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The Effect of Photocatalysis using TiO_2 and UV for COD Degradation of Wastewater in Linerboard Mill

Kwang-Ho Kang and Hyoung-Jin Kim†

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ABSTRACT

This study was carried out to investigate the effect of photocatalysis using TiO_2 and UV applied for the COD reduction of wastewater in linerboard mill. Trials were done to obtain the optimum addition amounts of TiO_2 and H_2O_2 to the wastewater and find an appropriate pH condition for photocatalysis on TiO_2 for degrading COD. The photocatalytic reaction was applied to the wastewater collected after secondary activated sludge treatment in WWTP of linerboard mill. The optimum application of photocatalysis reaction was obtained under the addition conditions of 2 g/L of TiO_2 and 200 mg/L of H_2O_2 at pH 3.0, respectively. The removal efficiency of $SCOD_{Cr}$ by photocatalytic treatment was 86.4 % and higher than Fenton treatment in which removal efficiency was 67.4 %. It was concluded that the photocatalytic process using TiO_2 and UV could be applied to the wastewater treatment in linerboard mill and also to the dramatic drop-off in NBDCOD load from wastewater of tertiary treatment in WWTP.

Keywords *: linerboard, wastewater, photocatalysis, TiO_2, H_2O_2, COD*

1. Introduction

Water shortage and environmental pollution have been serious problems on the point of economic, social and industrial aspects. Recently, in paper industry, the consumption of fresh water is reduced and also recycled process water by introduction of mill closing system is increased. Due to the expanded white water closing systems, the environmental load by soluble or insoluble types of contaminants is increased simultaneously. Many researches in the influential factors and treatment techniques to solve these problems have been carried out (1-3).

A large amount of water is used in the paper mills for dilution, washing, sealing, and other process operations. As the regulation of water environment has been more tightened than before, the water management in the paper mills has become the most important task. Topics on reducing fresh water and increasing recycling water have been studied. Further, an interest in zero-effluent system has been increased (4).

After Fujishima et al (5-6) studied electrochemical evidence for the mechanism of the primary stage of photosynthesis and electrochemical photolysis of water at a semiconductor electrode in early 1970's,

• Department of Forest Products, Kookmin University, Seoul 136-702, Korea
† Corresponding Author : E-mail ; hyjikim@kookmin.ac.kr

studies on the photocatalysis technique were increasingly concerned about the UV-photochemical conversion and storage.

Leah Kanzic Boyd et al (7) studied the application of photocatalysis on titanium dioxide (TiO_2) for degrading chemical oxygen demand (COD) in paper mill wastewater. In their study, photocatalysis with TiO_2 is a feasible method for degrading both COD and toxidity in various types of pulp and paper mill wastewaters and it could help reduce the environmental impact of effluents. Alternatively, it could make it more feasible to increase water recycling and possibly close the system.

Photocatalysis is an ambient-temperature process in which organic compounds in wastewater can be oxidized on a photocatalyst, such as TiO_2 (7). Energy from light (hv) is utilized in photocatalysis to oxidize organic pollutants. The mechanism of photocatalysis was fully described as follows (7); Photocatalysis is based on the production of electron hole pairs (Eq. 1) by illumination with light of band gap energy ($\lambda < 380$ nm for TiO_2) of a semiconductor powder dispersed in an aqueous medium. These charge carriers migrate to the surface of the particles and react with adsorbed species of suitable redox potential. The main reactions of this process are summarized (Eq. 2-4).

$$TiO_2 + h\nu \rightarrow h^+_{bv} + e^-_{bc} \quad [1]$$

$$h^+_{bv} + H_2O_{ads} \rightarrow OH^{\cdot} + H^+ \quad [2]$$

$$h^+_{bv} + OH^-_{ads} \rightarrow OH^{\cdot} \quad [3]$$

$$e^-_{bc} + O_2 \rightarrow O_2^{\cdot -} \quad [4]$$

Despite photocatalysis having been shown to be adequate for the degradation of a wide variety of compounds, the process is only efficient for rather dilute effluents, and involves consumption of a large amount of energy (8-9). Many workers tried to enhance the process by adding reagents with different chemical roles such as H_2O_2, O_3, Fe Ⅱ, and Fe Ⅲ (10-11).

In this research,we have attempted to obtain the optimum addition amounts of TiO_2 and H_2O_2 and appropriate pH condition for wastewater treatment using photocatalysis on TiO_2 with wastewater after secondary activated sludge and tertiary Fenton treatment in linerboard mill.

2. Materials and Methods

2.1 Materials

2.1.1 Titanium Dioxide

As shown in Table 1, 2 kinds of TiO_2 were considered for photocatalytic reaction of wastewater. The photoactivity efficiency between TiO_2 products could be characterized by the chemical and physical properties of catalyst, including crystal structure, crystal size, surface property and surface area (12). The main difference between two products used in this experiment is BET surface area and crystallite size in TiO_2 particles. The TiO_2 from Ishihara has higher surface area and anatase ratio than from Degussa. In this study, TiO_2 from Ishihara ST-01 was chosen because it had higher BET surface area of 300 m^2/g and smaller crystallite size of 10.4 nm, and had more uniform composition of 100 % anatase type.

2.1.2 Ultraviolet lamp

Fig. 1 shows UV lamp used in photocatalytic reaction. UV lamp (produced from Sankyo Denki, Co., Ltd.) was longitudinal fluorescent tube type, and diameter and length were 15 mm and 357 mm. The spectral energy distribution of UV lamp was shown in Fig. 2 and the maximum wavelength of UV lamp was 253.7 nm.

Table 1. Physical properties of catalysts

Catalyst	BET surface area, ㎡/g	Crystallite size, nm
Degussa P-25	52	20.7 (anatase), 29.9 (rutile)
Ishihara ST-01	300	10.4 (anatase)

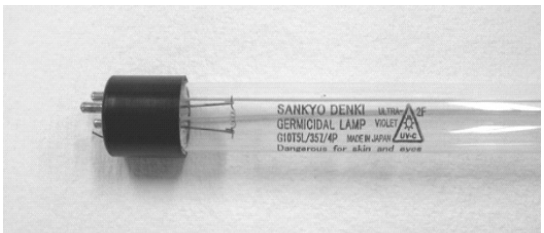

Fig. 1. UV lamp used in photocatalysis process.

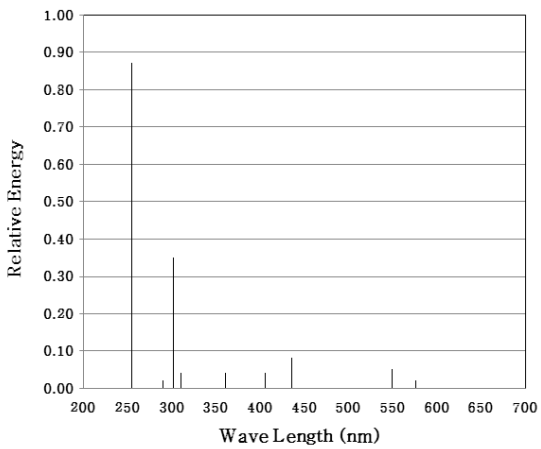

Fig. 2. Spectral energy distribution of UV lamp.

2.1.3 Effluents source

The source of effluents used in photocatalytic reaction was directly obtained from a linerboard mill. The secondary and tertiary wastewater were collected after the treatment of activated sludge and Fenton in wastewater treatment processes (WWTP), and the COD values collected after each stage of treatment were 390 mg/L and 127 mg/L.

2.2 Methods

2.2.1 Photocatalytic reaction system

As shown in Fig. 3, photocatalytic reaction system which is modified from DIP cell was consisted of 20 L capacity of main reaction vessel, and stirring apparatus which is located in bottom part of cell and available to control rotation speed. Oxygen or air was bubbled into the slurry of wastewater throughout the reaction

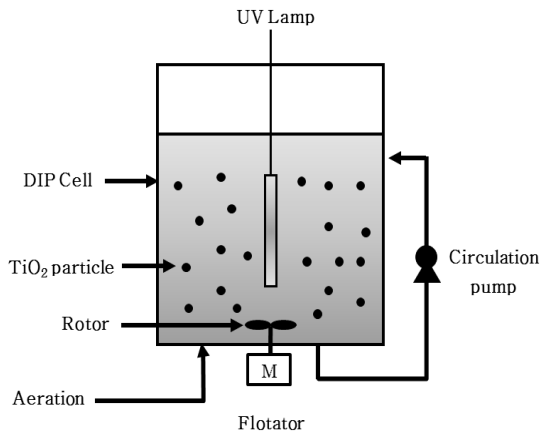

Fig. 3. Schematic diagram of the photocatalytic reaction system for COD degradation of wastewater.

period by free vacuum generated with flotation rotor. UV lamp was inserted into the wastewater with a pyrex sheath around the lamp from upper part of cell and fixed in the center of cell.

2.2.2 COD measurements

Before and after treatment of photocatalytic reaction, COD values were measured, and were the main parameter used for evaluating the performance of photocatalytic process in this study. $SCOD_{Cr}$ (Soluble COD_{Cr}) was measured by standard digestion method using HACH DR/2500 spectrometer.

2.2.3 Controls of TiO_2 and H_2O_2 concentration

In order to control optimum photocatalytic conditions, 20 L of wastewater after activated sludge and Fenton treatment was put into the flotation cell, and TiO_2 concentration was controlled from 0 to 2 g/L. Each photocatalytic reaction was run for 8 hr with stirring wastewater slurry and UV lamp on. To investigate the optimum pH condition, pH of wastewater after activated sludge treatment was controlled to 3, 5, 7, 9 and 11 at optimum TiO_2 dosage, and then H_2O_2 dosage was controlled to 50, 100, 200, 400 mg/L at optimum TiO_2 dosage and pH condition.

The controls of pH and H_2O_2 option were run for 4 hr.

Each 200 mL of wastewater sample was withdrawn in all tests and used in COD value measurement. Subsequent samples were withdrawn every hour, and all samples were filtrated using Whatman GF/C filter paper.

3. Results and Discussion

3.1 Effects of photocatalytic reaction according to the TiO_2 dosage

In order to assess optimum condition of TiO_2 dosage and photocatalytic reaction time, a selected wastewater after activated sludge treatment in WWTP of linerboard mill was controlled in photoreactor for 8 hr. TiO_2 concentration was varied to 0, 0.5, 1 and 2 g/L. Fig. 4 and 5 show the variations of $SCOD_{Cr}$ and the removal efficiency of COD according to the control conditions of photocatalytic reaction. As shown in Fig. 4, the initial COD of the wastewater was 390 mg/L, and kept to decrease during photocatalytic reaction time. The concentration of TiO_2 was greatly affected to the level of COD degradation. The degradation rates of $SCOD_{Cr}$ from TiO_2 dosage of 0 g/L to 1 g/L were shown as continuous decreases with reaction time, but

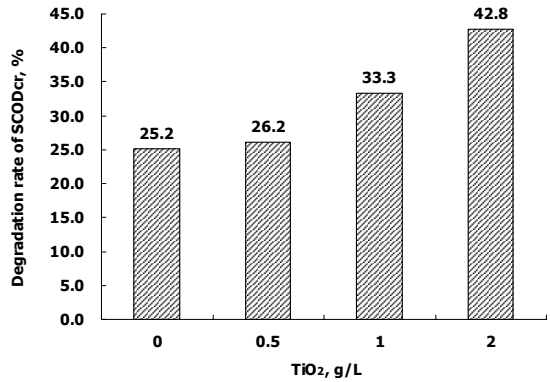

Fig. 5. Removal efficiency of $SCOD_{Cr}$ for 8 hr reaction by controlling TiO_2 addition to wastewater after activated sludge treatment.

those of $SCOD_{Cr}$ at TiO_2 dosage of 2 g/L shown as dramatic drops at initial reaction time up to 3 hr and then slightly decreased up to 8 hr. As also shown in the results of Fig. 5, the removal rate of $SCOD_{Cr}$ with increasing TiO_2 concentration up to 1 g/L was gently increased, and then rapidly increased at dosage amount above 1 g/L. The concentration of 2 g/L had a greatest COD reduction and the $SCOD_{Cr}$ was gained to 223 mg/L after 8 hr reaction time.

Fig. 6 and 7 show the variations of $SCOD_{Cr}$ to a selected wastewater after Fenton treatment in WWTP of linerboard mill with the increasing concentration of

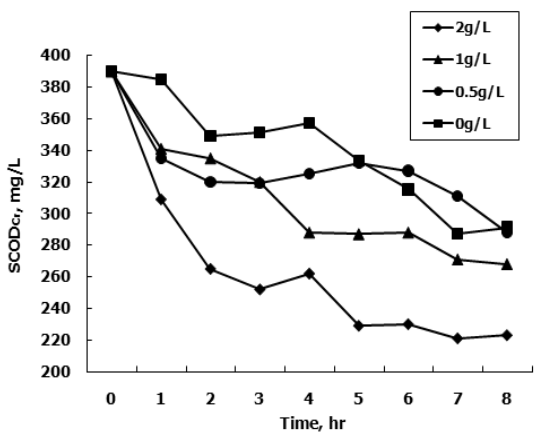

Fig. 4. Changes of $SCOD_{Cr}$ by controlling TiO_2 addition to wastewater after activated sludge treatment.

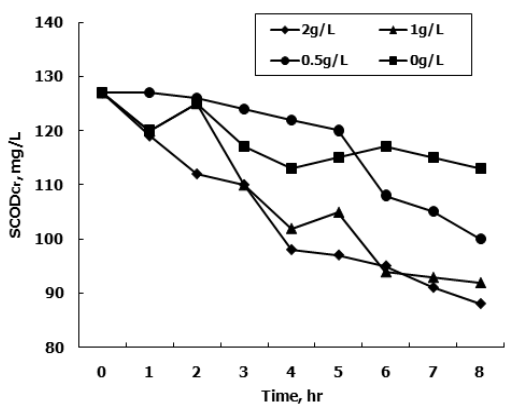

Fig. 6. Changes of $SCOD_{Cr}$ by controlling TiO_2 addition to wastewater after Fenton treatment.

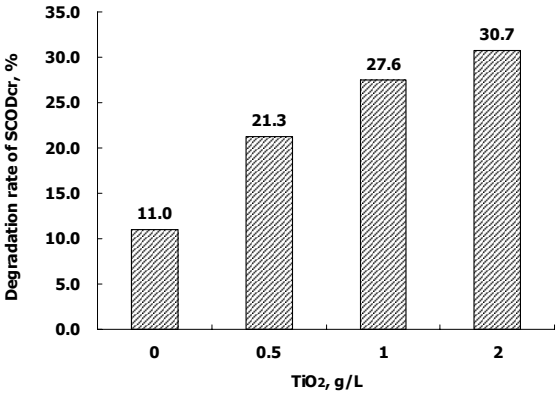

Fig. 7. Removal efficiency of $SCOD_{Cr}$ for 8 hr reaction by controlling TiO_2 addition to wastewater after Fenton treatment.

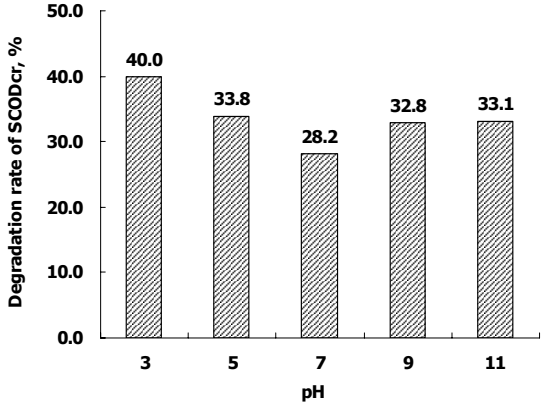

Fig. 9. Removal efficiency of $SCOD_{Cr}$ for 4 hr reaction at different levels of pH to wastewater after activated sludge treatment.

TiO_2 in photoreactor for 8 hr. Apart from the results of Fig. 4, the rate of $SCOD_{Cr}$ degradation was not shown big difference with increasing concentration of TiO_2 because of initial low $SCOD_{Cr}$ value, but still decreased to 88 mg/L at dosage point of TiO_2 2.0 g/L. However, these results mean that the photocatalysis on TiO_2 could be removed more NBDCOD materials remained in wastewater after Fenton treatment of the wastewater treatment process in linerboard mill.

3.2 Effects of photocatalytic reaction according to pH condition

The efficiency of photocatalysis on TiO_2 to a selected wastewater was recorded under the different conditions of pH. The wastewater in a photocatalysis reactor was adjusted to 5 levels of pH which were set in 3, 5, 7, 9 and 11 using NaOH and H_2SO_4. Fig. 8 and 9 show the changes and degradation rates of $SCOD_{Cr}$ at different pH levels to wastewater after activated sludge treatment from linerboard mill for 4 hr photocatalytic reaction at dosage point of TiO_2 2.0 g/L. The greatest degradation of $SCOD_{Cr}$ was obtained in condition of pH 3.0. The maximum reduction rate of $SCOD_{Cr}$ at pH 3.0 was 40 % and $SCOD_{Cr}$ was degraded to 234 mg/L. In alkaline medium, high level of hydroxide ions (OH^-) induced the generation of hydroxyl free radicals (HO•), which came from the photooxidation of OH^- by holes forming on the TiO_2 surface. This observation has been justified by Chu et al (13).

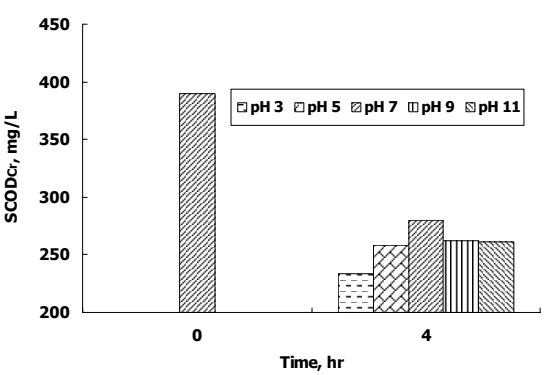

Fig. 8. Changes of $SCOD_{Cr}$ at different levels of pH to wastewater after activated sludge treatment.

3.3 Effects of photocatalytic reaction according to H_2O_2 dosage

Another trial, besides the presence of UV with TiO_2 and pH option, was carried out to improve the yield of photoactivity by adding an additive, H_2O_2. As reported references (11, 14), the role of H_2O_2 changes with concentration: at low concentrations of H_2O_2 plays a beneficial role, while at high concentrations it

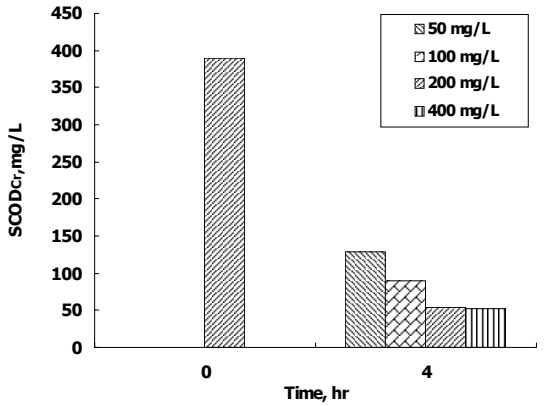

Fig. 10. Changes of $SCOD_{Cr}$ by controlling H_2O_2 addition to wastewater after activated sludge treatment.

becomes detrimental. Because H_2O_2 is a better electron acceptor than O_2, it may also absorb photons without producing a reaction, thus competing with the photocatalyst for light absorption. It can also compete with the organic substrates for adsorption at the catalyst surface sites (15).

Fig. 10 and 11 show the changes and removal efficiency of $SCOD_{Cr}$ according to addition amounts of H_2O_2 to wastewater after activated sludge treatment for 4 hr reaction at conditions of TiO_2 2.0 g/L and pH 3.0. In the presence of UV with TiO_2, the degradation

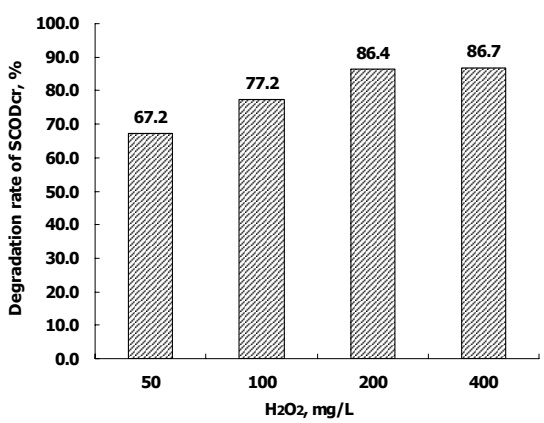

Fig. 11. Removal efficiency of $SCOD_{Cr}$ for 4 hr reaction by controlling H_2O_2 addition to wastewater after activated sludge treatment.

rates of $SCOD_{Cr}$ increased by adding hydrogen peroxide. The maximum reduction in $SCOD_{Cr}$ was obtained dosage of H_2O_2, 400 mg/L, and the $SCOD_{Cr}$ was removed to 52 mg/L. However, because the $SCOD_{Cr}$ was reached to 53 mg/L at the condition of H_2O_2 200 mg/L dosage, thus the optimum conditions of photocatalytic reaction were concluded at TiO_2 2.0 g/L, pH 3.0, and H_2O_2 200 mg/L. Under these conditions, $SCOD_{Cr}$ by photocatalysis on TiO_2 was finally reduced to 53 mg/L, and was lower than $SCOD_{Cr}$ (136 mg/L) by Fenton treatment.

4. Conclusions

Recently, due to the technical development of closed system in pulp and paper mills, non-biodegradable materials have more and more been accumulated in mill process water lines and wastewater treatment tank. Therefore, it has also been more and more difficult to reduce the environmental loads such as COD factor for recycling wastewater as well as to attain the limited COD level for discharging effluents. This study was carried out to consider the photocatalysis on TiO_2 for more effective degradation of SCOD or NBDCOD materials retained in wastewater of WWTP of linerboard mills. In this study, the optimum conditions for photocatalysis technique with TiO_2 and UV were studied for best available reduction of COD with hydrogen peroxide, as considered one of the advanced oxidation processes. The maximum yields of photocatalytic reaction were obtained in the conditions of TiO_2 2.0 g/L, pH 3.0, and H_2O_2 200 mg/L. Over 86% of the initial $SCOD_{Cr}$ from the wastewater after secondary activated sludge treatment were effectively degraded by photocatalytic treatment. It was thus concluded that the photocatalysis technique using TiO_2 and UV could be available to the application of wastewater treatment in linerboard mill, and the SCOD and NBDCOD load of the process and wastewater could be decreased dramatically.

Acknowledgement

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