INHIBITION OF THE ALGAL GROWTH USING TIO2-EMBEDDED EPS BALLS: LAB-SCALE OUTDOOR EXPERIMENT

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Abstract - TiO_2-embedded expanded polystyrene(TiEPS) balls with powdered TiO_2 particles embedded on the surface of EPS were developed, and the growth inhibition of Chlorella ellipsoidea, a green algae, was evaluated. Based on the analysis of cell number, cell morphology, concentrations of Chl-a andPhaeopigments,both surface reactions in heterogeneous photocatalysis and light shielding could inhibit the growth of C. ellipsoidea.Although dominant inhibitory effects on the growth of C. ellipsoidea were ambiguous, TiEPS balls were feasible to prevent and inhibit the excessive growth of algaes in eutrophic water body.Further experiments are in progress to evaluate the inhibitory effects of harmful algae growth in eutrophic rivers and lakes as a mesocosm field study.

Index Terms - Chlorella ellipsoidea, inhibitory effects,Photocatalyst, TiO_2-embedded EPS balls

I. INTRODUCTION

Algae in freshwater is an important role as a primary producer in aquatic ecosystem.However, if algal blooms occur continuously due to overgrowth of algae, algal blooms causes both aquatic ecosystem disturbance and aesthetic, physical adverse effects on human life[1-5].As rapid industrialization and urbanization progress, eutrophication is continuing in rivers and lakes.Also, climate change, abnormal high temperature, reduced precipitation, and increased sunlightresults in the excessive algal blooms[1-5].Therefore, various physical, chemical and biological algae countermeasure technologies are being developed. However, due to limitations such as economic efficiency, stability, and sustainability, it is required to use low-cost sustainable algal growth inhibition methods. Recently, polymer-based photocatalyst composites have received increased attention since various polymer supports (e.g., polyaniline, polycarbonate, polyethylene, polystyrene, polyvinyl alcohol, polyvinyl chloride, etc.) with outstanding mechanical properties and compatibilities can readily control both surface morphology and chemistry of composites through direct compounding, in situ synthesis, self-assembly, electro-spinning, etc. Accordingly, self-floating photocatalyst/support composites utilizing both continuous illumination of solar energy and oxygenation in the air/water interface are applied in contaminated lakes and wastewater reservoirs. In this study, expanded polystyrene(EPS) is used as a practical and floating support for photocatalyst/support composites since EPS is an innocuous floating material with its thermal-softness and long durability. Also, simple and cost-effective temperature-controlled melting method of EPS was developed as immobilization technique for mass production of TiO_2-embedded EPS (TiEPS) balls[6-7]. Finally, the photocatalytic activity of TiO_2-embedded EPS balls was evaluated using Chlorella ellipsoidea(C. ellipsoidea) as a probe algae under the natural solar light irradiation (285~660 nm & 0.10~0.14 mW/cm^2). From this study, the feasibility for usage of buoyant TiO_2-embedded EPS balls to inhibit the excessive growth of algae in rivers and lake was evaluated.

II. MATERIALS AND METHODS

A. Manufacturing method of TiO_2-embedded EPS balls

Commercial low density uniform EPS balls were purchased, and the diameter of the EPS balls used was 3 cm.In this study, powdered P25 TiO_2 (Evonik Degussa, Germany) was used. Glycerin was used as a dispersing medium for TiO_2 and was purchased (Daejung chemicals & metals co., Republic of Korea).The suspension of TiO_2 was heated to 140 ~ 150 ℃, which is the temperature at thermal denaturation of the polymer occurs, using a digital temperature controller and a heating pan equipped with a magnetic stirrer. EPS balls were repeatedly immersed,so that the TiO_2 particles were evenly embedded in the EPS balls surface.The surface of the EPS balls was wrapped with commercial packing vinyl, and then was completely immersed in cold water (1-4 ℃).Finally, the TiO_2-embedded EPS (TiEPS) balls were washed with distilled water at 700W for 10 minutes using an ultrasonic washing machine (POWER SONIC 420, Hwasin Tech) to remove excess TiO_2 particles that were not rigorously imbedded to the surface of the EPS balls.After washing, the TiEPS balls were allowed to air dry at roomtemperature[7].



Fig.1. Production procedures of TiO_2-embedded EPS (TiEPS)balls used in this study.

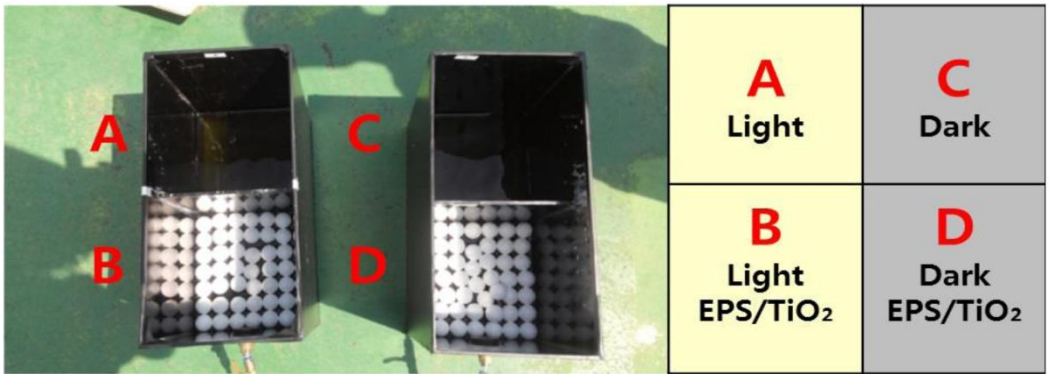

Fig.2. Pictorial view of lab-scale outdoor inhibition experiment against the growth of C. ellipsoidea.

The detail production process of TiEPS balls is shown in Fig. 1.

A. Experiment on inhibition of algae growth using TiO_2-embedded EPS balls

Chlorella ellipsoidea(C. ellipsoidea), which was used to verify the inhibitory effect of TiEPS ball on algae growth, was obtained from KRIBB(Korea Research Institute of Bioscience and Biotechnology) and cultured using BG-11 medium (MB cell co.).The culture conditions in the lab were as follows: light intensity of 1,800 lux, temperature of 25 ° C, light cycle of 12hr(light)/12hr(dark), and cultivation for 7 days before the outdoor experiment. The initial concentration of C. ellipsoideawas set at 4 L with$1x10^6$ cells/mL of the algal concentration.The outdoor experiment was performed using an acrylic reactor, the height of the water was 10 cm from the bottom, and total 49 TiEPS balls were inserted in each reactors of (B) and (D). The experiment was conducted using four reactors with various conditions of (A) natural sunlight, (B) natural sunlight+TiEPS balls, (C) dark, and (D) dark+TiEPS balls at the roof of the building during five days(see Fig. 2).

Both supernatant and mixture solution were sampled. During the experiment, the changes in both cell number of C. ellipsoidea and concentration of chlorophyll-a (Chl-a) and phaeopigments were observed.

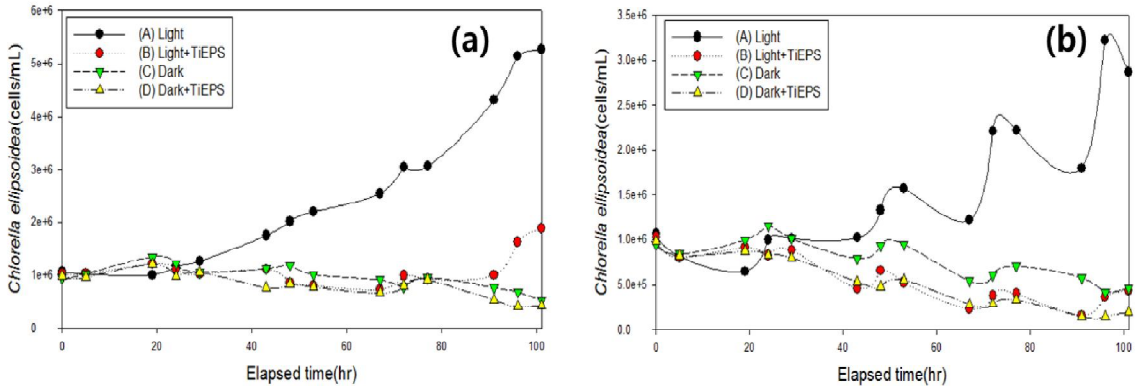

Fig.3. Changes in cell number the lab-scale inhibition experiment against the growth of C. ellipsoidea experiment. (a) number of algae cells in mixture; (b) number of algae cells in supernatant

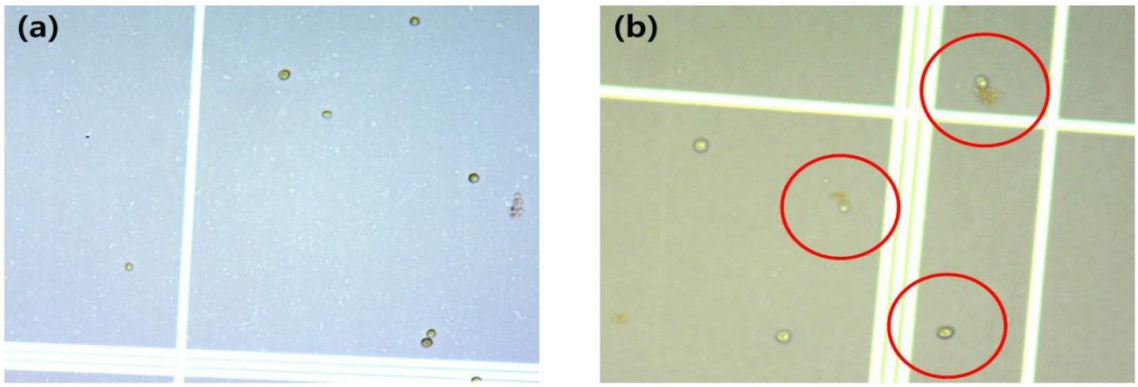

Fig.4. Changes in cell shape the lab-scale inhibition experiment against the growth of C. ellipsoidea experiment. (a) light; (b) light+TiO_2/EPS balls.

The number of C. ellipsoideawas counted using an optical microscope (DN-10A, Samwon Scientific Industries, Ltd.) using a hemocyte counter (Marinefeld, Germany) and the concentrations of chlorophyll-a and phaeopigments were measured using ICES Techniques [ICES Techniques in Marine Envirionmental Sciences (No. 30 Chlorophyll-a: Measurement by Spectroscopy ISSN 0903-2606)] [7].

III. RESULTS AND DISCUSSION

A. Cell number of C. ellipsoidea

In case of natural sunlight only during the experiment, the growth of C. elliipsoidea increased along the Monod growth curve, and no inhibition of the growth was observed. Therefore, it is considered that there is no significant growth inhibitory effect of C. ellipsoidea under the natural sunlight irradiation. However, the number of cells in the cases of (B), (C) and (D) was not significantly different up to 80 hours, displaying that the growth inhibition effect of C. ellipsoidea was observed. Based on the comparison of cell numberof C. elliipsoideabetween mixture (Fig. 3a) and supernatant (Fig. 3b), the cell numbers alter in case of (A), whereas the cell numbers decreased faster in cases of (B), (C) and (D) in the supernatant, indicating that cells of C. elliipsoideamigrate vertically during the experiment. Since the photocatalytic reactions occurred around the water surface, highly reactive transitory species effectively inhibit the growth of C. elliipsoideaon the water surface, thus, C. elliipsoideamight migrate to the bottom of reactors.

Considering the cell numbers decreased faster in cases of (B), (C) and (D) in both mixture and supernatant, both surface reactions in heterogeneous photocatalysis and light shielding could inhibit the growth of C. elliipsoidea. Although dominant inhibitory effects on the growth of C. elliipsoideawere ambiguous, TiEPS balls were found to be effective to inhibit the excessive growth of algae in the stagnant water body. As shown in Fig. 4, cell morphology was clear and healthy in the case of (A), whereas cell contents were eluted out of the cell, and the circular shape of cell was distorted in the case of (B). This might be attributed to the attack of OH radical generated by the light of TiO_2 against the algal cell membrane. Further study is warranted to elucidate more dominant effects on the algal growth inhibition using intact vs. TiEPS balls.

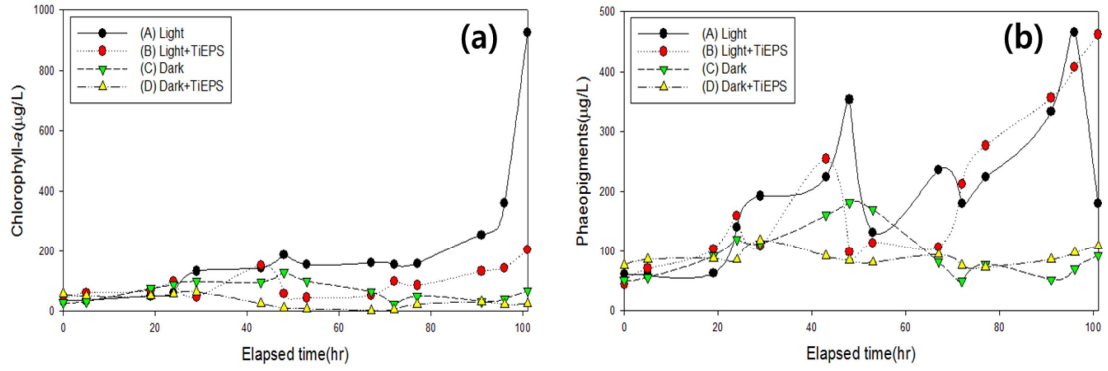

Fig.5. Changes in Chl-a and Phaeopigments the lab-scale inhibition experiment against the growth of C. ellipsoidea experiment. (a) Chl-a; (b) Phaeopigments

B. Chlorophyll-a and Phaeopigments

Chlorophyll-a (Chl-a) is an indirect indicator of the distribution coefficient of algae, and phaeopigments are indirect indicator of algae death[7-8]. As

displayed in Fig. 5a, Chl-a concentrations increasedwith time in case of light only whereas Chl-a concentrations decreased with time in case of (B), (C), and (D). Similar to the results of cell numbers, TiEPS balls were also found to be effective to inhibit the excessive growth of algaes based on the Chl-a.

As displayed in Fig. 5b, phaeopigment concentrations increasedwith time in cases of (A) and (B), whereas phaeopigment concentrations decreasedwith time in cases of (C) and (D). These results suggest that both algal growth and death occurred simultaneously in cases of (A) and (B), whereas both algal growth and death did not occur due to both surface reactions in heterogeneous photocatalysis and light shielding. Consequently, synergistic effects of both photocatalysic reactions and light shielding using TiEPS balls were significant in case of (B). Therefore, TiEPS balls were feasible to prevent and inhibit the excessive growth of algaes in eutrophic water body.

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