Photocatalytic Degradation of Algae and its By-product using Rotating Photocatalytic Oxidation Disk Reactor

Son Hee-Jong, Jung Chul-Woo¹, and Bae Sang-Dae^{2,*}

Busan Water Authority, Water Quality Research Institute, Busan, Korea

¹*Ulsan Industry Promotion Techno Park, Ulsan Regional Innovation Agency, Ulsan, Korea*

²*Department of Environmental Engineering, Silla University, Busan, Korea*

Received August 2008, accepted September 2009

Abstract

This study examined the special technique of photocatalytic degradation (RPODisk) for removal of taste and odor causing materials, algae, and algal toxin. The RPODisk was effective for removal of these troublesome contaminants. It outperformed the fixed media and the UV irradiation for geosmin removal. The RPODisk performance was comparable to the combination of the UV irradiation with TiO₂. The RPODisk performance was affected by the rotating speed. The faster the speed was, the better the performance. The RPODisk was also effective for removal of algae and algal toxin. The algal activity reduced by 80% after 30 mins of the treatment. More toxic microcystin (MC)-LR was more difficult to remove than MC-RR. The times for 50% removal were 23.7 mins for MC-LR and 14.1 mins for MC-RR. Almost 100 mins of the contact time was required to completely remove MC-LR at the rotating speed of 260 rpm.

Keywords: Photocatalytic degradation, Algae, Algal by-product, Taste and Odour, Rotating disk

1. Introduction

Recent industrialization and urbanization resulted in eutrophication of most surface waters in Korea. The typical example is the Nakdong river, which serves as raw water source to south-east region of Korea. Eutrophication was more serious at downstream, where hydration occurred.¹⁾ Subsequent algal bloom poses a serious threat to water treatment plants, relying on the Nakdong river. Algal bloom causes several problems including taste and odor (T & O), algal toxins, filter clogging. Since conventional treatment is ineffective to handle these problems, advanced processes such as activated carbon and ozonation were introduced to those plants. This study reports the results using the technique rotating photocatalytic oxidation disk reactor (RPODisk).

2. Materials and Methods

2.1. Materials

Geosmin was selected as the representative T & O causing

material in this study. The standard solution of geosmin (98%, Sigma-Aldrich, U.S.A.) was diluted in distilled water so that the solution concentration became 10 µg/L. Microcystin (MC)-LR and MC-RR were used as the representative algal toxin. The standard solution (Kanto Chemical, Japan) was diluted to 3.9 µg/L (MC-LR) and 2.9 µg/L (MC-RR) in distilled water. *Microcystis* sp. was collected from the Nakdong river during June to September, 2004 and were used to evaluate the algal activity reduction.

Titanium dioxide powder (Degussa P-25) was used without pretreatment to evaluate the photocatalytic oxidation performance. When an experiment did not involve the powder form of TiO₂, titanium isopropoxide (TTIP; 98%, Junsei Chemical Co., Ltd., Japan) was used. TTIP was attached into the fixed media such as the hollow glass bead with 2 cm of diameter, glass pellet with 2.5 mm of diameter, and glass disc with 15 cm of diameter. The germicidal lamp of 10 W (254 nm, Sankyo Denki, Japan) was used as the ultraviolet (UV) source. Fig. 1 shows the schematic diagram of the RPODisk used in this study.

2.2. TiO₂ Coating

The glass disc was washed with potassium dichromate before coating. TTIP was mixed with ethyl alcohol and HCl at the ratio of 10:100:1. The TTIP mixture was then coated into the dried

* Corresponding author
E-mail: baesd@silla.ac.kr
Tel: +82-51-999-6270, Fax: +82-51-999-5158

Fig. 1. RPODisk reactor.

glass disc. The titanium coated disc was then heated at 100°C. The temperature increased at the rate of 10~20°C/min up to 500°C, at which it stayed for 4 hrs. This process was repeated 20 times before the disc was placed into the reactor.²⁾

2.3. RPODisk reactor

The RPODisk used in this study was a batch reactor with a capacity of 3 liter. Two germicidal lamps were placed above the disc. A reflecting glass was put above these lamps so that the UV light heading the reactor roof can be directed into the disc. Seven discs with titanium coating (POD) were connected by a horizontal axis. It was rotated at 24~260 rpm. While POD was rotating, it would contact with water and air, alternatively. Photocatalytic capacity of the titanium oxide would be enhanced through the rotation.

2.4. Analysis

Geosmin and 2-MIB were analyzed by GC/MSD with twist pretreatment. For the microcystin analysis, sample of 500 mL was pretreated using solid phase extraction (Autotrace SPE Workstation, Tekmar, U.S.A.) so that microcystin could be adsorbed onto the sep-pak cartridge (C₁₈). It was washed and eluted into 20% methyl alcohol before filtration through 0.2 µm membrane filter (Sartorius Minisart RC4, Germany). HPLC was used for the analysis. Table 1 and 2 summarized the analy-

Table 1. Analytical Conditions of the GC/MSD and the Purge and Trap

GC/MSD	
- GC :	Varian Star 3400 CX
- MSD :	Varian Saturn 2000, EI mode
- Column :	DB-5MS, 60 m ID × 0.25 mm × 0.25 µm
- Oven Temp. :	Hold 10 min at 40°C
	- 1st step 5°C to 150°C, 2nd step 4°C to 250°C
Purge & Trap	
- Tekmar LSC-3000 Purge and Trap Concentrator	
- Purge Time :	8 min
- Trap :	# J (VOCARB 4000), Desorb 4 min (260°C), Bake 5 min (260°C)

Table 2. Analytical Conditions of the HPLC

- LC :	Waters 2690
- UV-Detector :	Waters 996, photodiode array detector
- Column :	Novac-Pak C ₁₈ , 3.9 × 150 mm
- Mobile phase :	MeOH : 0.05 M phosphate buffer (pH 2.5, 58:42)
- Flow rate :	1 mL/min.
- Detection :	238 nm

tical conditions.

For chlorophyll-a analysis, sample of 500 mL was first filtered through GF/C filter paper. The paper was then soaked into the 90% acetone solution of 20 mL. After storing in a dark room at 0°C for 12 hrs, it was sonicated for 1 min, and put back into the storage for another 12 hrs. Centrifuge supernatant was then analyzed UV-absorption at such wavelengths as 750, 664, 647, 630, 480 nm based on the Jeffrey and Humphrey method (CARY 100 conc, Varian, Australia).³⁾

For the algal activity measurement, sample was added into the BOD bottle with 1 mL of NaH₁₄CO₃ (55.0 mCi/mmol) at the concentration of 10 µCi/mL. After being incubated for 3 hrs, its radioactive concentration was measured using Liquid Scintillation Analyzer (Packard 2500TR/AB, Canberra, U.S.A.) for algal substrate uptake.⁴⁾

3. Results and Discussion

3.1. TiO₂ Coating

Fig. 2 shows the SEM picture of the POD surface. According to Fig. 2(a), the coating thickness was 480 nm. Fig. 2(b) shows

(a)

(b)

Fig. 2. SEM photograph of TiO₂ immobilized on a glass disk. [×100k]

that TiO₂ particles packed the glass disc surface.

3.2. T & O Removal

Photocatalytic removal of geosmin was evaluated using powder form of titanium oxide, the titanium fixed media, and the RPODisk. Fig. 3 and Table 3 show the results. The wavelength of 254 nm was used for the UV irradiation. TiO₂ powder was suspended in the solution without pretreatment. The solution was continuously mixed using a magnetic bar so that the powder and the media were kept in suspension. The RPODisk was rotated at 260 rpm.

According to Fig. 3, the UV irradiation alone was not effective for the geosmin removal. The fixed media of glass bead and pellet were also ineffective. Their removal efficiencies were less than 10% even after 1 hr of contact time. The addition of TiO₂ improved the removal. The removal efficiency approached 90% when the UV irradiation was combined with TiO₂. The more the TiO₂ was dosed, the better the efficiency. It was 87% at the TiO₂ dosage of 50 mg/L and 96% at the dosage of 100 mg/L after 1 hr of contact time. The RPODisk performance was close to the combination of the UV irradiation and TiO₂. As the contact time was increased, the removal efficiency improved. The UV irradiation alone removed about 36% of geosmin after 2 hrs. Similar results were obtained with the fixed media. Almost all geosmin were removed after 2 hrs with the RPODisk. The combination of the UV irradiation with TiO₂ produced the comparable results to the RPODisk only when the TiO₂ dosage was 100 mg/L. The RPODisk performed better than the fixed media in the geosmin removal. The fixed media was dispersed unevenly. Some settled, and others floated. Because of the uneven distribu-

tion, the photocatalytic reaction failed to occur all over the solution. However, the RPODisk promoted the photocatalytic reaction both in air and water, which resulted in the better removal efficiency. The RPODisk could be more beneficial than the combination of the UV irradiation with TiO₂ for application to water treatment plant because the UV-TiO₂ combination process needs one more step to separate the TiO₂ particle. After the photocatalytic reaction, the TiO₂ particles should be separated from water by filtration. On the other hand, the RPODisk does not need an additional step.

Fig. 4 shows the effect of the rotating speed of the RPODisk on the removal of gesomin and 2-MIB. While the The rotating speed varied to 24, 80, and 260 rpm, the removal of gesomin and 2-MIB were monitored. According to Fig. 4, the best performance was obtained at the highest speed (260 rpm). The fast rotating possible reduced the boundary layer thickness, which encourage the better contact between the POD and the contaminants. The removal efficiency was different with the contaminant type. Geosmin was more difficult to remove than 2-MIB. The time needed for 90 removal was 105 mins for geosmin and 83 mins for 2-MIB at 24 rpm. It was 58 and 52 mins at 260 rpm.

3.3. Removal of Algae and Algal Toxin

The use of the RPODisk was extended for removal of algae. It was rotated at 260 rpm. Microcystis sp. was directly added into raw water. Fig. 5 shows the results. According to Fig. 5, the algal activity reduced rapidly. The reduction was complete after 30 mins. The chlorophyll-a concentration was slower than the algal activity. It slowly decreased. The 83% reduction was obtained after 4 hrs.

Fig. 3. Photocatalytic degradation of geosmin under different conditions.

Fig. 4. Effect of the rotating speed of the RPODisk on the removal of geosmin and 2-MIB.

Table 3. Summary of Removal efficiency of geosmin under different conditions

Contact time	Item	UV only	TiO ₂ powder 50 mg/L	TiO ₂ powder 100 mg/L	RPODisk	Hollow Bead	Pellet
60 min.		<4.8%	>87.0%	>96.0%	>92.0%	<5.0%	<6.7%
120 min.		<36.0%	>89.0%	>98.0%	>99.0%	<36.1%	<37.0%

Fig. 5. Variation of Chlorophyll-a and algae-activation in the RPOD reaction.

Fig. 6. Variation of microcystin-RR and -LR removal in the RPOD reaction.

Fig. 7. Photograph of Microcystis sp. before and after photodegradation by the RPODisk reactor.

Fig. 6 shows the results of algal toxin removal. According to Fig. 6, more toxic MC-LR was more difficult to remove than MC-RR. MC-RR was almost completely removed after 90 mins of contact time, but MC-LR required 120 mins. The time required to remove 50% of these algal toxin was 14.1 mins for MC-RR and 23.7 mins for MC-LR. Fig. 7 shows the pictures of Microcystis sp. It formed colony originally. However, after 90 mins of contact time, the colony was completely dispersed.

4. Conclusions

The RPODisk removed geosmin effectively. It outperformed

the fixed media and the UV irradiation. The RPODisk performance was comparable to the combination of the UV irradiation with TiO_2 . The RPODisk performance was affected by the rotating speed. The faster the speed was, the better the performance. The speed of 260 rpm gave the best results in this study. The RPODisk was also effective for removal of algae and algal toxin. The algal activity reduced by 80% after 30 mins of the treatment. The chlorophyll-a concentration was slower than the algal activity. It took 4 hrs to reduce the chlorophyll-a concentration by 83%. More toxic MC-LR was more difficult to remove than MC-RR. The times for 50% removal were 23.7 mins for MC-LR and 14.1 mins for MC-RR. Almost 100 mins of the contact time was required to completely remove MC-LR at the rotating speed of 260 rpm.

References

1. Kim, W. H., Choi, A. R., and Lee, J. A., "The occurrence of microcystins in the Nakdong river," *Korean J. Algae*, **14**(4), 237-246. (1999).
2. Son, H. J., Jung, C. W., and Kim, S. H., "Photocatalytic degradation of bisphenol-A using a rotating photocatalytic-oxidation drum reactor (RPODR)," *Environ. Eng. Res.*, **13**(4), 197-202 (2008).
3. Jeffrey, S. W. and Humphrey, G. F., "New Spectrophotometric equations for determining chlorophyll a, b, c1 and c2 in higher plants, algae and natural phytoplankton," *J. of Biochem. physiol. pflanzen.*, **167**, 191-194 (1975).
4. Bell, R. T., Ahlgren, G. M., and Ahlgren, I., "Estimating bacterioplankton production by the $[^3\text{H}]$ thymidine incorporation in a eutrophic Swedish Lake," *Appl. Environ. Microbiol.*, **45**, 1709-1721 (1983).