*Korean J. Chem. Eng.*, **18**(6), 889-893 (2001)

# Photocatalytic Inactivation of Algal Growth in Eutrophic Water with Hollow Glass Beads

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(*Received 3 September 2001 • accepted 28 September 2001*)

**Abstract**–Photocatalytic inactivation of algae, *Anabaena*, *Microcystis*, and *Melosira*, was performed with $TiO_2$-coated pyrex glass beads under the illumination of UV light (370 nm wavelength). After being irradiated with UV light in the presence of the $TiO_2$-coated pyrex glass beads, *Anabaena* and *Microcystis*, known as typical cyanobacteria, lost their photosynthetic activity, and the string of *Anabaena* cells and the colonies of *Microcystis* cells were completely separated into individual spherical ones. In the case of *Melosira,* which is a typical diatom, however, somewhat lower photocatalytic inactivation efficiency was obtained, which was believed to be due to the presence of the inorganic siliceous wall surrounding the cells of *Melosira.*

Key words: Photocatalytic Inactivation, Algae, $TiO_2$-coated Hollow Pyrex Glass Bead, Photosynthesis, *Anabaena*, *Microcystis*, *Melosira*

## INTRODUCTION

$TiO_2$ in anatase crystal form is a semiconductor with bandgap energy of 3.2 eV or more. Upon excitation by light of wavelength less than 385 nm, the photon energy generates an electron-hole pair on the $TiO_2$ surface. This electron-hole pair produces highly reactive oxygen species [Hoffmann et al., 1995]. These highly reactive species oxidize organic compounds adsorbed on the catalyst surface. The application of photocatalysts to destroy organic pollutants from contaminated water has been extensively studied [Ollis et al., 1989].

The problems created by algal blooms in eutrophic water are today a serious threat to life. Large populations of algae in water supply reservoirs may result in the blocking of filters in the treatment works. The reservoir may have to be taken out of service sometimes for several weeks, because the water becomes untreatable. Especially when toxic cyanobacterial blooms in drinking water supplies appear, drinking water may cause potential human health problems [Feitz et al., 1999]. Presently, the most common method to control algal blooms is dosing with copper based algicides. While this invariably destroys algae, it is no longer considered an effective treatment method as it produces secondary environmental problems.

Microbial cells in water were reported to be killed by the action of $TiO_2$ photocatalysis [Matsunaga et al., 1988; Ireland et al., 1993; Chai et al., 2000]. This finding gave us an insight that the massive growth of algae in eutrophic water can *a priori* be prevented by applying the photocatalytic activity of $TiO_2$. Despite a broad spectrum of investigation, the potential use of this technology for the inactivation of algae has been presently unexplored.

In the present work the photocatalytic inactivation of algae in water was carried out with the $TiO_2$ thin film coated on the surface of hollow pyrex glass beads. The beads were designed to float in water in order to enhance the close contact with algae.

## EXPERIMENTAL

### 1. Preparation of Supported $TiO_2$ Film on Hollow Glass Beads

As can be seen in Fig. 1, hollow pyrex glass beads (average diameter 20 mm) were designed to float in water. $TiO_2$ was coated on the surface of the beads by the well established method of dip coating [Pulker, 1984]. After being carefully cleaned by sonication in acetone the beads were immersed in a solution of 0.1 M titanium tetraisopropoxide [$Ti(OCH(CH_3)_2)_4$, from Merck] in dry eth-

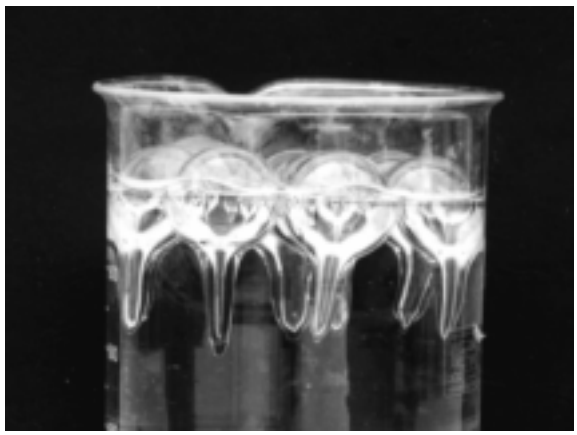

**Fig. 1. A representative photograph of the $TiO_2$-coated hollow pyrex glass beads floating in water.**

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anol (200 ml) and hydrochloric acid (2 N, 5.4 ml). The beads were removed from the solution at a constant rate of 2 cm/min. The samples were then dried in air for 15 minutes. Finally the samples were calcined at 673 K for 2 h.

**2. Characterization of the Samples**

The scanning electron micrographs were obtained with a Phillips (XL30) microscope working at 20 KV. The instrument was fitted with an energy dispersive X-ray (EDS) accessory. X-ray diffraction analysis (XRD) was carried out by using $CuK_{\alpha}$ radiation in a Siemens D5000 diffractometer.

**3. Photocatalytic Inactivation of Algae**

Three species of algae, *Anabaena*, *Microcystis*, and *Melosira*, which are commonly found in algal blooms in eutrophic water, were employed for the experiments of photocatalytic inactivation. The reactions were carried out in a batch reactor (2.0 m width, 2.0 m length, and 0.3 m depth). The reactor was placed below black light UV lamps [Model F4T5-BLB; wavelength, 370 nm (unfiltered); 20 W]. When the lamps were switched on, the lamps' irradiance was 0.60 $mWcm^{-2}$, as determined with a radiometer (Optronic Laboratories, Inc., Model OL730C) at the reaction solution surface. This UV intensity was selected so that test results could be relevant to solar-excited treatment designs [the average intensities of UV-A (330-390 nm) in sunlight in Seoul, Korea on the surface of rivers were 4.3 $mWcm^{-2}$ and 0.6 $mWcm^{-2}$ on cloudless days at 2 pm and cloudy days at 9 am, respectively].

Pure cultures of the three kinds of algae were obtained from the National Institute of Environmental Research (NIER), Korea. The algae were grown in a laboratory incubator through the procedures as indicated by NIER. Algae used in the experiments were obtained from axenic cultures that were started every 10-14 days to keep the cells growing in log phase.

$TiO_2$-coated hollow pyrex glass beads were added to the reactor, and suspension of the algae was introduced into the reactor to have the initial chlorophyll-a concentration of 150 $mg/m^3$.

**4. Measurements of Photosynthetic Activity of the Algae**

An indication of photosynthetic efficiency of algae was determined by carbon 14 method, which is known to be basically more sensitive than other methods [Greenberg et al., 1992]. Samples were withdrawn from the reactor during the reaction at different reaction times, and were charged into light and dark bottles. A solution of radioactive carbonate ($^{14}CO_3^{-2}$) was then added to the sample bottles. After being incubated *in situ*, the algae were collected on a membrane filter, were treated with hydrochloric acid (HCl) fumes to remove inorganic carbon 14, and were assayed for radioactivity with a liquid scintillation counter (Packard Co. Tri-carb model 1500). The quantity of carbon fixed by algae is proportional to the fraction of radioactive carbon assimilated. A more detailed procedure of this method is described in the reference [Greenberg et al., 1992].

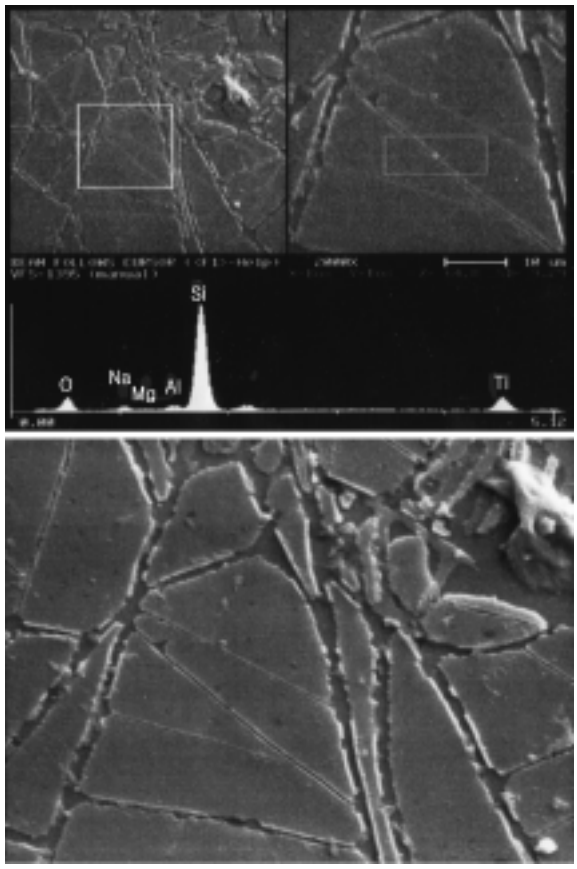


**Fig. 2. SEM micrograph and EDX analysis of the $TiO_2$ film immobilized on the pyrex glass bead.**

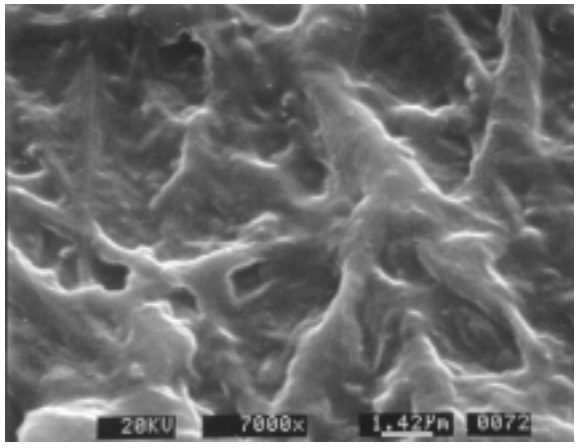


**Fig. 3. Detailed SEM micrograph of the $TiO_2$ film immobilized on the pyrex glass bead.**

## RESULTS AND DISCUSSION

**1. Characterization of $TiO_2$ Film**

SEM micrographs of $TiO_2$ film on the hollow pyrex glass bead are shown in Fig. 2. SEM analysis of the $TiO_2$ film on the glass bead shows a fractured appearance. The fracturing of the film is believed to be due to contraction and stress on drying. Additional fracturing may have occurred during the calcination process due to the different thermal coefficients of the overlayer and the substrate. From the EDX analysis of the film, titanium is found to be one of the major components.

When the $TiO_2$ film is observed in more detail with SEM (Fig. 3), the $TiO_2$ film is known to have porous surface morphology. The thickness of the $TiO_2$ film could be measured from the SEM image of the cross section of the glass bead (Fig. 4). The average thickness of the film was estimated to be 0.3 μm.

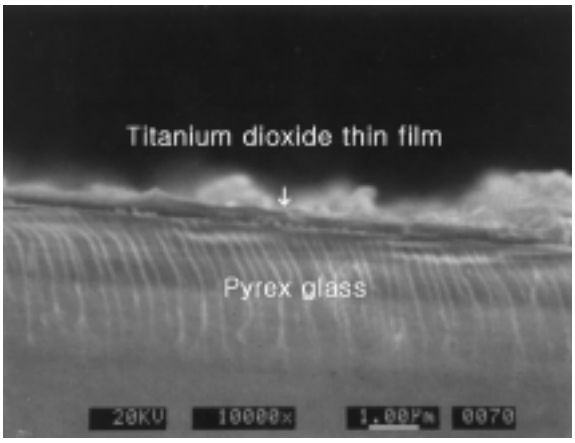


**Fig. 4. SEM micrograph of the cross section of the $TiO_2$-coated hollow pyrex glass bead.**

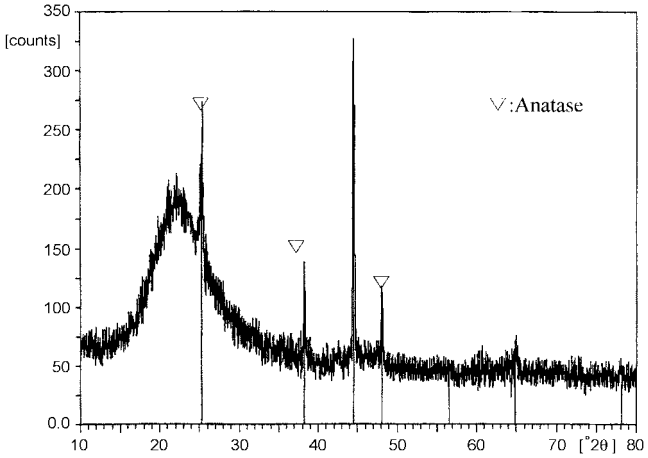


**Fig. 5. XRD diffractogram of the $TiO_2$ film immobilized on the pyrex glass bead.**

Fig. 5 shows the XRD pattern of the $TiO_2$ film. The peak appearing at 44.5° is attributed to the crystalline silica of the hollow pyrex glass bead. The $TiO_2$ film on the glass bead has anatase structure. Since anatase samples are generally, but not always, more active than rutile ones [Sclafani et al., 1990; Suri et al., 1993; Lee and Cho, 2001], the immobilized $TiO_2$ film is expected to show high efficiency for the inactivation of algae.

**2. Photocatalytic Inactivation of Algae**

Fig. 6 shows the optical microscopic images of the algae before reaction and after 30 minutes reaction with the $TiO_2$-coated hollow glass beads. Photograph A was obtained for *Anabaena*. *Anabaena* is a typical filamentous cyanobacterium. Constrictions between adjacent cells of *Anabaena*'s unbranched filaments give the appearance of a string of beads [Sze, 1998]. When irradiated by UV light in the presence of $TiO_2$-coated glass beads, the string of *Anabaena* came to be separated, and each spherical cell was completely isolated. The luminant bright yellow color (shown in the colorful photograph) of the cells before reaction is indicative of the vigorous photosynthetic activity of *Anabaena*. But most of the isolated cells of *Anabaena* lost their photosynthetic activity.

*Microcystis* is a typical nonfilamentous and a colonial cyanobacterium [Sze, 1998]. Colonies of *Microcystis* consist of hundreds of spherical cells in a mucilaginous sheath. As shown in photograph B, the colonies of spherical cells were completely isolated after 30 minutes reaction with the $TiO_2$-coated glass beads, and each cell almost lost its photosynthetic activity.

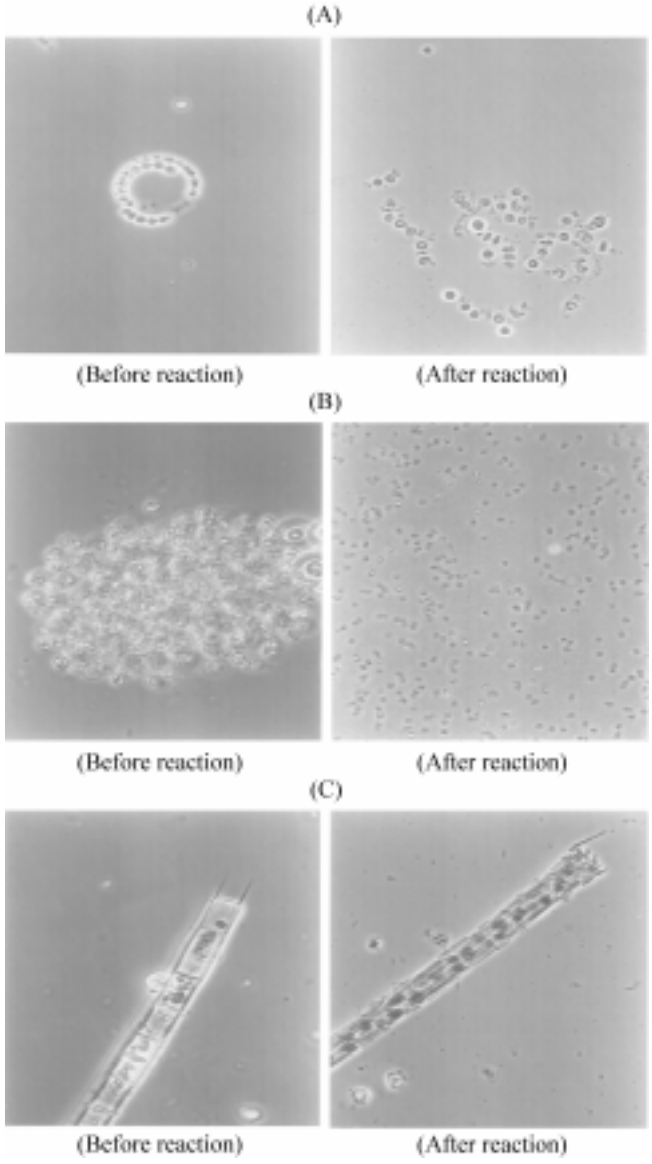


**Fig. 6. Optical microscopic images of the algae before and after photocatalytic reaction with the $TiO_2$-coated hollow glass beads for 30 minutes (A: *Anabaena*, B: *Microcystis*, C: *Melosira*).**

*Melosira* is a kind of diatom, which is an important component of planktonic communities in water habitats [Sze, 1998]. A distinctive siliceous wall, called a frustule, surrounds its nonflagellated vegetative cells [Sze, 1998]. As in the cases of *Anabaena* and *Microcystis*, the cell of *Melosira* was severely damaged and lost its photosynthetic activity after 30 minutes reaction with the $TiO_2$-coated glass beads (photograph C).

The results in Fig. 6 could be a direct evidence for the photocatalytic role of the $TiO_2$-coated glass beads on the inactivation of the algae.

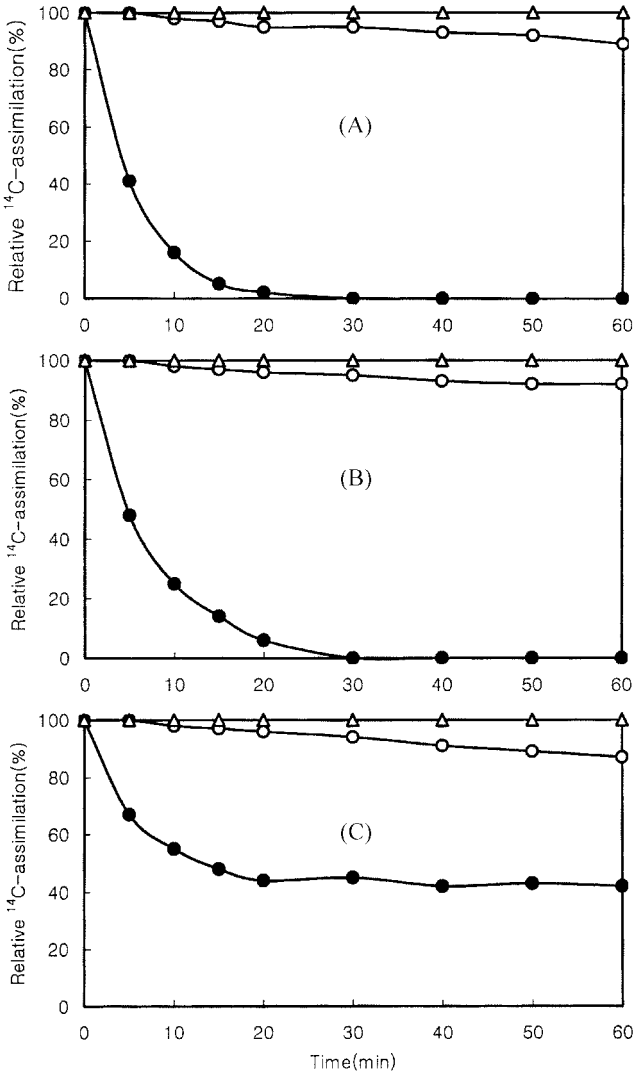


**Fig. 7. Changes in photosynthetic activity of *Anabaena* (A), *Microcystis* (B) and *Melosira* (C) with reaction time (●: photocatalytic reaction with the $TiO_2$-coated glass beads, △: dark reaction without the $TiO_2$-coated glass beads, ○: blank reaction under UV illumination without the $TiO_2$-coated glass beads).**

The photosynthetic activities of the algae during the reaction were also measured by carbon 14 method. Fig. 7 shows the photocatalytic reaction occurring with *Anabaena*, *Microcystis* and *Melosira* at different reaction times. The relative $^{14}$C-assimilation recorded on the Y-axis is the ratio of the $^{14}$C-assimilation before reaction and that during reaction. Most of the inactivation of the photosynthetic activity of *Anabaena* and *Microcystis* took place within 30 min. But in the case of *Melosira* much lower photocatalytic inactivation efficiency was observed. About 60% of the cells lost their photosynthetic activity in 40 minutes. The lower inactivation of *Melosira* is believed to be due to the presence of inorganic siliceous wall, called a frustule, surrounding the cells.

## CONCLUSION

$TiO_2$ was coated on the surface of the hollow pyrex glass beads through a sol-gel method. The $TiO_2$-coated hollow glass bead was employed as a photocatalyst to inactivate the algae under the illumination of UV light.

$TiO_2$ could successfully be immobilized as a film on the surface of the glass bead. The $TiO_2$ film had anatase form and a porous structure. The average thickness of the film was estimated to be 0.3 μm.

Three species of algae, *Anabaena*, *Microcystis* and *Melosira*, were taken for the inactivation experiments. When irradiated by UV light in the presence of the $TiO_2$-coated glass beads, the structure of the algae changed greatly. The string of *Anabaena* cells and the colonies of *Microcystis* cells were completely separated into individual spherical ones, and most of the isolated cells lost their photosynthetic activity. The cells of *Melosira* were also damaged severely after being contacted with the $TiO_2$-coated glass beads. Complete photocatalytic inactivation of *Anabaena* and *Microcystis* was obtained in about 30 min, while the inactivation efficiency for *Melosira* was somewhat lower than the cyanobacteria. The lower efficiency was believed to be due to the presence of the inorganic siliceous wall surrounding the cells of *Melosira*.

## ACKNOWLEDGEMENTS

This research was supported by G-7 program sponsored by Ministry of Environment, Korea.

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