

INVESTIGATION OF PHOTOCATALYTIC DEGRADATION OF PHENOL USING TITANIUM DIOXIDE PARTICLES

D.T.T. TRINH ^{1,2}, S.T.T. LE ^{1,2}, W. KHANITCHAIDECHA ^{1,2} AND A. NAKARUK ³

¹Department of Civil Engineering, Faculty of Engineering

²Centre of Excellence for Innovation and Technology for Water Treatment

³Department of Industrial Engineering, Faculty of Engineering
Naresuan University, Phitsanulok 65000 Thailand

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ABSTRACT

The commercial TiO₂ particles were used in the present work to investigate the photocatalytic degradation (photodegradation) of phenol solution with 100 ppm of concentration in an aqueous suspension of TiO₂ under UVC (215 nm) light irradiation. The commercial TiO₂ was analysed using X-ray diffraction (XRD), surface area analysis (BET), and dynamic light scattering (DLS), in order to obtain important parameters. The results indicated that the commercial TiO₂ consisted of 96% of anatase and 4% of rutile. Further, the data also revealed that the particle size was 400 nm and the specific surface area was 9.73 m²/g. The photodegradation was done under UV irradiation for 24 hours. The evaluation of photocatalytic efficiency was done by measuring the absorbance peak of phenol at 270 nm using UV-VIS spectroscopy. The absorbance spectra of phenol's peak indicated that after 12 hour of irradiation time the phenol's peak decreased approximately 50%. In the meantime, the red shift of absorbance peak also appeared. This means the degradation of phenol occurred during the irradiation process. However, the absorbance peak decreased dramatically after 16 hours of irradiation. In addition, the COD data confirmed the mentioned results by showing that the COD concentration of phenol solution slightly decreased from initial condition to 12 hours of irradiation time and decreased dramatically after 16 hours of irradiation. All the results in proved that phenol can be removed using photocatalytic of TiO₂. Additionally, the intermediate phase of phenol during the degradation process might be considered in the further work.

INTRODUCTION

At the present time, phenol and its related compounds have been widely used in industrial applications. However, phenol and its related compounds are very

toxics. Even at very low concentrations; it can impact ecosystems and human health. Further, the present of phenol in waters is highly dangerous because carcinogenic compounds as chlorophenols can be formed during disinfection and oxidation processes

* Corresponding author's email : auppathamn@nu.ac.th

(Hasanoglu, 2013). Many literature reviews indicated that drinking phenol contaminated water can cause mouth sores, nausea, and dark urine. In addition, high doses of phenol is known to cause mucosal necrosis in the mouth, vomiting, esophagus stomach pain, and bloody diarrhea are more dangerous diseases (McCall *et al.*, 2009). Therefore, the phenol removal from water is one of the most important issues at the moment.

Currently, the conventional methods such as activated carbon (Giraldo and Moreno-Piraján, 2014), membrane filtration (Ipek *et al.*, 2012), and ion exchange (Yamada *et al.*, 2013) have shown the high in phenol removal. However, mentioned techniques can generate solid wastes which are required the further treatment. On the other hands, photocatalytic process using titanium dioxide (TiO₂) and UV light has been emerged as a promising technique for the photodegradation of organic pollutants (Saratale *et al.*, 2014). Briefly, electro-hole pair is generated by irradiating semiconductor with UV light. These charge carriers migrate to the particles surface and react to form hydroxyl radicals. With strong oxidizing ability, hydroxyl radicals can decompose most organic contaminants into carbon dioxide and water (Konstantinou and Albanis, 2004). Although, there are several semiconductors (ZnO, Fe₂O₃, CdS, GaP and ZnS), TiO₂ is the most widely used catalyst because of its photostability, non-toxicity, low cost and water insolubility under most environmental conditions (Chong *et al.*, 2010).

Therefore, in the present work, the commercial TiO₂ particles have analysed basic properties before using. The photocatalysis process was used to investigate the required time to remove phenol from water and the processes occurred during irradiation by degradation of phenol's peak and COD test.

METHODOLOGY

The commercial TiO₂ particles supplied from Sigma-Aldrich (Reagent grade) were used in this research as a source of TiO₂. The particles was basically analysed on mineralogy, particle size, and specific surface using X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS) and Brunauer-Emmett-Teller (BET), respectively.

The 100 ppm of phenol solution was used as a standard phenol, prepared by dissolving 0.1 g of phenol in 1 L of distilled water. The TiO₂ particles were added into phenol solution at 2 g/L of concentration. The suspended solution was irradiated under 215 nm

of UV light up to 24 hours. The phenol removal efficiency was evaluated by measuring the absorbance peak at 270 using UV-VIS spectroscopy (Zhang *et al.*, 2000). In addition the COD of solution was also measured using COD analyser.

RESULTS AND DISCUSSION

The XRD pattern of commercial TiO₂ particles is presented in Figure 1. It is clearly indicated that the commercial TiO₂ consisted of anatase and rutile phases of titanium dioxide. The actual percentage can be calculated using XRD data (Nakaruk *et al.*, 2010), the result is shown in Table 1. The size of particles and specific surface area also are shown in Table 1.

Table 1. Summary 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

It is known that phenol obtained the absorption peak at 270 nm (Zhang *et al.*, 2000). Therefore, the reduction of phenol peak can refer to the phenol degradation in the solution. Figure 2 shows the absorption spectra of phenol as a function of irradiation time. It can be seen that the peak at 270 decreased with increasing irradiation time. It has to be noted that the red shift also occurred, this means the phenol degraded to intermediate phases which were not identified in the present work.

Figure 2 suggests that for 4 to 12 hour of irradiation time the phenol decreased linearly. However, after 16 hour of irradiation, the absorption peak decreased dramatically. Phenol completely disappeared after 24 hour of irradiation. Despite, phenol has only 6 atom of carbon, however, the structure of phenol is similar to benzene ring which is known as a highly stable form of hydrocarbon (Tanev *et al.*, 1994; Fukuzumi and Ohkubo, 2013). Then the degradation time was slightly longer comparing to degradation of methylene blue (Lin *et al.*, 2014; Houas *et al.*, 2001).

It has to be noted that the degradation of phenol can be divide into 2 step. Firstly, the phenol degraded intermediate phases. In this step, there was only a few carbon that was removed from solution, as shown in Figure 3. It can be seen that COD was slightly decreased during 12 hours of irradiation time. Second

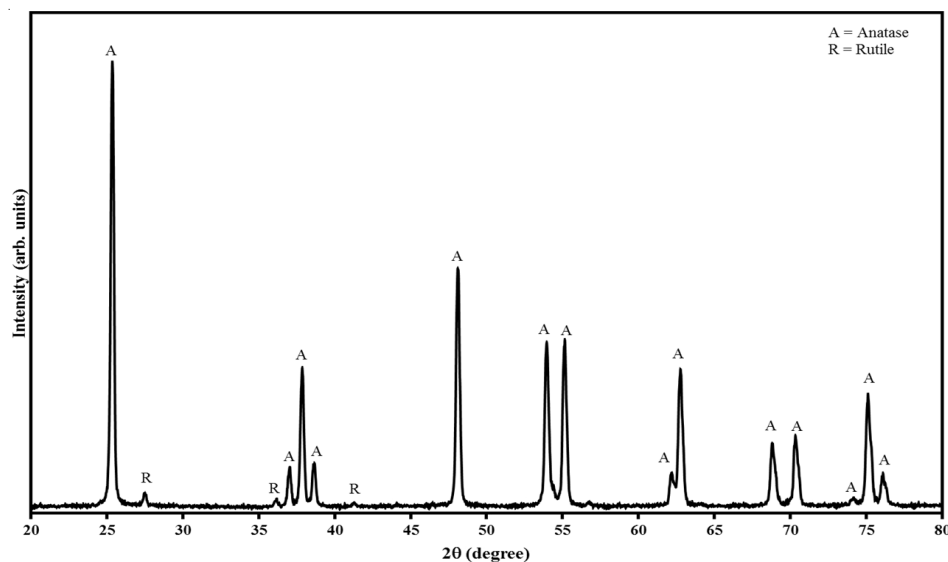


Fig. 1 X-Ray diffraction pattern of commercial TiO_2 particles

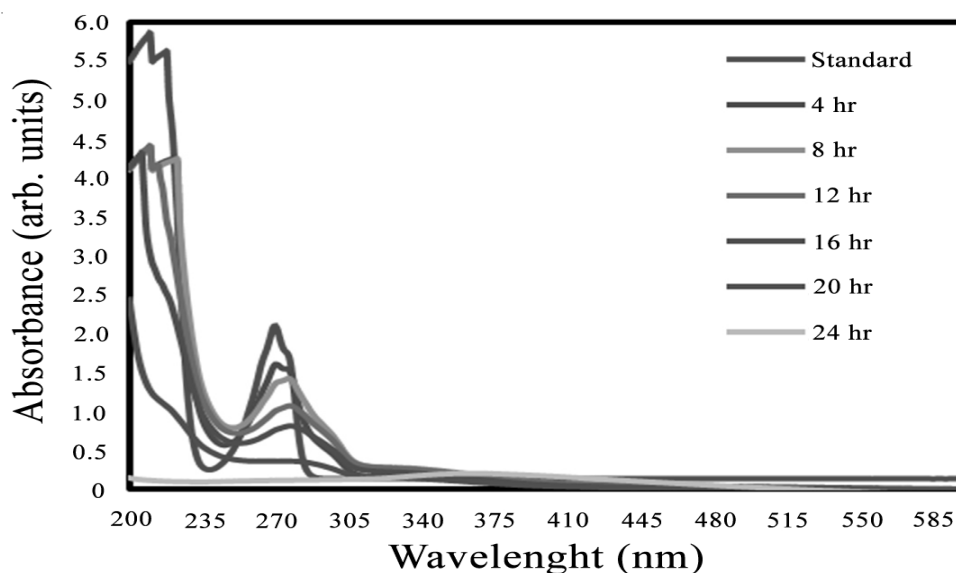


Fig. 2 The absorption spectrum of pure phenol at various irradiation time.

step, after 16 hours of irradiation, COD dropped dramatically, this is because hydrocarbon chain was mineralised into CO_2 form. The result of COD measurement confirmed the UV- VIS test.

CONCLUSION

In the present work, the commercial TiO_2 particles were used as catalyst for photodegradation of phenol. The particles consisted of 96% of anatase phase and 4% of rutile phase. The particle size was 400 nm and the specific surface area was $9.73 \text{ m}^2/\text{g}$. The phenol can

be completely removed after 24 hour of irradiation time. However, the results also indicated two step of photodegradation process that are -

- 1) Creating intermediate phase: during this process the phenol was degraded into other forms, however, there were only a few carbon can be removed from the solution,
- 2) Mineralisation of hydrocarbon: during this step the intermediate phases were mineralised into CO_2 and H_2O . In summary, this work suggest that photocatalysis mechanism was suitable for phenol removal.

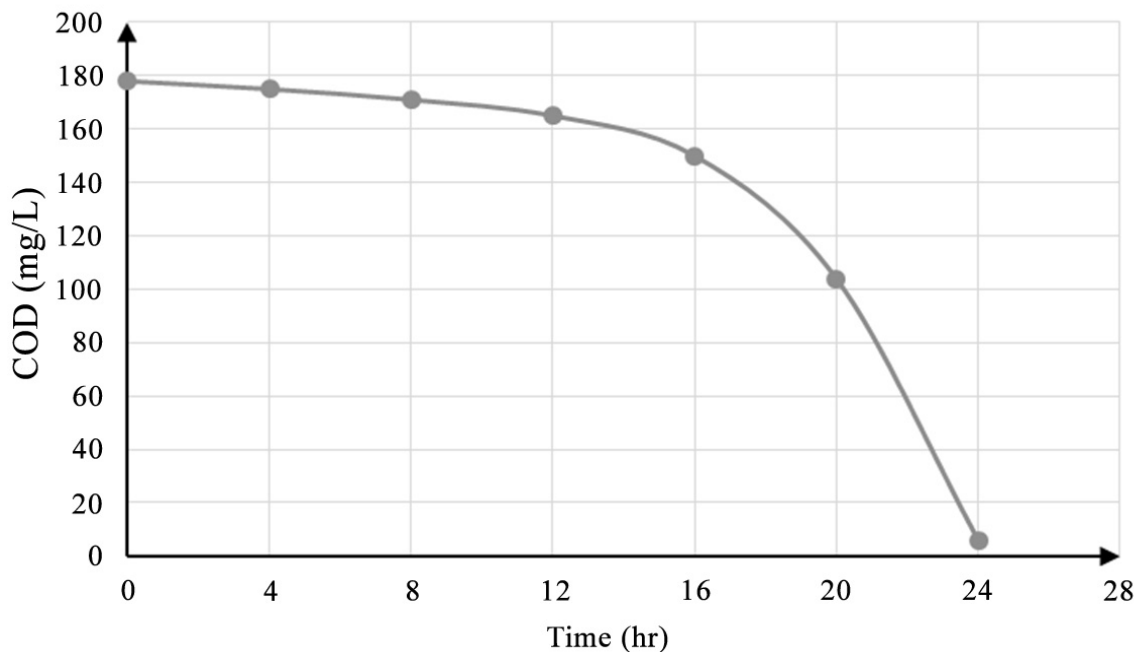


Fig. 3 The COD concentration of phenol at various irradiation times

REFERENCES

- Chong, M.N., Jin, B., Chow, C.W.K. and Saint, C. 2010. Recent developments in photocatalytic water treatment technology. *Water Res.* 44 : 2997-3027.
- Fukuzumi, S. and Ohkubo, K. 2013. Selective photocatalytic reactions with organic photocatalysts. *Chem. Sci.* 4 : 561-574.
- Giraldo, L. and Moreno-Piraján, J.C. 2014. Study of adsorption of phenol on activated carbons obtained from eggshells. *J. Anal. Appl. Pyrolysis.* 109 : 41-47.
- Hasanoglu, A. 2013. Removal of phenol from wastewater using membrane contactors: Comparative experimental analysis of emulsion perturbation. *Desalination.* 309 : 171-180.
- Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C. and Herrmann, J.M. 2001. Photocatalytic degradation pathway of methylene blue in water. *Appl. Catal. B-Environ.* 31 : 145-157.
- Ipek, T.Y., Kabay, N., Yüksel, M., Yapici, D. and Yüksel, T. 2012. Application of adsorption-ultrafiltration hybrid method for removal of phenol from water by hypercrosslinked polymer adsorbents. *Desalination.* 306 : 24-28.
- Konstantinou, I.K. and Albanis, T.A. 2004. TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. *Appl. Catal. B-Environ.* 49 : 1-14.
- Lin, C.P., Chen, H., Nakaruk, A., Koshy, P. and Sorrell, C.C. 2013. Effect of annealing temperature on the photocatalytic activity of TiO₂ thin films. *Energy Procedia.* 34 : 627-636.
- McCall, I.C., Betanzos, A., Weber D.A., Nava, P., Miller, G.W. and Parkos, C.A. 2009. Effects of phenol on barrier function of a human intestinal epithelial cell line correlate with altered tight junction protein localization. *Toxicol. Appl. Pharm.* 241 : 61-70.
- Nakaruk, A., Kavei, G. and Sorrell, C.C. 2010. Synthesis of mixed-phase titania films by low-temperature ultrasonic spray pyrolysis. *Mater. Lett.* 64 : 1365-1368.
- Saratale, R.G., Noh, H.S., Song, J.Y. and Kim, D.S. 2014. Influence of parameters on the photocatalytic degradation of phenolic contaminants in wastewater using TiO₂/UV system. *J. Environ. Sci. Heal. A,* 49 : 1542-1552.
- Tanev, P.T., Chibwe, M. and Pinnavaia, T.J. 1994. Titanium-containing mesoporous molecular sieves for catalytic oxidation of aromatic compounds. *Nature.* 368 : 321-323.
- Yamada, A., Matsui, A. and Tsuji, H. 2013. Removal of phenol from saline water by polyamine chelating resin. *Water Sci. Technol.* 68 : 1819-1824.
- Zhang, Q., Gao, L. and Guo, J. 2000. Effects of calcination on the photocatalytic properties of nanosized TiO₂ powders prepared by TiCl₄ hydrolysis. *Appl. Catal. B-Environ.* 26 : 207-215.