

Investigation of Intermediate Compounds of Phenol in Photocatalysis Process

D. T. T. Trinh, S. T. T. Le, D. Channei, W. Khanitchaidecha, and A. Nakaruk

Abstract—Determining the degradation mechanism of phenol under illumination of titanium dioxide (TiO_2) is main task in this present work. The experiment carried out with 100 ppm of phenol solution and 0.9 g/L TiO_2 under UV-C light. The COD and UV-Vis measurement were applied in the present work to evaluate the efficiency of phenol removal. The results showed that photocatalysis removed effectively phenol from water after 24 hours of UV-C illumination. In the first 16 hours, there was a slight decrease in the COD value. However, it decreased dramatically after 24 hours of illumination. Similarly, the result from UV-Vis spectrophotometer also showed the same reduction of phenol peak. These proved that the photocatalytic degradation of phenol include two main phases. Phenol was transformed to by-products in the intermediate compound phase. Subsequently, these intermediate compoundss were removed from water under the form of carbon dioxide and water in the mineralization phase. Therefore, it is necessary to identify intermediate phase of phenol photodegradation in the further work.

Index Terms—Phenol, titanium dioixde, photodegradation, intermediate compounds.

I. INTRODUCTION

The presence of organic compounds in aqueous environment has caused several serious problems. Among recalcitrant organic compounds, phenol is considered generally to be one of the most toxic organic pollutants which cause several environmental problems [1]. The phenol pollution can come from various pollution sources such as paint, pesticides, coal conversion, polymeric resin, petroleum and petrochemical industries [2]. In aquatic environment, phenol is harmful to organisms at low concentration due to its toxicity, persistence and bioaccumulation. Additionally, it can also effect on human health, including fainting, vomiting, headache and paralysis, when people expose to phenol polluted water [3]. Additionally, potential carcinogenic compounds may be formed during disinfection and oxidation processes that cause health problem relating to mutation [4].

Therefore, the phenol removal is a considered issue for current researches. In past decades, several technologies have been used and showed their efficiency in phenol removal. However, stabilization and solubility of phenol in water are obstacles in treatment processes. Conventional methods such as solvent extraction, activated carbon adsorption, common chemical oxidation, biodegradation and ion exchange have serious drawbacks including high cost or formation of hazardous by-products in phenol treatment [5]-[7]. Consequently, advanced oxidation processes (AOPs) are promising techniques to handle with phenol contaminated waters.

In recent years, AOPs are considered as optimum alternative methods that have received much attention in the phenol removal. The main principle of AOPs are based on using hydroxyl radicals (OH^\bullet) which are known as one of the most powerful oxidizing species, these radicals oxidize strongly contaminants exist in water [8]. Among AOPs, the photocatalytic process using semiconductor catalysts has been demonstrated as an effective method in decomposing organic pollutants into biodegradable matters, and/or mineralizing completely to carbon dioxide (CO_2) and water (H_2O) [9]. The basic mechanism of photocatalytic process is that semiconductor catalysts are excited under UV illumination leading to the movement of electrons from valence band to conduction band. This results in the formation of electron-hole pairs at the surface of catalyst. These electrons and holes continue to react with water and oxygen molecules to yield strongly oxidizing free radicals as OH^\bullet and superoxide species (O_2^\bullet). The reactive agents then attack molecules of organic compounds in water and cause hydroxylation, oxidation, and mineralization in forming final products of carbon dioxide (CO_2) and water (H_2O) [10], [11]. Therefore, the semiconductor catalyst is an important part of photocatalytic process. Zinc oxide (ZnO), cadmium sulfur (CdS), zinc sulfur (ZnS), titanium dioxide (TiO_2), ferric oxide (Fe_2O_3), gallium phosphide (GaP) are typical semiconductor catalysts which often applied in photocatalytic process [12]. Among of them, titanium dioxide (TiO_2) is one of the most effective catalyst because its advantaged abilities such as non-photocorrosive, non-toxic, high oxidation and chemical stability [13], [14]. In addition In addition to these advantages, TiO_2 catalyst has been proved to be the most active catalyst in earlier researches [15], [16].

Therefore, the aim of the present work was to investigate the photodegradation of phenol via chemical oxygen demand (COD) and UV-Vis measurement. In addition, the study also conducted experiment with different dosage of TiO_2 to find the optimum concentration for phenol degradation.

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II. METHODOLOGY

Photodegradation of phenol was carried out in batch reactor. 0.1g of phenol solid was dissolved in 1 L of distilled water to make phenol solution. The present work used commercial TiO₂ powder from Sigma-Aldrich as main catalyst in phenol photodegradation. The characteristic of TiO₂ powder were described in the Table I [17].

TABLE I: SOME PROPERTIES OF COMMERCIAL TiO₂ PARTICLES

Parameter	Value
Anatase (%)	95.97
Rutile (%)	4.03
Particle size (nm)	400
Specific surface area (m ² /g)	9.73
Band gap (eV)	3.74

Beakers contained 50 mL of phenol solution with suspended TiO₂ powders. In the present work, 215 nm of UV-C light was used to illuminate the suspended solution. Besides, magnetic stirrer operated with the rate of 100 rpm to avoid the settling of TiO₂ particles during photodegradation of phenol. Before measurement, the phenol solution containing TiO₂ were centrifuged for 15 min at 5000 rpm.

The effect of catalyst concentration on photodegradation of phenol was examined to find out the optimum concentration by using different concentrations of TiO₂ ranging from 0.01 to 2.00 g/L.

The optimal dosage of TiO₂ was then used to degrade phenol solution under the following conditions: in the presence of UV light with and without TiO₂, and in the combination of TiO₂ and UV light.

The efficiency of phenol removal was evaluated via COD measurement by COD analyzer. Additionally, the present work also used UV-Vis spectroscopy (UV-6100 Double Beam Spectrophotometer) to measure the absorption of phenol solution. Basing on the measured spectrum, the degradation of phenol was evaluated through the absorbance peak at 270 nm [18].

III. RESULTS AND DISCUSSION

The removal efficiency of the concentration of TiO₂ on phenol photodegradation is illustrated in Fig. 1. It clearly indicates that the degradation of phenol increases with increasing concentration of TiO₂ and reaches optimal concentration at 0.9 g/L. On the other hands, the efficiency of phenol photodegradation is reduced slightly at higher concentration of catalyst (e.g., 2 g/L). The explanation of this phenomenon is that the penetration of light will be decreased by the suspension of catalyst at high concentration [19]. Therefore, the present work applied 0.9 g/L of TiO₂ concentration for further experiments.

Fig. 2 shows the degradation of phenol under different conditions as mentioned in the methodology section. The results indicated that phenol was only degraded under the combination of TiO₂ and UV light. In the meantime, phenol was also absorbed around 5% on the surface of TiO₂ particles. For only UV illumination, there is no any reaction occur over the time. This is because phenol contains a benzene ring which is known as the highly-stable structure resisting to decomposition reactions.

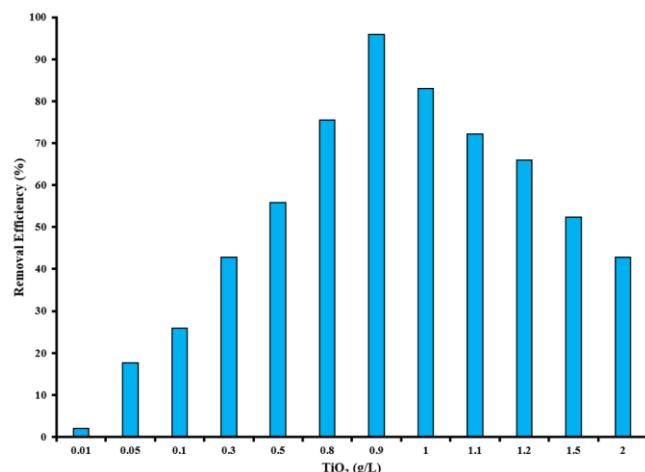
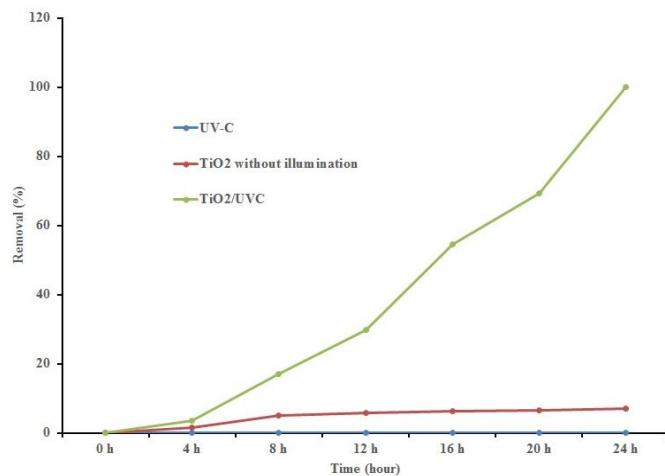
Fig. 1. The removal efficiency of phenol with different concentration of TiO₂.

Fig. 2. Degradation of phenol under different conditions.

In the next step, the COD value was measured at every 2 hours, as shown in Fig. 3. The data shows that the COD value slightly decreased during the first 16 hours of illumination. This means that only a little phenol has been removed from water under the form of carbon dioxide (CO₂). However, the COD value reduced dramatically and reaches around 40 mg/L after 24 hours of illumination. This reveals that there are 2 phases in the photodegradation mechanism of phenol. The first phase is intermediate compound phase, in which phenol is degraded into intermediate products. After that, intermediate compounds continue to be oxidized and reach final products as carbon dioxide (CO₂) and water (H₂O) in the mineralization phase.

The COD results are confirmed by UV-Vis measurement, as illustrated in Fig. 4. Similarly, the reduction mechanism of COD also occurred to the absorbance peak of phenol at 270 nm. For 16 hours of illumination, the phenol peak slowly decreased. However, it decreased quickly and disappears after 24 hours of illumination. It has to be noted that there are the presence of red shifts at around 300 nm of wavelength during photodegradation of phenol. The red shifts appeared only after 2 hours of illumination. It continued to increase until 12 hours of illumination, but there are the decreases of these shifts after 16 hours. These changes of red shifts proved more clearly that phenol underwent intermediate compounds phases before it was removed completely from water.

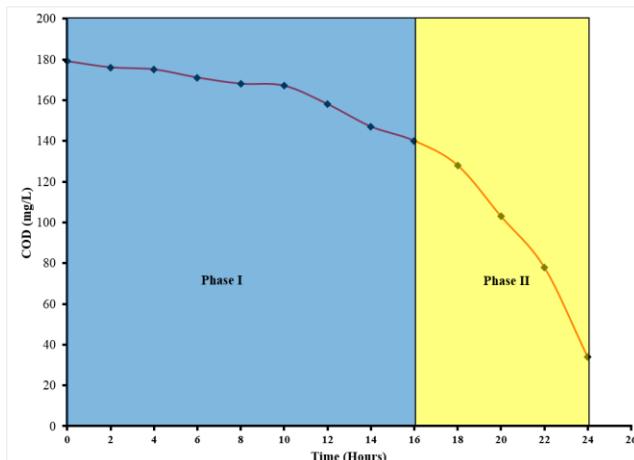


Fig. 3. The COD results of phenol solution at every 2 hours.

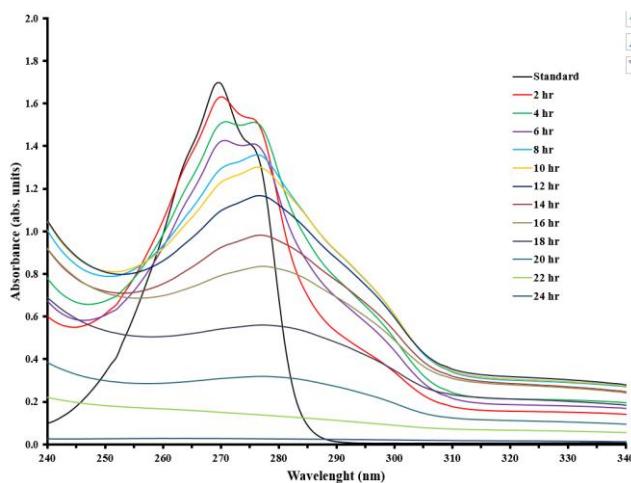


Fig. 4. The absorption spectrum of phenol at various illumination time.

These results reflected complex reaction mechanism in the degradation of phenol by photocatalysis using TiO_2 catalyst that preliminarily reported in previous researches as shown in Fig. 5. This has contributed to prove that there are two main phases in the photodegradation mechanism of phenol including intermediate phase and mineralization phase.

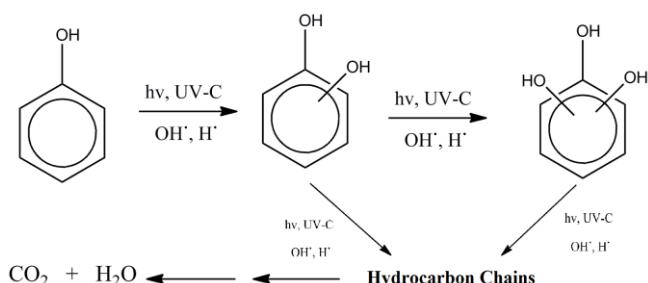


Fig. 5. The possible degradation mechanism of phenol in photocatalysis.

In the intermediate phase, phenol can transform into compounds such as catechol, benzoquinone or resorcinone by the addition of OH group at *ortho* or *para* position. As a result, ring-opening reactions subsequently happened leading to the formation of hydrocarbon chains. Due to weak energy of C-H, H-O, C-O, these organic short-chains were oxidized easily to carbon dioxide and water [20]. These are considered as complete mineralization phase of phenol. Therefore, it is recommended that intermediate compounds in phenol photodegradation need to be identified more clearly in the further work.

IV. CONCLUSIONS

The photocatalytic process using commercial TiO_2 powders can remove phenol from water after 24 hours of illumination. The found adequate concentration of TiO_2 is 0.9 g/L for 100 ppm of phenol solution. Due to the highly-stable structure, phenol was only decomposed by TiO_2 catalyst under illumination of UV light. The COD measurement showed that COD value decreased slightly in the first 16 hours of illumination, but it reduced rapidly after that. This occurred similarly to the result of UV-Vis spectrum. Therefore, it can be concluded that the photodegradation of phenol include two phases. In the intermediate phase, by-products were generated from direct oxidation of phenol including aromatic compounds and hydrocarbon chains. Subsequently, these intermediates were completely mineralized to carbon dioxide and water in mineralization phase. Therefore, the investigation of intermediate phases needs to be studied more clearly in the further work.

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