Removal of microcystin-LR from drinking water with TiO₂-coated activated carbon

S.-C. Kim and D.-K. Lee

Department of Chemical Engineering/School of Environment Protection, Environment and Regional Development Institute, Environmental Biotechnology National Core Research Center, Gyeongsang National University, Kajwa-dong 900, Jinju, Gyeongnam 660-701, Korea

Abstract  TiO₂-coated granular activated carbon was employed for the removal of toxic microcystin-LR from water. High surface area of the activated carbon provided sites for the adsorption of microcystin-LR, and the adsorbed microcystin-LR migrated continuously onto the surface of TiO₂ particles which located mainly at the exterior surface in the vicinity of the entrances of the macropores of the activated carbon. The migrated microcystin-LR was finally degraded into nontoxic products and CO₂ very quickly. These combined roles of the activated carbon and TiO₂ showed a synergistic effect on the efficient degradation of toxic microcystin-LR. A continuous flow fluidized bed reactor with the TiO₂-coated activated carbon could successfully be employed for the efficient photocatalytic of microcystin-LR.

Keywords  Microcystin-LR; photocatalytic oxidation; TiO₂-coated activated carbon; drinking water; fluidized bed reactor

Introduction

The worldwide appearance of toxic cyanobacterial blooms in drinking water supplies has raised concerns about systemic effects on human health. One of the most acutely toxic cyanobacterial toxins is microcystin-LR which is a hepatotoxic material produced by several cyanobacteria generally including Microcystis, Anabaena and Planktothrix, which are increasingly found in water bodies at high densities (water blooms) as a result of eutrophication (Carmichael, 1992). This compound is a cyclic heptapeptide containing 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (ADDA), with leucine (L) and arginine (R) in the variable positions. Microcystin-LR has caused the death of both animals and humans as a result of ingestion of contaminated water. It is also believed that long-term exposure to sublethal levels of microcystins may promote primary liver cancer by disruption of protein phosphates 1 and 2A.

Different sources of activated carbon have been investigated for their ability to adsorb microcystin-LR. Wood-based products were found to be most effective because of their high mesopore volume. It was found that treatment with 25 µg/L of wood-based powdered activated carbon, with a contact time of 30 minutes, could reduce the concentration of microcystin-LR from 50 to < 1 µg/L. Granular activated carbon filters were found to be effective in reducing microcystin-LR levels from 20 to 1 µg/L (Drikas, 1994). Although both powdered and granular activated carbon have proven effective, the activated carbon adsorption method might become expensive due to frequent replacement or regeneration.

In recent years photocatalytic oxidation using TiO₂ powder has received considerable attention. TiO₂ is a semiconductor with a bandgap energy of 3.02 eV or more. Upon excitation by UV light of wavelengths less than 411 nm, the photons generate a pairs of electron-hole. These pairs migrate to the surface of the photocatalyst, where the holes may react with water molecules or hydroxyl groups adsorbed at the surface, thus forming reactive hydroxyl radicals. On the other hand, the electrons may react with oxygen molecules
adsorbed on the surface, thus producing highly reactive oxygen species (Hoffmann et al., 1995). These highly reactive oxygen species oxidize organic compounds adsorbed on the catalyst surface. The application of photocatalysts to destroy organic pollutants from contaminated water has extensively been studied (Lee and Cho, 2001a,b; Ollis et al., 1989). It was shown that microcystin-LR was rapidly destroyed by TiO$_2$ powder, even at extremely high toxin concentrations (Feitz et al., 1999; Lawton et al., 1999; Cornish et al., 2000). TiO$_2$ powder has, however, some detrimental shortcomings for practical application. TiO$_2$ powder is not only difficult to be separated from water after being used, but also reduces photocatalytic efficiency due to light scattering.

In order to make the environmental application of TiO$_2$ photocatalysis more practical immobilization of TiO$_2$ on a certain suitable substrate is inevitably required. Granular activated carbon can be a successful substrate due to its adsorption ability of microcystin-LR and easy separation from water. When combining the roles of both the adsorption and photocatalytic destruction, the TiO$_2$-immobilized granular activated carbon is expected to show successful performance for the removal of microcystin-LR from water.

In the present study TiO$_2$ was coated mainly at the exterior surface neighboring the macropore entrances of the granular activated carbon, and this TiO$_2$-coated activated carbon was employed for the adsorption followed by photocatalytic oxidation of microcystin-LR. The photocatalytic performances of the TiO$_2$-coated activated carbon were also investigated in a continuous flow fluidized bed reactor.

**Experimental**

**Materials**

Microcystin-LR was purchased from Sigma-Aldrich Co. Granular activated carbon was prepared by exposing carbonized coconut shell to steam at 900°C. The average particle size was adjusted to be 1 mm through crushing process. Titanium tetraisopropoxide [Ti(OCH(CH$_3$)$_2$)$_4$] and isopropyl alcohol, obtained from Merk, were used as the precursor of TiO$_2$ and solvent, respectively. All solutions were prepared in Milli-Q water, and all other organic solvents used were analytical grade.

**TiO$_2$ coating procedures**

In order to locate TiO$_2$ mainly at the exterior surface in the vicinity of macropores of the activated carbon, a modified sol-gel preparation method was employed. Twenty grams of the activated carbon were placed in a flask of a rotary evaporator. After filling the pores of the activated carbon with pure isopropyl alcohol at 20°C, the temperature was dropped to $-4^\circ$C immediately. The mixture of 15 mL titanium tetraisopropoxide and 15 mL water was then introduced into the activated carbon drop by drop during 24 h under continuous stirring. The prepared samples were then dried in vacuo at 50°C for 24 h. The dried samples were finally treated in a microwave oven with a microwave power generator (Hitachi, 600 W) for 3 h.

**Adsorption and photocatalysis**

The adsorption and photocatalysis of microcystin-LR were performed with a water-jacketed borosilicate glass vessel incorporating a quartz window for ultraviolet (UV) light illumination. The light source was a 4-Watt black light lamp (370 nm, F4T5-BLB). When the lamp was switched on, the lamp irradiance was 0.6 mW/cm$^2$, as determined with a radiometer (Optronic Laboratories, Inc., Model OL730C). The water cooling jacket provided a constant temperature of $20 \pm 0.5^\circ$C in the vessel. The vessel contained the granular activated carbon without TiO$_2$(GAC) or the granular activated carbon with TiO$_2$(GAC-Ti) completely dispersed in an aqueous phase with microcystin-LR. The initial concentration of
microcystin-LR (200 μg/mL) used in this investigation was considerably higher than might be expected to occur in natural environment (Hrudrag et al., 1994; James, 1996). However, this enabled direct analysis of toxin by HPLC without multistep processing that would be necessary to quantify the much lower levels found in the environment. A GAC or GAC-Ti dosage of 1.0 g/L was used in the experiments if not mentioned otherwise.

Analytical methods
Analysis of microcystin-LR was performed by HPLC with photodiode array detection (column, Symmetry C18 250 × 4.6 μm i.d.; detection, Waters 996 high-resolution diode array monitoring between 200 and 300°C) (Cornish et al., 2000). The extent of mineralization of microcystin-LR during photocatalysis was monitored using methods similar to those described by Cornish et al. (2000). A closed system containing GAC-Ti and microcystin-LR solution was sparged with pure oxygen. The gas stream from the vessel was bubbled through a Ba(OH)₂ conductivity cell. The generation of CO₂ from photocatalysis results in the production of insoluble BaCO₃, reducing the conductivity of the solution in the conductivity cell.

The prepared TiO₂-coated activated carbon was characterized with a scanning electron microscopy (SEM, Phillips XL30) and a transmission electron microscopy (JEOL 200CX).

Fluidized bed reactor
Adsorption and photocatalytic oxidation of microcystin-CR with GAC and GAC-Ti was carried out in a cylindrical continuous flow fluidized bed reactor (Figure 1) with 65 cm height and 68 cm inside diameter. Four black light UV lamps were installed inside the reactor. 4.5 kg of GAC or GAC-Ti was loaded inside the reactor and aqueous solution of microcystin-LR (50 μg/mL concentration) was fed into the bottom of the reactor. The exit stream of the reactor was analyzed for microcystin-LR concentration.

Results and discussion
Characterization of GAC-Ti
Figure 2 shows the SEM micrograph of the TiO₂-coated granular activated carbon used in this study. As can be seen in this figure, pores are well developed and their average diameter was estimated to be 1.0 nm.

When looking the pores in more detail with TEM, fine particles of TiO₂ are known to be dispersed at the exterior surface in the vicinity of the pores (Figure 3).

Figure 1 Schematics of the fluidized bed reactor (A: inlet, B: UV-lamp, C: pressure gauge, D: outlet)
Adsorption of microcystin-LR with GAC

The concentrations of microcystin-LR remaining in the solution over time in the absence and presence of GAC and in the absence and presence of light are shown in Figure 4. $C_0$ in the y label denotes the initial microcystin-LR concentration, and $C_t$ is the microcystin-LR concentration at corresponding reaction times. It is clear that essentially no decrease in microcystin-LR concentration occurs in the absence of GAC, while in the presence of GAC more than 50% initial microcystin-LR disappears within 30 min. The presence of light, however, does not give any additional detectable effects on the removal efficiency of microcystin-LR. These results support the hypothesis that an adsorption process by GAC accounts for the reduction in concentration of microcystin-LR and homogeneous photolysis of microcystin-LR is not a significant process. The adsorption of microcystin-LR on GAC proceeded slowly and more than 12 h exposure was required for the complete removal of microcystin-LR.

Photocatalytic degradation of microcystin-LR with GAC-Ti

Figure 5 demonstrates the effects of GAC-Ti on the removal of microcystin-LR in the presence and absence of light. Microcystin-LR disappears very rapidly on exposure to GAC-Ti and light. This rapid disappearance, however, is not observed in the absence of light. Almost complete removal of microcystin-LR under illumination can be achieved in approximately 20 min. This extremely rapid removal rate of microcystin-LR on TiO$_2$-coated
activated carbon (GAC-Ti) might be due to the photocatalytic destruction of microcystin-LR on the surface of TiO₂ particles. As can be seen in Figure 2, fine TiO₂ particles were located mainly in the vicinity of the pore entrances of the activated carbon. Microcystin-LR might adsorb onto the surface of TiO₂ particles and/or on the surface of the activated carbon. The adsorbed microcystin-LR on TiO₂ particles is believed to be degraded quickly. Microcystin-LR was already reported to be degraded photocatalytically by TiO₂ powder at very fast rate (Feitz et al., 1999; Lawton et al., 1999; Cornish et al., 2000).

After being exposed to microcystin-LR aqueous solution in the absence and presence of light for different times, GAC-Ti was subjected to solvent extraction with 1 L methanol for 2 h to determine if residual microcystin-LR was remained, and the results are shown in Figure 6. The extracted concentrations of microcystin-LR from GAC-Ti which was exposed to microcystin-LR aqueous solution in the presence of light were much lower than the corresponding concentrations obtained from GAC-Ti which was exposed to microcystin-LR aqueous solution in the absence of light. The extracted concentration of microcystin-LR from the illuminated GAC-Ti for 30 min was 0.12 μg/mL. This concentration is about one hundred times lower than the extracted one (13.4 μg/mL) from GAC-Ti without light. In addition, the extracted concentration from GAC-Ti without light increases gradually with increasing exposure time, while the extracted concentration from the illuminated GAC-Ti goes through maximum and then decreases rapidly. After being exposed for longer than 40 min, no residual microcystin-LR was detected from GAC-Ti.

These behaviors indicate that TiO₂ particles in the activated carbon must have played an important role on accelerating the continuous degradation of microcystin-LR in the presence of light. Part of microcystin-LR in the aqueous solution will directly adsorb onto the surface of TiO₂ particles, and will then photocatalytically be degraded quickly. The other part of microcystin-LR, which was adsorbed to the surface of activated carbon, is suggested to migrate continuously onto the surface of TiO₂ particles for the subsequent photocatalytic degradation.

In order to confirm the suggested migration of adsorbed microcystin-LR from the surface of activated carbon onto the surface of TiO₂, a separate experiment was carried out. GAC-Ti was exposed to microcystin-LR aqueous solution up to 30 min in the absence of light. After 30 min operation the UV lamp was switched on, and the concentrations of microcystin-LR in the solution were measured (Figure 7).

The removal of microcystin-LR proceeds somewhat slowly in the absence of light. Upon illumination the concentration of microcystin-LR decreases rapidly, and most of microcystin-LR was removed within another 20 min. After 90 min operation, GAC-Ti was
extracted with methanol. No detectable amount of microcystin-LR was measured in the extracted solvent. This result provides a further evidence for the aforementioned suggestion that the adsorbed microcystin-LR on the surface of activated carbon migrates continuously onto the surface of TiO₂ for the subsequent photocatalytic degradation.

**Extent of mineralization**

The extent to which microcystin-LR was mineralized through photocatalytic degradation with GAC-Ti was measured using a simple conductivity method as described in the experimental section. Although complete removal of microcystin-LR was observed after 20 min operation in the presence of light, just 48.9% of the total microcystin-LR was mineralized. Many kinds of byproducts, which could not successfully be identified through HPLC-MS spectroscopy, were produced in small quantities during the reaction. They must be stable against photocatalytic destruction and do not undergo complete degradation.

Since it was shown that microcystin-LR is not completely degraded, it is important to confirm that the photocatalytic breakdown byproducts are non-toxic. Lawton et al. (1999) also observed the similar formation of the stable byproducts during the photocatalytic degradation.

![Figure 8](image1.png)  
**Figure 8** Changes in the height of the fluidizing activated carbon particles with the volumetric flow rates of water

![Figure 9](image2.png)  
**Figure 9** Concentration of microcystin-LR at the exit of the fluidized bed reactor with GAC and GAC-Ti at different volumetric flow rates (●: 155 cm³/s, GAC; ■: 199 cm³/s; ○: 155 cm³/s, GAC-Ti; □: 199 cm³/s, GAC-Ti)
reaction with TiO₂ powder. They assessed the toxicity of the byproducts using brine shrimp bioassay method, and they could not detect any measurable toxicity of the byproducts. However, the degradation of microcystin-LR via GAC-Ti and pure TiO₂ might proceed in different manners. Accordingly the byproducts could not be said to be non-toxic. Additional assessment is needed to be carried out.

**Performance of the fluidized bed reactor**

In order to investigate the fluidizing patterns of the activated carbon particles, 4.5 kg activated carbon was loaded inside the reactor. The initial depth \( (H_0) \) of the packed activated carbon bed was approximately 2.5 cm. Upon introduction of upward-flowing water, the bed began to expand, and at higher flow rates of water the expanded bed became fluidized. In Figure 8 is shown the height of the fluidized bed \( (H_f) \) as a function of the volumetric flow rate of water. When the flow rate is lower than 50 cm³/s, the expansion of the bed is almost negligible. At the flow rates higher than 50 cm³/s detectable expansion of the bed is observed. Successful fluidization without carryover of the activated carbon particles could be obtained at the flow rates of upward-flowing water between 150 and 200 cm³/s.

Microcystin-LR solution (50 \( \mu g/mL \) concentration) was fed into the reactor at the fluidizing flow rates, and the microcystin-LR concentrations at the exit stream of the reactor were measured. Figure 9 illustrates the microcystin-LR removal efficiencies obtained with the 4.5 kg TiO₂-free activated carbon (GAC) and with 4.5 kg TiO₂-coated activated carbon (GAC-Ti) under the illumination of UV-light at different fluidizing velocities. The concentration of microcystin-LR at the exit of the reactor after 30 min operation with GAC were 12.8 and 20.2 \( \mu g/mL \) at the flow rates of 155 and 199 cm³/sec, respectively. About 60–75% of the microcystin-LR in the feed solution can be said to be removed. Then exit concentration of microcystin-LR increase gradually, and reach at around 37 \( \mu g/mL \) after 540 min operation. These results indicate that the surface of the activated carbon becomes saturated due to the containing uptakes of microcystin-LR. On the contrary, more than 95% of the microcystin-LR in the feed solution is steadily removed up to 540 min operation with GAC-Ti. As mentioned previously, this stable and high removal efficiency is due to the adsorption of microcystin-LR on the surface of the activated carbon followed by continuous migration onto the surface of TiO₂ particles where subsequent fast oxidation of microcystin-LR proceeds.

**Conclusion**

Microcystin-LR in water could successfully be degraded by using TiO₂-coated granular activated carbon. Most of microcystin-LR was degraded within 20 min under UV light. Microcystin-LR, adsorbed to the surface of the activated carbon, migrated continuously onto the surface of TiO₂ particles locating near the entrance of macropores in the activated carbon. Continuous migration and subsequent photocatalytic oxidation on the surface of TiO₂ accelerated microcystin-LR removal efficiency greatly, and made the application of the TiO₂-coated granular activated carbon more practical. Photocatalytic oxidation of microcystin-LR with the TiO₂-coated activated carbon in the continuous flow fluidized bed reactor yielded more than 95% removal efficiency stably up to 540 min operation.

**Acknowledgement**

This work was supported by a grant from the KOSEF/MOST to the Environmental Biotechnology National Core Research Center (grant #: R15-2003-012-02002-0).

S.C. Kim and D.K. Lee
References