the destruction removal efficiency (DRE) of 2,4-DCP was raised about 10 % when 250 μ M of Fe (II) and Fe (III) were added and this phenomenon was suggested that the Fenton-like reaction occurred.

Keywords: Titanium dioxide, Ultrasonic procedure, Advanced oxidation processes (AOPs), 2,4-dichlorophenol, Wastewater, Fenton-like.

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Contribution/ Originality

This study uses new estimation methodology to combine the advantages of ultrasonic procedure and photodegradation procedure of TiO_2 to treat 2, 4-DCP wastewater. In this study, the low ultrasonic energy was used and the Fenton-like reaction occurred to raise about 10 % destruction removal efficiency.

1. INTRODUCTION

Chlorophenols (CPs) is one of the organic pollutants and are most widespread in aqueous environment. They usually come from the water disinfection, industrial effluent and other artificial activities. Common control techniques for CPs include combustion, adsorption, biological treatment and air stripping etc. Advanced oxidation processes (AOPs) have been extensively utilized for the decomposition of hazardous or recalcitrant pollutants in the environment. Various AOPs such as UV/semiconductor procedure, ultrasonic procedure, ozone oxidation, and Fenton processes are the more mature technologies under development currently, but these processes have limitations. Titanium dioxide (TiO₂) photocatalyst, with advantages including photostability, non-toxicity, affordable price, and insolubility in water, has been studied and used by both industrial and academic communities (Cheng *et al.*, 2008; Chang *et al.*, 2009; Hsieh *et al.*, 2009; Cheng *et al.*, 2010a; Shen *et al.*, 2011). Ultrasonic procedure was employed to treat wastewater because its treatment efficiency is less affected by turbidity and colors of wastewater. Moreover, it does not incur separation problem following the treatment, and does not require

chemicals to be added. In view of these benefits, the ultrasonic procedure is an AOP with great potential. Previous studies discovered that the combination of ultrasonic procedure and UV/TiO₂ procedure showed excellent additive treatment effects (Kau and Singh, 2007; Kritikos *et al.*, 2007; Kazuhiko *et al.*, 2008; Maezawa *et al.*, 2007). However, previous research employed ultrasonic output of higher energy and most focused on the dye wastewater. The present study used ultrasonic output of lower energy (10 W in 800 mL of solution) to examine whether there exists a threshold for the additive effect between the two reactions, and to further clarify the causes of the additive effect. The ultimate objective of this research is to combine the advantages of the two procedures for enhancing treatment efficiency of 2, 4-DCP wastewater.

2. EXPERIMENTAL DETAILS

2.1. Materials

The reagents such as tetraisopropyl orthotitanate (TTIP) used in the preparation of catalysts, 2,4-DCP (Sigma) and all the other chemicals of analytical reagent grade used in the present study were purchased from Merck Co., Riedel-del Haen Co., Sigma, and J.T. Baker. The deionized water ($\geq 18M_{cm}^{-1}$) used for preparing the chemical solutions was processed by the Milli-Ultrapure R/O System (Millipore, USA) to ensure the quality of the prepared solution.

2.2. Procedure

2.2.1. Preparation of TiO₂ Photocatalyst

First, the TiO₂ photocatalyst was prepared using the modified sol-gel method (Cheng *et al.*, 2010b). Ti(OC₃H₇)₄, C₃H₇OH, and CH₃COOH of molar ratio 1:2:8 were added into the Erlenmeyer flask, which was sealed with a parafilm, and stirred for 8 hours on the stirrer to form the soluble gel. The gel produced was dried in the oven at 105 °C for 1 hour to remove water and solvents, and then at 150 °C for another hour. The gel was cooled, ground coarsely, and baked in the oven at 550°C for 90 minutes to eliminate any excess or unreacted organic substances and to form TiO₂ crystals. After the final cooling process, the crystals were ground in the agate mortar to produce the powder of the TiO₂ photocatalyst.

2.2.2. Experimental Setup

A self-designed liquid-phase photocatalytic system was employed in this study. The photocatalytic system comprised a 365-nm packed UV light (13W) positioned at the central core (z-axis) in an annular tube, a 1-L circular mixing and reaction chamber, a probe sonicator, a magnetic stirrer, and a cooling water system. The setup was placed in the reaction cabinet of 80 cm high, 66 cm wide and 55 cm deep. The reaction cabinet comprised an angle steel frame with black UV-resistant screens on each side of the cabinet. The front side was covered with a movable screen to prevent interference from outside light radiation. The experimental setup was illustrated in Fig. 1.

2.2.3. Ultrasonic/ Photocatalytic Reaction

The present liquid-phase photocatalytic system was employed to investigate the oxidation process in completely mixed batch reactions under various experimental conditions. The experimental parameters included pH values, initial 2,4-DCP concentrations, and amounts of TiO₂, Fe (II), and Fe (III) added. First, 25 mg L⁻¹ 2,4-DCP solution was prepared to the designed concentrations and then poured into the reaction chamber, followed by the adjustment in pH value using HClO₄ and NaOH. The required amount of photocatalyst was added and the mixture was stirred for 10 minutes in the dark to allow the reaction to reach adsorption equilibrium. The UV light was turned on and the reaction proceeded at the stirring rate, temperature, light intensity and ultrasonic intensity

designed for the experiment. All samples collected at different reaction times were analyzed by the High Performance Liquid Chromatography-Ultraviolet Detector (HPLC-UV; Agilent Co., Model HP1100 Series) equipped with the LC-8 column (25 cm x 4.6 mm, 5 μ m, Supelco, Inc.). The buffer solution containing 0.1M acetic acid, 58% CH₃CN and deionized water was used as the eluent for HPLC to determine the yield of 2,4-DCP. The other indicator of photocatalytic activity was mineralization of 2,4-DCP analyzed using TOC (total organic carbon, TOC-V_{CSN}, Shimadzu, Japan).

3. RESULTS AND DISCUSSION

3.1. Photocatalyst Properties

The FE-SEM images of TiO₂ photocatalysts at magnification of 100,000 times is shown in Fig.2. As seen clearly, TiO₂ photocatalysts existed homogeneously as round granules and the diameters of were estimated to be approximately 10~20 nm. The specific surface areas of the photocatalysts were analyzed by BET instrument (Micromeritic ASAP 2010) and the size was 108 m² g⁻¹. The result reveals the prepared photocatalysts had bigger reaction surface areas and the better efficiency might be occurred. At the same, the photocatalysts prepared by the modified sol-gel method were analyzed by the XRD (MAC MXTIII) to examine the crystals form. As illustrated in Fig. 3, the main peak appears at the 2 θ values of 25.4 at the scanning rate of 40.0 KV, 150 mA and 1.0 deg min⁻¹. In the JCPDS database (No. 21-1276 and 21-1272), the three major diffraction peaks of anatase crystal structure appear at the 2 θ values of 25.4, 37.9 and 48.2 (with respect to the diffraction surfaces of 101, 200 and 004, respectively). Therefore, the crystal structure of all the photocatalysts prepared in the experiment was anatase and there was no variation during preparing procedure.

3.2. Background Tests

3.2.1. Direct Photodegradation

To determine whether direct photodegradation excessive to the oxidation efficiency of the entire system would affect the accuracy and credibility of the study on photocatalytic reaction, the photocatalyst was not added in this part of the experiment. The irradiation of a UV lamp at the wavelength of 365 nm was used. The experimental conditions were: 2,4-DCPat the concentration of 25 mg L⁻¹, temperature of 25 °C, and direct photodegradation at pH 4, 7 and 10 in the reaction chamber for 240 minutes. The result showed that there was no significant DRE under acidic, neutral and basic conditions. Therefore, the effect of direct photodegradation was not taken into consideration in the following experiment, which did not affect the interpretation of the data acquired.

3.2.2. Independent Ultrasonic Degradation

To determine the effect of ultrasonic procedure on the entire system, the experiment was conducted for 240 minutes in the dark at pH 4, 7 and 10, 2,4-DCP at the concentration of 25 mg L⁻¹, temperature of 25 °C, TiO₂ of 1 g L⁻¹, and ultrasonic output of 10 watts. The result indicated that the DRE of 2,4-DCP were approximately 43 % under basic conditions and the following experimental data were based on this data to be deducted.

3.3. Combination of UV/TiO₂ and Ultrasonic Procedure

In this part of the experiment, the reaction conditions included 25 mg L⁻¹ 2,4-DCP, pH 10, temperature of 25°C, 10-watt ultrasonic output and TiO₂ of 1 g L⁻¹. The variations in DRE thus obtained are illustrated in Fig. 4. As can be seen, the treatment efficiency of the combined procedure was superior to the sum of the two individual treatments and reached to 91%. This result indicates the presence of additive effect and was identical to that obtained by combining the ultrasonic procedure and UV/TiO₂ to degrade Acid Orange 52, Reactive Red 198, and

Reactive Black 5 dyes in previous studies (Kau and Singh, 2007; Kritikos *et al.*, 2007; Maezawa *et al.*, 2007). Since the rate of the heterogeneous photocatalysis system varies with the mass transfer, it was hypothesized that the ultrasonic procedure caused the compression of the electric double-layer, thus facilitating the diffusion and adsorption of pollutant molecules on the surface of TiO_2 and their degradation by electric holes and hydroxyl radicals. As a result, the rate of desorption of the intermediate or final products from the surface of TiO_2 was improved, thus accelerating the overall reaction. Moreover, if the asymmetric collapse of the cavitation bubbles occurred on the surface of the catalyst, a local high pressure was able to remove the adsorbents on the TiO_2 surface while generating micro-streaming at the same time to bombard the TiO_2 surface, leading to the purging effect for the activation of functional groups on the surface (Mrowetz *et al.*, 2003; Gogate and Pandit, 2004; Shimizu *et al.*, 2007; Kazuhiko *et al.*, 2008; Hsieh *et al.*, 2009).

3.4. Effect of Addition of Photocatalyst

The degradation of 2,4-DCP is dependent on the direct oxidation by electric holes or indirect oxidation by hydroxyl radicals formed indirectly on the TiO₂ surface. As a consequence, the more TiO₂ was added, the more reaction sites became available, and the more electric holes and hydroxyl radicals are generated, thus enhancing the treatment efficiency. The objective of the present study was to identify the optimal quantity of TiO₂ added according to economic consideration. This part of the experiment was carried out under the following conditions: initial 2,4-DCP concentration of 25 mg L⁻¹, pH 10, temperature of 25 °C, and 10-watt ultrasonic output. The variations of DRE are illustrated in Fig. 5. As can be seen, when the TiO₂ added was increased from 0.25 g L⁻¹, the DRE of 2,4-DCP was improved from 22% to 57%. When the amount of TiO₂ added was increased to 1.0 g L⁻¹, the DRE of 2,4-DCP was further reached to the maximum. However, when the amount of TiO₂ added was increased from 1.0 g L⁻¹ to 2.0 g L⁻¹, the DRE of 2,4-DCP dropped by 13%. It was speculated that excessive amount of TiO₂ added to the solution caused shielding of the UV light. Thus, both the light path and amount of TiO₂ available for UV radiation were reduced, resulting in a decrease in overall treatment efficiency.

3.5. Effect of Initial Concentration of 2,4-DCP

To investigate the influence of various initial concentrations of 2,4-DCP on the photocatalytic activity, the experiment was conducted in a reactor for 240 minutes at the initial concentrations of 2,4-DCP of 10 mg L⁻¹, 25 mg L⁻¹, 50 mg L⁻¹, and 100 mg L⁻¹, pH 10, temperature of 25 °C, TiO₂ of 1 g L⁻¹, and 10-watt ultrasonic output. Fig. 6 illustrates the DRE of 2,4-DCP was enhanced with decreasing initial concentration. The suggestion is that the oxidative species, such as hydroxyl radicals, were not only enough but also completely destruct all of the 2,4-DCP molecules in this experimental conditions. In addition, the higher the concentration, the more the intermediates were formed in the reaction. These intermediates could absorb UV light or compete for being adsorbed on the active functional groups of the TiO₂ surface, thus reducing the treatment efficiency. Therefore, the lower the concentration of pollutants or the fewer the intermediates derived from the pollutants, the higher the photo-activity of the photocatalyst would be.

3.6. Effect of pH

In general, the yield of hydroxyl radicals in the photocatalytic reaction increases with increasing pH of the aqueous solution and it usually produces the higher removal of organic pollutants. However, the distribution ratios of the intermediates produced in the solution were directly related to the pH values. Moreover, the pH value alters the electrical behavior on the surface of the photocatalyst leading to changes in the absorption and desorption properties and capabilities of the intermediates produced by the catalyst. Therefore, the control of pH was very

important for the overall treatment efficiency during the operation. This study investigated the photocatalysis of 2,4-DCP solution under acidic, neutral and basic conditions. Figure 7 illustrates the DRE of 2,4-DCP after 240 min of ultrasonic-photocatalytic reaction. As can be seen, the DRE of 2,4-DCP was higher under basic conditions. The result coincided with previous studies (Fabbri *et al.*, 2006; Aal *et al.*, 2008; Karunakaran and Dhanalakshm, 2008; Kazuhiko *et al.*, 2008; Dhanus and Kiyoshi, 2010; González *et al.*, 2010; Temel and Münevver, 2011; Liu *et al.*, 2012). For explaining this phenomenon, because the pH_{zpc} value of TiO₂ is 6.4, therefore, the TiO₂ surface carries a positive charge at pH below 6.4. However, more and more oxygen ions dissociate from the TiO₂ surface at pH above 6.4, causing a negative charge to develop on the catalyst surface. The substances formerly attached to the catalyst surface as a result of electrostatic adsorption begin to leave the catalyst under the influence of electric repulsion between the substances and the catalyst, thus lowering the oxidation/reduction rate of the reactants. Therefore, the ionic reactants are more affected by the pH of the environment due to electrostatic interaction. The

pKa value of 2,4-DCP is 7.89 (
$$C_6H_3Cl_2OH \rightarrow C_6H_3Cl_2O^- + H^+$$
, $pK_a = 7.89$). When the pH value of the

solution is higher than its pKa, it exists mainly in ionic form and is more affected by the electric nature of the TiO_2 surface. More 2,4-DCP is adsorbed on the TiO_2 surface at pH between the pKa of 2,4-DCP and the pH_{zpc} of TiO_2 due to electrostatic attraction. The absorption process is the first step in the photocatalytic reaction mechanism. Therefore, the conversion rate of 2,4-DCP increases with increasing opportunities for hydroxyl radicals to attack 2,4-DCP. However, the amount of 2,4-DCP adsorbed decreases due to the increase in negative charge on the TiO_2 surface and the formation of repulsion to the negatively charged 2,4-DCP ions ($C_6H_3Cl_2O^-$) after dissociation at pH higher than pH_{zpc} . As a consequence, the 2,4-DCP ions ($C_6H_3Cl_2O^-$) adsorbed are less likely to be attacked by hydroxyl radicals in the photocatalytic reaction, leading to decrease in oxidation intermediates with increasing pH.

3.7. Effect of Addition of Fe (II) and Fe (III)

Previous studies (Papadaki *et al.*, 2004; Vassilakis *et al.*, 2004; Abu-Hassan *et al.*, 2006) indicated that about 8 mg L⁻¹ of hydrogen peroxide was formed after the sonication of pure water for 120 minutes at the ultrasonic frequency of 20 to 80 kHz and the output power of 125 to 150 W. Furthermore, the concentration of hydrogen peroxide decreased in the presence of matrix in water. Since both the UV/TiO₂ and ultrasonic procedures were able to produce hydrogen peroxide, the present study added Fe (III) and Fe (II) in the reaction to induce the Fenton-like reaction in order to achieve better treatment efficiency. This part of the experiment was conducted in the reactor for 240 minutes at 25 mg L⁻¹ 2,4–DCP, 25°C, 1g TiO₂ photocatalyst, 10-watt ultrasonic output and 250 μ M of Fe (II), 250 μ M of Fe (III), but pH was not adjusted (original pH of 6.7). The experimental results are shown as Fig. 8. Although the higher pH can raise the ultrasonic-photocatalytic effect, but it also easily occur the precipitation of Fe ions. For this reason, the pH value didn't be adjusted. According to the experimental results, the Fenton-like reactions seemed to be induced and the 8 and 13% efficiency were raised when the Fe (II) and Fe (III) were added respectively. However, the ultrasonic output energy and the light intensity in this experiment were too low to produce the enough hydrogen peroxide; otherwise, the Fenton-like phenomenon will be obviously and the efficiency will be higher.

4. CONCLUSIONS

This research combined low-energy ultrasonic output with the UV/TiO₂ procedure to degrade the harmful 2,4-DCP. Experimental results on the optimal quantity of photocatalysts added and concentration of 2,4-DCP showed that higher treatment efficiency was achieved by adding 1.0 g L⁻¹ of TiO₂ and at the initial 2,4-DCP concentration of 25 mg L⁻¹ under the basic condition. Furthermore, this study attempted to produce the Fenton-like effect by the

addition of Fe ions to improve the overall treatment efficiency. The results gave a good answer, Fenton-like effects seemed to be induced and about 10% efficiency was raised. It was also found that the treatment efficiency of Fe (II) was superior to that of Fe (III) under the same conditions.

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Contributors/Acknowledgement: All authors contributed equally to the conception and design of the study.

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Fig-2. SEM image of TiO2 photocatalysts prepared by modified sol-gel method (magnification 100,000 times)



Fig-5. Amount effect of photocatalyst on the DRE of 2,4-DCP $\,$



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