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Photocatalytic oxidation of microcystin-LR with TiO_2-coated activated carbon

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Abstract

TiO_2-coated granular activated carbon was employed for the removal of toxic microcystin-LR from water. Surface areas of the activated carbon in the vicinity of TiO_2 particles provided sites for the adsorption of microcystin-LR, and the adsorbed microcystin-LR migrated continuously onto the surface of TiO_2 particles which were 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 CO_2 very quickly. These combined roles of the activated carbon and TiO_2 showed a synergistic effect on the efficient degradation of toxic microcystin-LR. For this purpose, 0.6 wt.% TiO_2 loading in the TiO_2-coated activated carbon was proved to be the most effective.

1. 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 hepatoxic material produced by several cyanobacteria general including *Microcystis*, *Anabaena*, and *Planktothrix*, which are increasingly found in water bodies at high densities water blooms) as a result of eutrophication [1]. The structure of microcystin-LR, the subject of this study, is shown in Fig. 1. 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.

Conventional water treatment methods of chemical coagulation, flocculation, and sand filtration are poor at removing low concentrations of cyanotoxins [2]. Treatment using chlorination requires high doses and long contact times, and there is the possibility of generating toxic byproducts such as trihalomethanes. Biological methods typically require a reaction time of hours to days. Thereby, special treatment methods need to be developed.

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 mg/L of wood-based powdered activated carbon, with a contact time of 30 min, could reduce the concentration of microcystin-LR from 50 to $<1\,\mu g/L$. Granular activated carbon filters were found to be effective in reducing microcystin-LR levels from 20 to $1\,\mu g/L$ [3]. Although both powdered and granular activated carbon have proven effective, the presence in the water of other organic pollutants that could be adsorbed by the activated carbons needs to be considered. Due to frequent replacement or regeneration, the activated carbon adsorption method might become expensive.

In recent years, photocatalytic oxidation using TiO_2 powder has received considerable attention. TiO_2 is a semiconductor with a band gap 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 TiO_2 surface. This electron–hole pair produces highly reactive oxygen species [4]. These highly reactive oxygen species oxidize organic compounds adsorbed on the catalyst surface. The application of photocatalysts to destroy organic pollutants

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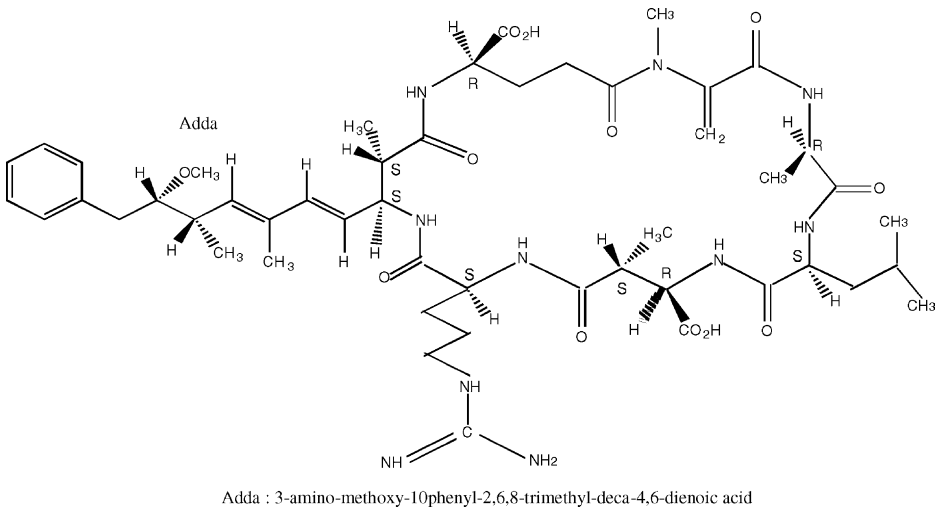

Fig. 1. The structure of microcystin-LR.

from contaminated water has extensively been studied [5–8]. It was shown that microcystin-LR was rapidly destroyed by TiO_2 powder, even at extremely high toxin concentrations [2,9,10]. 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 in the vicinity of 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.

2. Experimental

2.1. Materials

Microcystin-LR was purchased from Sigma–Aldrich. 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.

2.2. 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 °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. By repeating these processes several times, the amount of TiO_2 loaded could be changed.

2.3. Adsorption and photocatalysis

The adsorption and photocatalysis of microcystin-LR were performed with a water-jacketed borosilicate glass vessel (1 L capacity) incorporating a quartz window for ultraviolet (UV) light illumination. The light source was a 4-W 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 ± 0.5 °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 [11,12]. However, this enabled direct analysis of toxin by HPLC without multistep processing that would be necessary to

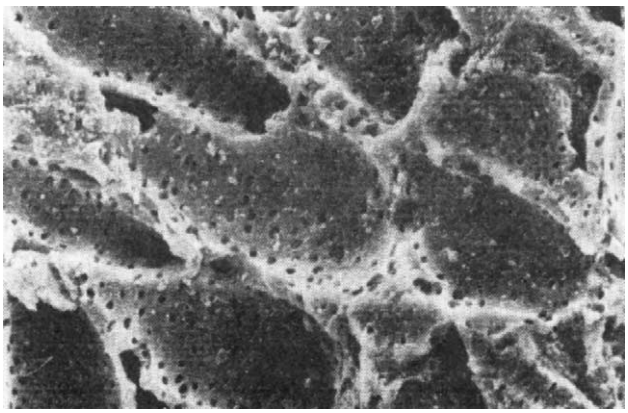

Fig. 2. SEM micrograph of the TiO_2-coated activated carbon (GAC-Ti (0.6 wt.%)).

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.

2.4. Analytical methods

Analysis of microcystin-LR was performed by HPLC with photodiode array detection (column, Symmetry C18 250 × 4.6 nm i.d.; detection, Waters 996 high-resolution diode array monitoring between 200 and 300 nm) [9]. The extent of mineralization of microcystin-LR during photocatalysis was monitored using methods similar to those described by Cornish et al. [9]. 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 CO_2 from photocatalysis results in the production of insoluble $BaCO_3$, reducing the conductivity of the solution in the conductivity cell.

The prepared TiO_2-coated activated carbon was characterized with a scanning electron microscopy (SEM, Phillips XL30) and a transmission electron microscopy (JEOL 200CX). Surface areas and pore volumes of the samples were determined by using nitrogen as the sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP 2010).

3. Results and discussion

3.1. Characterization of GAC-Ti samples

The quantities of TiO_2 in the GAC-Ti samples changed with the numbers of repetition of the preparation steps as described in the Section 2.2. GAC-Ti samples were dissolved with excess concentrated HCl solution and the Ti concentration in the solution was quantified with ICP. Chemical analyses showed that the TiO_2 loads were 0.6, 1.1, 1.5, and 1.9% in weight for the samples underwent one, two, three, and four times preparation steps, respectively.

Fig. 2 shows the SEM micrograph of the TiO_2-coated granular activated carbon with 0.6 wt.% TiO_2 loading used in this study. As can be seen in this figure, macropores are well-developed and their average diameter was estimated to be 1.0 μm.

When looking the macropores in more detail with TEM, fine particles of TiO_2 are known to be dispersed at the exterior surface in the vicinity of the macropores(Fig. 3). XRD analysis showed that TiO_2 particles are in anatase crystalline form.

3.2. 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 Fig. 4. 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. This result indicates that the

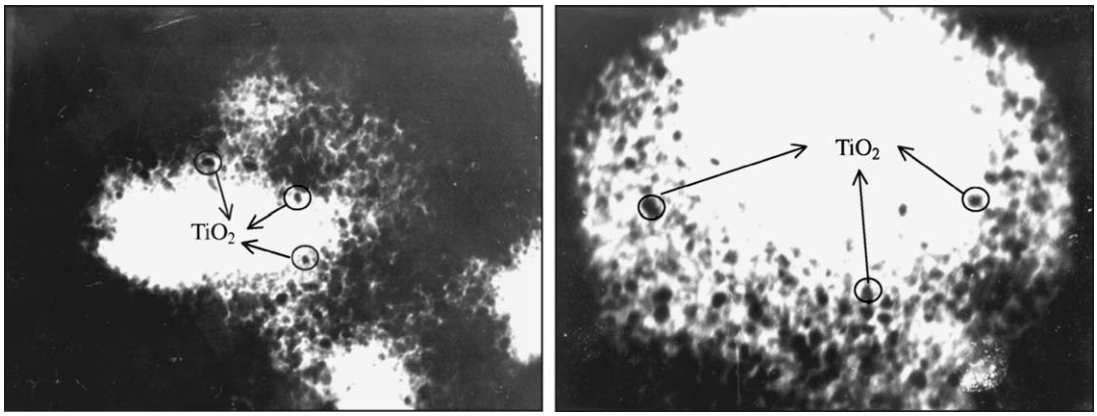

Fig. 3. TEM micrographs of the TiO_2-coated activated carbon (GAC-Ti) (0.6 wt.%)) (left: 40,000× magnification and right: 85,000× magnification).

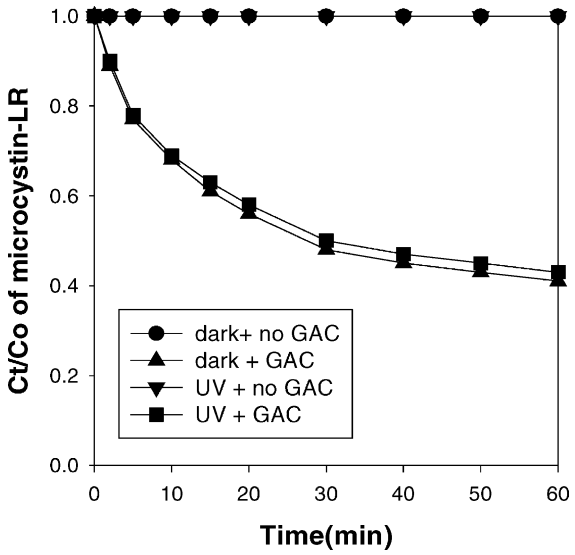

Fig. 4. Changes in microcystin-LR concentration with time in the absence and presence of GAC and in the absence and presence of light.

adsorption of microcystin-LR on the surfaces far from the entrances of macropores is hindered by diffusion limitation.

3.3. Photocatalytic degradation of microcystin-LR with GAC-Ti (0.6 wt.%)

Fig. 5 demonstrates the effects of GAC-Ti (0.6 wt.%) 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 GAC-Ti (0.6 wt.%) might be due to the photocatalytic oxidation of

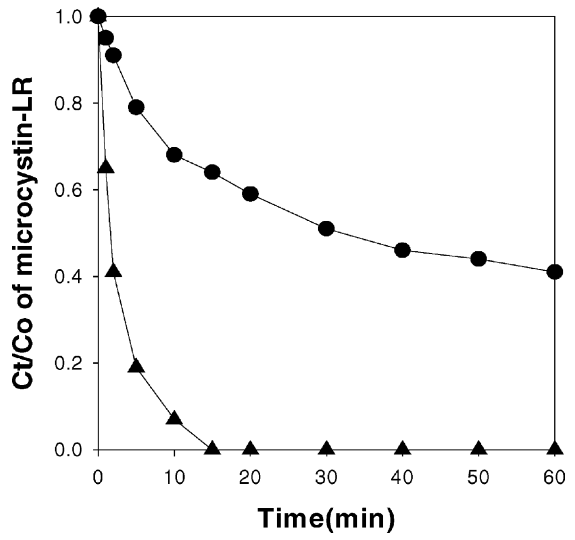

Fig. 5. Effects of GAC-Ti (0.6 wt.%) on the removal of microcystin-LR in the absence (●) and presence (▲) of light.

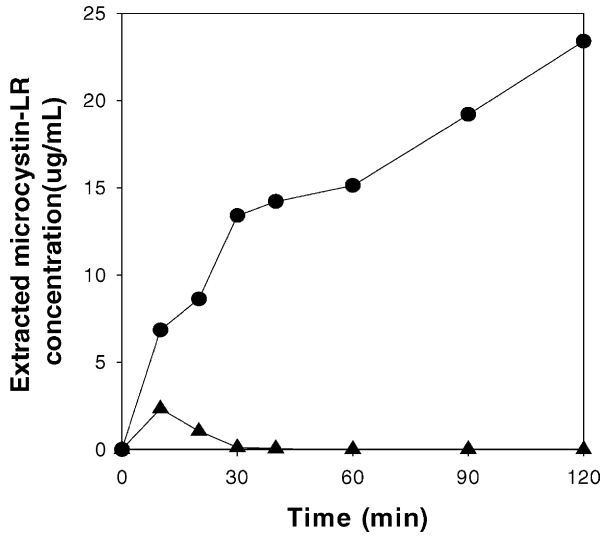

Fig. 6. Concentration of microcystin-LR extracted from GAC-Ti (0.6 wt.%) after being exposed to microcystin-LR aqueous solution for different times in the absence (●) and presence (▲) of light.

microcystin-LR on the surface of TiO_2 particles. As could be seen in Fig. 3, fine TiO_2 particles were located mainly in the vicinity of the pore entrances of the activated carbon. Microcystin-LR might adsorb onto the surface of TiO_2 particles and/or on the surface of the activated carbon. The adsorbed microcystin-LR on TiO_2 particles is believed to be oxidized quickly. Microcystin-LR was already reported to be oxidized photocatalytically by TiO_2 powder at very fast rate [2,9,10].

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 Fig. 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 (0.6 wt.%) which was exposed to microcystin-LR aqueous solution in the absence of light. The extracted concentration of microcystin-LR from the illuminated GAC-Ti (0.6 wt.%) 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 (0.6 wt.%) 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 (0.6 wt.%) goes through maximum and then decreases rapidly. After being exposed for longer than 40 min, no residual microcystin-LR was detected from GAC-Ti (0.6 wt.%).

These behaviors indicate that TiO_2 particles in the activated carbon must have played an important role on accelerating the continuous degradation of microcystin-LR in the presence of light. Blank experiment with 6 mg TiO_2 powder (corresponding loading of the GAC-Ti (0.6 wt.%) sample)

alone showed that the conversion of microcystin-LR was just 7.6% after 60 min reaction. Accordingly the effect of TiO_2 in the GAC-Ti (0.6 wt.%) sample is not additive but synergistic. Since microcystin-LR is a large size molecule, long distance migration from the internal surface of the activated carbon onto TiO_2 particles which were located mainly at the entrances of macropores will be really difficult.

In the GAC-Ti (0.6 wt.%) sample, part of microcystin-LR in the aqueous solution will directly adsorb onto the surface of TiO_2 particles, and will then photocatalytically be oxidized quickly. The other part of microcystin-LR seems to adsorb on the surface of the activated carbon in the vicinity of TiO_2 particles, and the adsorbed microcystin-LR migrates onto neighboring TiO_2 particles for its subsequent photocatalytic degradation. That is, the surfaces of the activated carbon in the vicinity of the TiO_2 particles provided sites for continuing adsorption of microcystin-LR, which results in the synergistic effect of the GAC-Ti (0.6 wt.%) samples on the efficient removal of microcystin-LR.

In order to confirm the suggested migration of adsorbed microcystin-LR from the surface of activated carbon onto the surface of TiO_2, a separate experiment was carried out. GAC-Ti (0.6 wt.%) 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 concentration of microcystin-LR in the solution were measured (Fig. 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 (0.6 wt.%) 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 TiO_2 for the subsequent photocatalytic degradation.

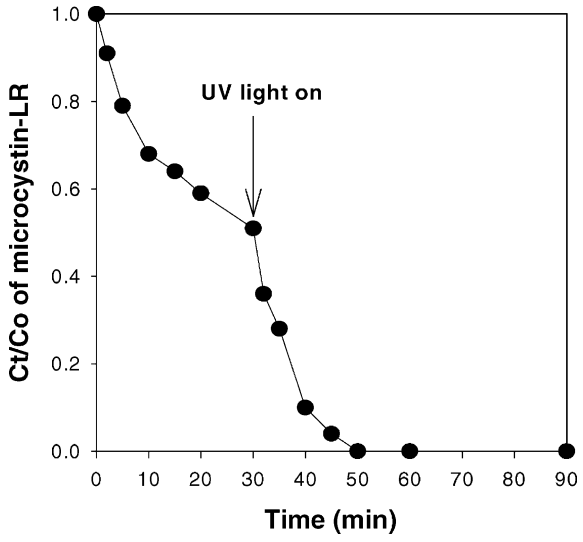

Fig. 7. Effects of UV illumination on the removal of microcystin-LR with GAC-Ti (0.6 wt.%).

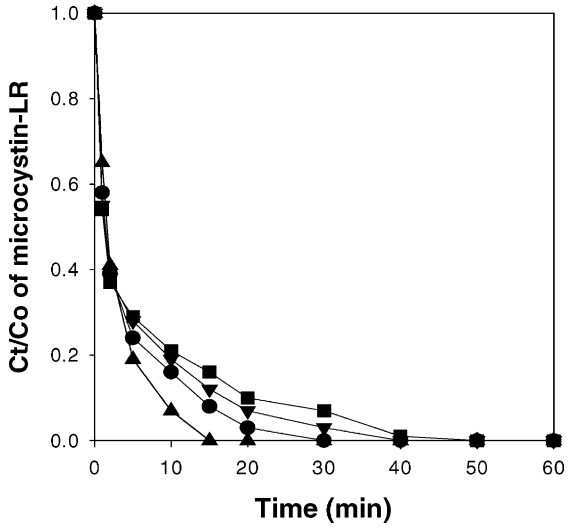

Fig. 8. Changes in microcystin-LR concentrations during the reaction with the GAC-Ti (0.6 wt.%) (▲), GAC-Ti (1.1 wt.%) (●), GAC-Ti (1.5 wt.%) (▼), and GAC-Ti (1.9 wt.%) (■) in the presence of light.

3.4. Effects of TiO_2 loadings

Fig. 8 shows the effects of TiO_2 loading on the microcystin-LR removal efficiencies on the GAC-Ti samples. With increasing TiO_2 loading, the microcystin-LR concentrations drop more rapidly up to the first 2 min. After 2 min reaction, however, the microcystin-LR concentrations in the solution are higher during the reaction with the GAC-Ti sample having higher TiO_2 loadings. In the case of the GAC-Ti (0.6 wt.%), compete removal of microcystin-LR from the solution is achieved within 15 min, while it takes 40 min with the GAC-Ti (1.5 wt.%) sample.

Ti concentrations present in the activated carbon particle were analyzed with a SEM/EDX (X-ray energy dispersive analysis). Most of TiO_2 were mainly located at the exterior surface of the activated carbon particle irrespective of the weight loadings of TiO_2. Too much quantities of TiO_2 may result in the partial blocking of the macropore and micropores of the activated carbon. The pore volume and surface area of the GAC-Ti (1.5 wt.%) were 0.36 cm^3/g and 615 m^2/g, respectively which were much lower than those of the GAC (0.48 cm^3/g pore volume and 996 m^2/g surface area) and the GAC-Ti (0.6 wt.%) (0.43 cm^3/g pore volume and 862 m^2/g surface area). In the case of the GAC-Ti (1.5 wt.%) sample part of the pores of the activated carbon must have been blocked during the coating processes of TiO_2. The partial blocking of the pores will make the diffusion of the huge microcystin-LR molecules onto the interior surface of the activated carbon more difficult, thereby inhibiting the continuous migration of the adsorbed microcystin-LR onto TiO_2 particles.

Although this progressive inhibition of the synergistic effects between the adsorption on the activated carbon and photocatalytic oxidation on TiO_2 with increasing blocking of the pore (or with increasing TiO_2 weight loading in the GAC-Ti samples), the direct photocatalytic oxidation of microcystin-LR on TiO_2 particles becomes more predominant. Accordingly the GAC-Ti (0.6 wt.%) seems to be the most effective for the removal of microcystin-LR through the adsorption followed by photocatalytic oxidation.

3.5. Extent of mineralization

The extent to which microcystin-LR was mineralized through photocatalytic oxidation with GAC-Ti (0.6 wt.%) was measured using a simple conductivity method as described in Section 2. 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 oxidation.

Since it was shown that microcystin-LR is not completely oxidized, it is important to confirm that the photocatalytic breakdown byproducts are nontoxic. Lawton et al. [10] also observed the similar formation of the stable byproducts during the photocatalytic reaction with TiO_2 powder. They assessed the toxicity of the byproducts using brine shrimp bioassay method, and they could not detect any measurable toxicity of the byproducts.

4. Conclusions

Microcystin-LR in water could successfully be degraded into non-toxic materials by using TiO_2-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 TiO_2 particles locating near the entrance of macropores in the activated carbon. Continuous migration and subsequent photocatalytic oxidation on the surface of TiO_2 accelerated microcystin-LR removal efficiency greatly, and made the application of the TiO_2-coated granular activated carbon more practical. Two much weight loading of TiO_2 in the TiO_2-coated activated carbon samples resulted in the partial blocking of the pores of the activated carbon, and much longer times were required for the complete removal of microcystin-LR. 0.6 wt.% TiO_2 loading was the most appropriate for the effective removal of microcystin-LR through the continuous adsorption, migration and the subsequent photocatalytic oxidation.

Acknowledgements

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