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Photocatalytic Decomposition of Nonbiodegradable Substances in Wastewater from an Acrylic Fibre Manufacturing Process

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Abstract–The testing samples in this experiment were obtained from an acrylic fibre manufacturing companys industrial wastewater. The water was the waste of the acrylic polymerization process. The company is located in Ulsan, Korea. The concentration of acrylonitrile (AN) in the wastewater was about 25-35 mg/L. Concentrations of 3-10 mg/L of methyl acrylate (M-35) were also found. The samples were treated by the TiO_2/UV system and were analyzed to determine the values of COD_{cr}, ammonia, nitrite nitrogen, and nitrate nitrogen by using an Auto Analyzer (Bran+ Luebbe, Germany) and a TOC (Tekmar Dohrmann, USA). Various reaction parameters, such as TiO_2 content, light intensity and wavelength, and the number of UV lamps were varied and their effects or decomposition efficiency were analyzed. The adsorption onto TiO_2 surfaces by organic materials in the wastewater was negligible. The reaction-rate constant was also calculated. The reaction rate constant for the G36T6L lamp at both 185 nm and 256 nm was 0.0661 hr^{-1} which is 1.3 times higher than that of the TUV36T5 lamp at 256 nm. While the reaction rate was increased by increasing the surface area of the photocatalyst, the excess photocatalyst blocked the light sources, causing a photo-enclosure effect. The stability of the treated wastewater was greatly increased because the elimination of the concentration of nitrite was followed by an increase in the concentration of nitrate. Generally, the ratio of BOD_5/COD_{cr} is used as the criterion for determining biodegradability. A ratio of 0.3 is needed for biological degradation. The ratio of the treated wastewater increased to 0.5 after 12 hours of reaction. The ratio increased to 0.8 after 20 hours.

Key words: Acrylonitrile, BOD/COD_{cr} Ratio, Industrial Wastewater, Photocatalytic Reaction, TiO_2/UV

INTRODUCTION

For wastewater treatment, most fibre manufacturing companies are generally adopting a conventional biological treatment system followed by physico-chemical methods of neutralization, coagulation, and sedimentation. Since wastewater discharged from most acrylic fibre manufacturing companies is difficult to degrade biologically, research to improve the removal efficiency is necessary [Nigam et al., 1996]. The wastewater including the rinse water from the acrylic polymerization process shows a low ratio of 0.1-0.2 of BOD_5/COD_{cr}. Due to the nonbiodegradable substances this wastewater is not easily treated by a single biological process. Therefore, it has been recommended that nonbiodegradable substances be decomposed into smaller ones before applying a biological process to consume the resulting smaller compounds. The TiO_2/UV system was known to be one of the most feasible methods to convert these nonbiodegradable compounds into smaller non-toxic compounds. Na et al. [2004] reported that an analysis of EC50 of TiO_2/UV treated Rhodamine B solution showed no toxicity. The intensity of light was increased by increasing the output of UV light. Lee et al. [2003] reported that the photon rate increased linearly as the number of the lamps increased.

Earlier investigators reported that there are large amounts of various inorganic anions, such as Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-} in industrial wastewater, which reduce the photocatalytic reaction rate by blocking active TiO_2 catalyst sites or competing with radicals [Abdullah et al., 1990; Wang et al., 2000]. Chen et al. [1997] detailed the effect of anions on adsorption of DCE on the surface of TiO_2 in aqueous solution. The anions competed with the adsorption of DCE on the surface of TiO_2 and the photolysis reaction. However, research using photocatalysts has been carried out mostly with a view to investigate parameters, but this research has focused on confirming the practical possibility of the photochemical treatment process of industrial wastewater.

This study attempted to determine the effects of the amount of photocatalyst, the intensity of UV light, the ratio of BOD_5/COD_{cr}, and nitrogen anions in the photocatalytic degradation process while

Table 1. Characteristics and flow rate of the wastewater from the acrylic polymerization process

Conditions	Value	Components	Concentration (mg/L)
Flow rate (m^3/day)	3,000-4,000	AN	25-35
COD_{cr} (mg/L)	800-1,000	M-35	3-10
BOD_5 (mg/L)	100-200	Na^+	735
SS (mg/L)	50	SO_4^{2-}	1,340
pH	7.0	Cl^-	60 -70
Temp. (°C)	50 °C	CN^-	0.16 -3.00
		NH_4^+	40
		Total sulfur	600

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Table 2. Specifications of the VU lamps used in this experiment

Type	Sankyo denki GL20	Ster-L-Ray G36T6L	Ster-L-Ray GHO1055T5	TUV 36T5 (Philips)
Wattage	20 W	40 W	104 W	40 W
Lamp Current (A)	0.36	0.426	0.8	0.425
Ultraviolet Output (W)	4.2	13.8	-	15
		120 μW/cm^2/1 m	290 μW/cm^2/1 m	
Wavelength(nm)	254 nm	184 nm+254 nm	184 nm+254 nm	254 nm

treating wastewater discharged from an acrylic fibre manufacturing company.

MATERIALS AND METHOD

The amount of outflow and the quality of the wastewater from the acrylic polymerization process plant are listed in Table 1. The batch reactor used in the experiment was a 70 mm diameter (outside) cylinder (60 mm inside), and 1,000 mm long. The reactant inside the reactor was perfectly mixed by a magnetic stirrer and air flowed at the rate of 1 L/min from the bottom. The anatase-form of TiO_2 (Junsei Chemical Company) and GL20, G36T6L, GHO1055T5, and TUV36T5 lamps (see Table 2 for specifications) were used in this experiment. The reaction temperature was controlled by circulating water through the jacket.

To determine the degradability of the wastewater, samples were taken after photocatalytic decomposition by the TiO_2/UV system and were centrifuged at 2,500 rpm (1,200 G) for 15 minutes to remove the TiO_2 powder. Once the samples were free of TiO_2 powder, they were analyzed for COD_{cr}, ammonia, nitrite nitrogen and nitrate nitrogen by using an Auto Analyzer (Bran+Luebbe, Germany) and a TOC analyzer (Tekmar Dohrmann, USA). The effect of various reaction conditions, such as the TiO_2 content, the configurations of UV lamps, and nitrogen ions on the decomposition efficiency were determined and the reaction-rate constants were also calculated.

RESULTS AND DISCUSSION

1. Effect of Surface Adsorption

The effect of the adsorption of organic materials in the solution on the surface of TiO_2 was investigated. The 2.0 g/L TiO_2 solution was stirred for 3 hours in a Jar Tester without light at 200 rpm, and the TOC and COD_{cr} of the solution were determined at regular time intervals. Analyzing the differing concentrations between the initial wastewater and the TiO_2 treated samples showed that the adsorption onto TiO_2 surfaces by organic materials in the wastewater was negligible.

2. Decomposition Efficiency According to Different Wavelengths

The quantum yield of direct photolysis increased as the molar absorption coefficient increased and decreased as the UV wavelengths increased [Chu et al., 1998]. Experiments into the decomposition of wastewater were performed at a fixed temperature (T= 30 °C) using TUV36T5 or G36T6L lamps. The G36T6L lamp used wavelengths of 185 nm and 256 nm, but the TUV36T5 lamp used only 256 nm. Although the UV output capacity of the TUV36T5 (15 W) lamp was higher than that of the G36T6L (13.8 W) lamp, the efficiency of decomposition with the G36T6L lamp which included a wavelength of 184 nm was higher than that with the TUV36T5 lamp. The decomposition-rate constant of the samples treated with the G36T6L lamp was 0.0661 hr^{-1} which was 1.3 times higher than that of the samples treated with the TUV36T5 lamp (0.0490 hr^{-1}). The higher UV light energy that results from the shorter wavelengths decomposes organic compounds faster (Fig. 1).

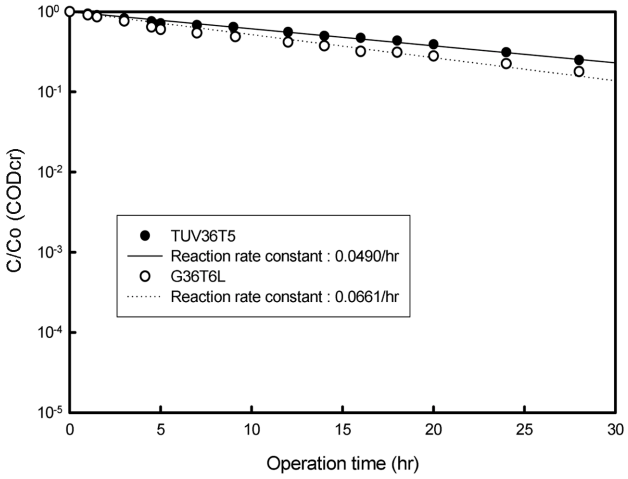

Fig. 1. Kinetics of the photocatalytic degradation of the wastewater at various UV wavelengths with operation time (C/Co: relative concentration of wastewater).

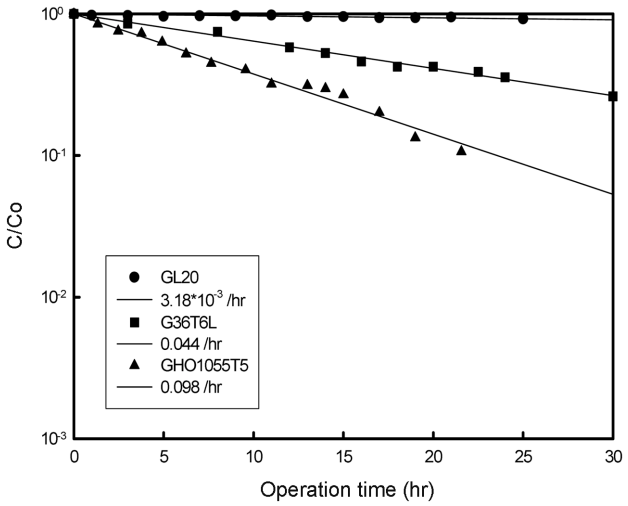

Fig. 2. Kinetics of the photocatalytic degradation of the wastewater at various UV intensities with operation time (C/Co: relative concentration of wastewater).

Table 3. Variation of the reaction rate constant at various TiO_2 concentrations with operation time

TiO_2 (mg/L) \ UV lamp	k ($\times 10^{-3}$ hr^{-1})	
	TUV36T5	GHO1055T5
0.1	12.36	-
1.0	19.14	-
2.0	24.84	50.7
4.0	30.12	137
6.0	32.28	110
8.0	29.7	118

3. Effect of light intensity

Daneshvar et al. [2004] reported that the reaction rate was proportional to the intensity of light through the photocatalytic degradation of Acid Red 27 (AR27) in the presence of TiO_2-P25.

Fig. 2 shows the effect of the intensity of UV-lamps on photocatalytic decomposition at a fixed temperature of T=30 °C. Various UV lamps (GL20=4.2 W, TUV36T5=13.8 W, GHO1055T5=15 W) were tested for up to 30 hours. The values of COD_{cr} did not decrease noticeably when the GL20 lamp (low UV output, wavelength of 254 nm) was used, but decreased sharply when the TUV36T5 lamp or the GHO1055T5 lamp was used. The reaction-rate constants were calculated as 3.18×10^{-3} hr^{-1} (GL20), 0.044 hr^{-1} (TUV36T5), and 0.098 hr^{-1} (GHO1055T5), respectively.

4. Effect of Photocatalyst Concentration

Since more catalysts provide more effective photons, the reaction rate should increase when the concentration of photocatalyst increases under the TUV36T5 or GHO1055T5 lamp.

However, when the amount of catalyst exceeds a certain value, the screening effect and the shelter among catalyst particles becomes dramatic, which then blocks some portion of the sensitive surfaces of TiO_2 [Hong et al., 2004]. Table 3 shows that the photo-enclosure effect appeared when the concentration of TiO_2 was 8 g/L for the TUV36T lamp and 6 g/L for GHO1055T lamp.

5. Change of Nitrogen Ions

The presence of free and metal-complex cyanides in industrial wastewaters is considerably toxic to living organisms. Augugliaro et al. [1999] reported that ammonia, nitrate, and nitrite were observed when the photocatalytic oxidation of CNO^- and NH_2OH was carried out under mild oxidation conditions in a laboratory photoreactor, and only nitrate and nitrite were detected with the addition of H_2O_2.

This research showed that CN^- ion in the wastewater was converted to ammonia, nitrite, and nitrate. It was found that the concentration of ammonium nitrogen increased to 60 mg/L after 24 hours from an initial concentration of 40 mg/L. Fig. 3 shows that the concentration of nitrite nitrogen was very low but the concentration of nitrate nitrogen increased up to 15 mg/L at an operation time of 25 hours. The concentration of nitrite was very low because the nitrite ions were converted into nitrate ions by the photocatalytic reaction using oxygen from the air. Nitrite in drinking water is a known carcinogenic. The stability of the treated water was greatly increased because the concentrations of CN^- ion and nitrite were eliminated followed by an increase in the concentration of nitrate.

6. Ratio of BOD_5 and COD_{cr}

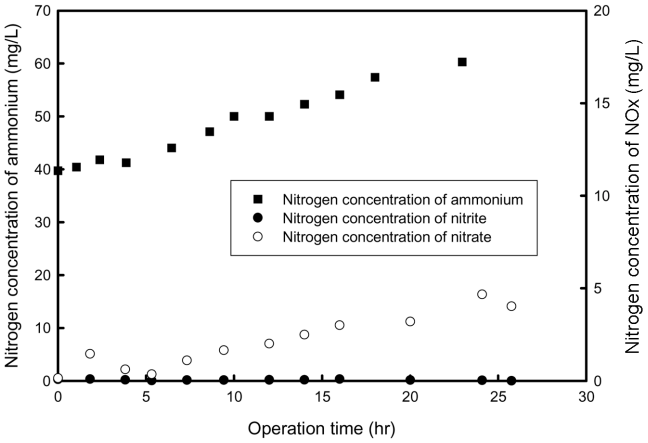

Fig. 3. Variation of nitrogen ions in the wastewater with operation time.

Generally, biodegradability is estimated by the BOD_5/COD_{cr} ratio. When the ratio is 0.3 or greater, biological degradation is possible. At ratios less than 0.3, reports indicate that the biological decomposition process cannot be used [Chun and Wang, 1999]. Biological degradation was examined by using various intensities of radiation. There was almost no change in BOD_5 when the GL20 lamp (4.2 W) was used. Therefore, the wastewater was not degraded by a UV output of 4.2 W whose UV irradiation is too weak to convert nonbiodegradable material into smaller biodegradable materials. Fig. 4 indicates the change in the BOD_5 and COD_{cr} of the wastewater when the TUV36T5 lamp was used. The original BOD_5 of the wastewater was about 120 mg/L, but increased up to 300 mg/L after 5 hours of reaction. This meant that the nonbiodegradable compounds were converted into biodegradable ones by the photocatalytic treatment. Fig. 5 presents the ratio of BOD_5/COD_{cr}, which is the criterion for establishing biodegradability and could be used as a predictor for using the photocatalytic process in an active sludge

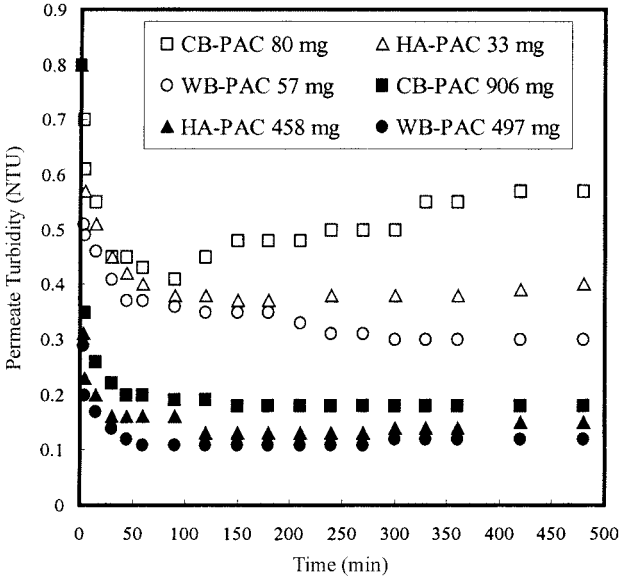

Fig. 4. Turbidity removal performance of the PAC pre-coated membrane (Initial turbidity of wastewater=1 NTU).

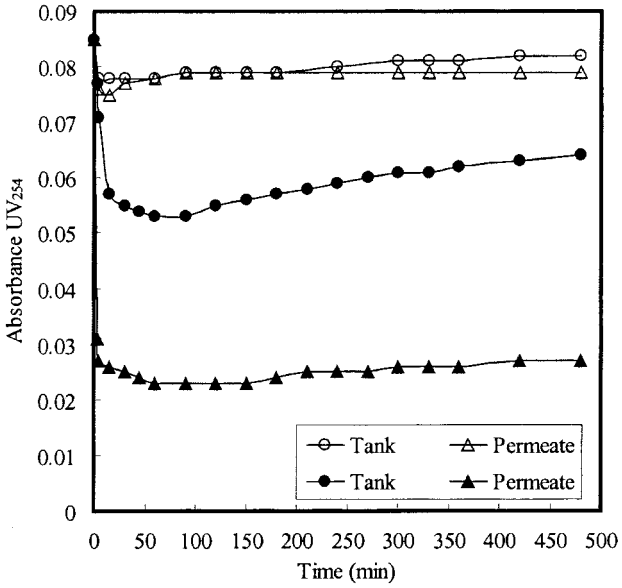

Fig. 5. Organic removal performance of the WB-PAC pre-coated membrane (For non-shaded symbols WB coating amount= 57 mg, shaded symbols WB coating amount=497 mg, Initial UV_{254} absorbance=0.085).

process after pre-treatment. The wastewater used in this experiment showed that the initial ratio of BOD_5 to COD_{cr} was 0.1, which indicated nonbiodegradability. After 12 hours of reaction, the ratio of BOD_5 to COD_{cr} increased to 0.5, and then to more than 0.8 after 20 hours of reaction. Therefore, it would be possible to use an active sludge process on this nonbiodegradable wastewater after it was pretreated by the photocatalytic decomposition process for 12 hours.

CONCLUSION

There was no significant difference in concentration between the original wastewater and the wastewater treated by TiO_2 powder only. It indicates that the decomposition of wastewater by TiO_2 powder was negligible. When G36T6L lamp using wavelengths of 185 nm and 256 nm was used, the reaction rate constant (0.0661 hr^{-1}) was 1.3 times higher than that of the TUV36T5 lamps (0.0490 hr^{-1}, and wavelengths of 256 nm). The value of COD_{cr} did not decrease when the GL20 lamp was used. However, the concentration of the wastewater significantly decreased when the TUV36T5 lamp or the GHO1055T5 lamp was used. As a result of the changes in the photocatalyst concentration caused by the TUV36T lamp or the GHO1055T5 lamp, the reaction rate increased by increasing the surface area of the photocatalyst. The increased levels of photocatalyst blocked light source resulting in a photo-enclosure effect. The initial concentration of ammonium nitrogen (40 mg/L) increased to 60 mg/L after 24 hours of reaction. While there was a very low concentration of nitrite nitrogen during the operation time, the concentration of nitrate nitrogen increased up to 15 mg/L. The value of BOD_5 of the initial wastewater was about 120 mg/L but increased about three times after 5 hours of reaction with the TiO_2/UV system using the TUV36T5 lamp. This indicated that the nonbiodegradable wastewater was converted to biodegradable wastewater as a result of the photocatalytic treatment.

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REFERENCES

Abdullah, M., Low, G. K. and Matthews, R. W., "Effects of Common Inorganic Anions on Rates of Photocatalytic Oxidation of Organic Carbon over Illuminated Titanium Dioxide," *J. Phys. Chem.*, **94**, 6820 (1990).

Augugliaro, J. Blanco, Gálvez, J. Cáceres, Vázquez, E. García, López, V. Loddo, López, Muñoz M. J., Rodríguez, S. Malato, Marcì, G., Palmisano, L., Schiavello, M. and Ruiz, J. Soria, "Photocatalytic Oxidation of Cyanide in Aqueous TiO_2 Suspensions Irradiated by Sunlight in Mild and Strong Oxidant Conditions," *Catalysis Today*, **54**, Issues 2-3, 245 (1999).

Bozzi, A., Guasaquillo, I. and Kiwi, J., "Accelerated Removal of Cyanides from Industrial Effluents by Supported TiO_2 Photo-catalysts," *Applied Catalysis B: Environmental*, **51**, Issue 3, 203 (2004).

Chen, H. Y., Zahraa, O. and Bouchy, M., "Inhibition of Adsorption and Photocatalytic Degradation of an Organic Contaminant in Aqueous Suspension of TiO_2 by Inorganic Ions," *J. Photochem. & Photobio. A: Chem.*, **108**, 37 (1997).

Chu, W., Jafvert, C. T., Diehl, C. A., Marley, K. and Larson, R. A., "Phototransformations of Polychlorobiphenyls in Brij 58 Micellar Solutions," *Environ. Sci. Technol.*, **32**(13), 1989 (1998).

Chun, H. and Wang, Y., "Decolorization and Biodegradability of Photocatalytic Treated Azo Dyes and Wool Textile Wastewater," *Chemosphere*, **39**(12), 2107 (1999).

Daneshvar, N., Rabbani, M., Modirshahla, N. and Behnajady, M. A., "Kinetic Modeling of Photocatalytic Degradation of Acid Red 27 in UV/TiO_2 Process," *Journal of Photochemistry and Photobiology A: Chemistry*, **168**, Issues 1-2, 39 (2004).

Hong, Z., Suohong, X., Junbo, Z. and Xinhe, B., "Kinetic Study on the Photo-catalytic Degradation of Pyridine in TiO_2 Suspension Systems," *Catalysis Today*, **93**, 857 (2004).

Lee, J. C., Kim, M. S., Kim, C. K., Chung, C. H., Cho, S. M., Han, G. Y., Yoon, K. J. and Kim, B. W. "Removal of Paraquat in Aqueous Suspension of TiO_2 in an Immersed UV Photoreactor," *Korean J. Chem. Eng.*, **20**(5), 862 (2003).

Na, Y. S., Kim, D. H., Lee, C. H., Lee, S. W., Park, Y. S., Oh, Y. K., Park, S. H. and Song, S. K., "Photocatalytic Decolorization of Rhodamine B (RhB) by Fluidized Bed Reactor with Hollow Ceramic Ball Photocatalyst," *Korean J. Chem. Eng.*, **21**(2), 430 (2004).

Nigam, P., Banat, I. M., Singh, D. and Marchant, R., "Microbial Process for the Decolorization of Textile Effluent Containing Azo/Diazo and Reactive Dyes," *Process Biochemistry*, **31**(5), 435 (1996).

Wang, K. H., Hsieh, Y. H., Wu, C. H. and Chang, C. Y., "The pH and Anion Effects on the Heterogeneous Photocatalytic Degradation of o-Methyl Benzoic Acid in TiO_2 Aqueous Suspension," *Chemosphere*, **40**, 389 (2000).