Solar-driven photocatalytic decomposition of microcystin-LR: from laboratory development to on-site demonstration

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ABSTRACT

Harmful algal blooms (HABs) found in various water bodies worldwide have been a huge concern due to their adverse impacts on human health and ecosystems. In particular, HABs associated with cyanobacteria have been of great interest because of their potential to generate and release biological toxins, especially, lethal microcystins (MCs). The overall goal of this study was to develop a new sustainable approach to decompose MCs, preferably on-site and in real-time with minimal effort, fewer chemicals, and low energy inputs. To achieve the goal, a high efficiency nitrogen-doped TiO₂ photocatalytic film immobilized onto a glass substrate was fabricated via integrated sol-gel synthesis employing nitrogen-containing surfactants as pore-templating agent and nitrogen-dopant. The film exhibited visible light-activated, nanoporous, and transparent properties. Effects of surfactant type, calcination temperature, coating layers, and reaction pH on the photocatalytic decomposition of microcystin-LR (MC-LR) were investigated under visible light. Eventually, the TiO₂ film was able to successfully decompose MC-LR on-site in a lake under solar radiation in real-time. This study implies the high potential of the TiO₂ film for on-site and real-time decomposition of many organic contaminants in water by using sustainable solar energy.

Key words | biological toxins, harmful algal blooms, microcystins, on-site treatment, solar radiation, TiO₂ photocatalysis

INTRODUCTION

Contamination of water resources with natural and anthropogenic chemicals has been a huge concern worldwide. Particularly, the increasing occurrence of harmful algal blooms (HABs) alarms water and health authorities and the general public (Nfodzo et al. 2015). Specifically, HABs associated with cyanobacteria (so-called cyano-HABs) produce and release lethal biological toxins such as microcystins (MCs) (Bownik 2016). MCs are a group of natural toxins that act as hepatotoxins and promote formation of tumors (Antoniou et al. 2005). Animal poisoning and fish killing have been reported in conjunction with MCs, resulting in significant economic losses (Svircev et al. 2015; Bownik 2016). Among more than 100 MC congeners, microcystin-LR (MC-LR) is the most notorious due to its high toxicity and prevalence and thus the United States Environmental Protection Agency has placed the toxin on the drinking water health advisories (USEPA 2015).

Particulate algae can be easily removed by conventional water treatment processes but cyanobacterial toxins dissolved in water are usually recalcitrant and hard to remove (Lawton & Robertson 1999). Many technologies, including activated carbon adsorption, coagulation/sedimentation, membrane separation, and chemical oxidation, have been tested for treatment of MC-LR (Campinas & Rosa 2010; Li et al. 2014; Roegner et al. 2014; Jasim & Saththasivam 2017). However, these ex-situ treatment approaches benefit only those who directly use treated water. They do not provide a systematic tool to protect the ecosystem in HAB sites. As a result, the overall goal of this study is to develop an on-site (or in-situ) treatment
approach for removal of cyanobacterial toxins. Considering many limitations occurring during on-site applications, such a treatment approach should be characterized, if possible, with minimal effort, fewer chemicals, and low energy inputs. Once developed, the approach is also important with respect to source water management.

In order to achieve the goal and to fulfill the requirements, this study proposes to use a high efficiency nitrogen-doped TiO2 photocatalytic film immobilized onto a glass substrate. TiO2 photocatalysis is one of the most effective water treatment processes (Choi et al. 2010; Lazar et al. 2012; Pelaez et al. 2012). Strong hydroxyl radicals generated from TiO2 non-selectively and readily attack and decompose organic contaminants in water including MCs. The catalytic process does not either require addition of other chemicals or consume TiO2 materials. However, the only requirement is to irradiate the TiO2 surface with UV with high photon energy above the band gap of TiO2. This greatly inhibits the utilization of solar radiation as a sustainable energy source for the TiO2 activation because only 4–5% of the incoming solar energy onto the earth’s surface is in the UV range. Consequently, activation of TiO2 under visible light can facilitate the development of promising processes for on-site remediation of contaminated water under solar radiation without introduction of complicated facilities for generating and introducing UV. Dye-sensitized or metal ion-doped TiO2 has shown promising results for the activation of TiO2 under visible light, as summarized by Pelaez et al. (2012). More recently, doping of TiO2 with anions such as nitrogen is also the most common method to narrow the band gap of TiO2 (Yang et al. 2010; Pelaez et al. 2012, 2016; Petala et al. 2015; Ansari et al. 2016).

Meanwhile, for on-site applications of TiO2 photocatalysis, TiO2 should be immobilized firmly onto a substrate such as glass. Both TiO2 film and substrate should also be transparent to improve light penetration and utilization in particular when TiO2 films are installed and stacked on-site in parallel (Choi et al. 2006). To exhibit high reactivity and thus to decompose MCs in real-time under solar radiation, the structural properties of TiO2 films should also be controlled. In particular, a porous structure is beneficial to light absorbance of TiO2 and accessibility of reactants to TiO2 (Zakersalehi et al. 2013). Surfactants and block copolymers as pore templates have been widely used to control the porous structure during sol-gel synthesis of TiO2 (Bosc et al. 2004). Use of nitrogen-containing surfactants is interesting. They can play dual roles as a pore template to make porous TiO2 and as a nitrogen source to dope the porous TiO2 with nitrogen (Choi et al. 2007).

In this study, such a high efficiency nitrogen-doped mesoporous transparent TiO2 photocatalytic thin film (N-TiO2) immobilized onto a glass substrate was fabricated via an integrated materials synthesis process, employing surfactant template-based sol-gel, dip coating, and calcination. Effects of surfactant type, calcination temperature, multiple coating layers, and reaction pH on the photocatalytic decomposition of MC-LR under visible light were investigated. Most importantly, we demonstrated the TiO2 works under solar radiation for on-site decomposition of MC-LR in real-time.

MATERIALS AND METHODS

Fabrication of N-TiO2 film

Three nonionic long chain nitrogen-containing surfactants, diethanolamine (DEA), benzyltrimethylammonium chloride (BTAC), and dodecylamin (DDAD) purchased from Aldrich, were used as a pore-directing agent and a nitrogen-doping source. Briefly, each surfactant was dissolved in isopropanol (i-PrOH, Fisher) and then acidic acid (Fisher) was added to the solution for the esterification reaction with i-PrOH, as demonstrated elsewhere (Choi et al. 2006). Titanium tetra-2-propoxide (TTIP, Aldrich) was added under vigorous stirring. The molar ratio of surfactant/i-PrOH/acetic acid/TTIP was 1:45:6:1. Transparent TiO2 sol was prepared.

A borosilicate glass with an effective surface area of 10 cm² (20 cm² for both sides) was dip-coated with the TiO2 sol by using PTL-MM01 dip-coater (MTI Corporation) at a coating rate of 15 cm/min. After coating, the TiO2 film was dried at room temperature for 1 hr and calcined in a programmable furnace (Paragon HT-22-D, Thermcraft). Temperature was increased at a ramp rate of 60 C/hr to 100 C and maintained for 1 hr, then further increased to different target temperatures at 350, 400, 450, and 500 C for 2 hr, and then cooled down naturally, forming N-TiO2.

To increase the number of coating layers up to seven, the dip-coating and calcination process was repeated. Control
TiO₂ prepared without the surfactants was also prepared only at 500 °C which generally results in high crystallinity and thus high reactivity (Aphairaj et al. 2011).

### Reactivity evaluation of N-TiO₂ film

To check quickly whether N-TiO₂ film can be activated under visible light, decomposition of methylene blue (MB) was initially tested because its decomposition can be easily quantified and even visually sensed. Two 15 W fluorescent lamps (Philips) were used at an intensity of 3.52 mW/cm² measured by a photonics power meter (Ophir version 15.01). The lamps were mounted with a UV block filter (UV420, Bower) to cut off the spectral range below 420 nm. The concentration of MB was 5 mg/L and the volume of the solution was 10 ml, where one TiO₂ film was submerged. The solution was mixed by using a shaker. Temperature was maintained at around 25 °C and initial pH at 6.5 was not adjusted. The solution was initially kept in dark conditions for 1 hr and then irradiated with visible light for 4 hr, as this was proven by preliminary tests as an appropriate reaction time to best distinguish the reaction kinetics over experimental conditions.

After the test with MB, decomposition of MC-LR (Cayman Chemicals) was targeted under the same conditions except for the initial concentration of MC-LR at 1 mg/L. The effects of various parameters on the decomposition of MC-LR, including calcination temperature, multiple coating layers, and reaction pH, were investigated. Standard conditions (calcination temperature of 500 °C, coating layers of 3, and natural pH of 6.5) were fixed while one parameter was varied. Reaction pH towards acidic conditions was adjusted in sodium phosphate buffer (Fluka) by using H₂SO₄ (Fluka).

### On-site decomposition of MC-LR

To evaluate the field application potential of the TiO₂ film, an on-site test was briefly conducted in Lake Arlington (Arlington, TX), in which HABS have often occurred. The MC-LR concentration was periodically monitored from July to October in 2016. However, the level of MC-LR during this period was too low to implement a field test and thus some lake water was removed, placed into a confined area, and spiked with MC-LR to a target of 0.1 mg/L. The volume of the reaction solution was 10 ml. After installing one TiO₂ film, the whole system was directly exposed to solar radiation for 4 hr without a UV filter, as intended. Solar intensity at the top of the reactor was measured with a photonics power meter (Ophir version 15.01).

### TiO₂ characterization and chemical analysis

A Tristar II 3020 (Micromeritics) porosimetry analyzer was used to determine the structural properties of TiO₂ including surface area, pore volume, and pore size and distribution. The zeta potential of the TiO₂ surface at different pH values was measured using a Zeta potential analyzer (SZ-100, Horiba, Japan) and thus the point of zero charge (PZC) of TiO₂ was determined. A Kristalloflex D500 diffractometer (Siemens) was employed to examine the crystal phase of TiO₂. Nitrogen content in TiO₂ was measured with an X-ray photoelectron spectroscope (Kratos Analytical). Concentration of MB was measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu). MC-LR was monitored with a reversed-phase high performance liquid chromatograph (1200 series, Agilent) and UV detector at 238 nm. Concentration of natural organic matter (NOM) in Lake Arlington was measured by using a total organic carbon (TOC) analyzer (Shimadzu TOC-Vcsn).

### RESULTS AND DISCUSSION

#### Physiochemical properties of N-TiO₂ and control TiO₂

The physicochemical properties of N-TiO₂ made with DEA, which showed the best reactivity under visible light later, are summarized in Table 1. A series of N-TiO₂ films were synthesized at different calcination temperatures. The synthesis temperature is known to greatly influence the properties of TiO₂, in particular, the crystal phase, structural properties and nitrogen content, and thus its overall reactivity (Sathish et al. 2005). The surface area decreased from 151 to 61.1 m²/g and porosity also decreased from 41% to 22% when the calcination temperature increased from 350 to 500 °C. Calcination is required to remove surfactant templates...
for creating a porous structure while prolonged calcination at high temperatures also collapses the formed porous structure (Choi et al. 2006). All N-TiO₂ films were found to have an anatase crystal phase and to be optically transparent.

Nitrogen content decreased from 6.3 to 3.1% over the temperature increase from 350 to 500 °C because nitrogen is subject to thermal decomposition during the calcination process. The PZC of N-TiO₂ was around 6.2 – 6.7. When comparing N-TiO₂ (made with DEA) and control TiO₂ prepared at 500 °C, N-TiO₂ had a slightly higher surface area (61.1 m²/g) than control TiO₂ (50.1 m²/g) and superior porosity (22%) to control TiO₂ (4.0%). In addition, N-TiO₂ contained 3.1% nitrogen while control TiO₂ showed negligible nitrogen (0.5%, most probably from the impurities of the ingredients used as well as from gaseous nitrogen in the air). The properties proved the dual role of DEA as a nitrogen-doping source and a pore-directing agent.

### Photocatalytic decomposition of MB under visible light

To check quickly whether TiO₂ films prepared with different surfactants are reactive under visible light, decomposition of MB was investigated, as shown in Figure 1. Although MB absorbs visible light mainly at 609 nm and 668 nm, there was no photolysis most probably due to the low light intensity at 3.52 mW/cm² (Vaiano et al. 2015). Around 4–8% of MB was absorbed onto N-TiO₂ and control TiO₂ under dark conditions. Control TiO₂ showed negligible reactivity under visible light above 420 nm while all N-TiO₂ films demonstrated significant decomposition of MB. The result implies that the surfactants worked effectively as a nitrogen-doping source for visible light activation of TiO₂. In particular, N-TiO₂ made with DEA showed the fastest MB decomposition kinetics, i.e., 67% decomposition after 4 hr.

### Photocatalytic decomposition of MC-LR under visible light

The N-TiO₂ film made with DEA was further tested with MC-LR, as shown in Figure 2. There was no photolysis of MC-LR since MC-LR does not absorb visible light (Graham et al. 2010). Adsorption of MC-LR to TiO₂ films was negligible in this specific case mainly due to almost neutral charge of TiO₂ surface at natural pH of around 6.5 (PZC is 6.7 for N-TiO₂ prepared at 500 °C), and partly a small amount of TiO₂ catalyst used in this test. Under visible light, control TiO₂ showed negligible reactivity with MC-LR while N-TiO₂ exhibited significant reactivity, i.e., 47% decomposition of MC-LR after 4 hr. The result confirms that DEA worked effectively as a nitrogen-doping source. Considering that different concentrations for...
MC-LR (1 mg/L) and MB (5 mg/L) were used, decomposition of MC-LR was much slower than that of MB due to its cyclic structure that is known to provide more chemical stability (Kenefick et al. 1993; Sui et al. 2014).

**Decomposition of MC-LR under various conditions**

A series of N-TiO$_2$ films prepared at different calcination temperatures were examined for the decomposition of MC-LR under visible light, as shown in Figure 3. All N-TiO$_2$ films showed high reactivity. When the calcination temperature was increased from 350 to 400 and 450 °C, the reactivity significantly increased although the nitrogen content decreased and the porous structure collapsed. This can be explained by a trade-off effect between crystallization and nitrogen content over calcination temperature (Aphairaj et al. 2011). Initial amorphous TiO$_2$ is transformed to the most active anatase phase at calcination temperatures above 300 °C and to a less active rutile phase at calcination temperatures above 550 °C (Yu & Wang 2010). It has been well reported that TiO$_2$ prepared at around 450–550 °C shows the greatest reactivity due to the formation of the anatase phase with high crystallinity (Kang & Chen 2013; Lin et al. 2015; Vaiano et al. 2015). A further increase in calcination temperature to 500 °C resulted in a slight decrease in the reactivity most probably due to too low nitrogen content (Choi et al. 2007).

Reaction pH is another important factor that can affect the photocatalytic decomposition of MC-LR under visible light. Significant decomposition of MC-LR was observed under natural pH of 6.5. When pH was adjusted to acidic conditions, MC-LR was decomposed much faster, as shown in Figure 4. Acidic pH was reported to be favorable for the photocatalytic degradation of MC-LR (Song et al. 2006). Under acidic pHs, the surface of MC-LR is negatively
charged due to dissociation of its free carboxylic group while N-TiO$_2$ with PZC of 6.7 is positively charged, which leads to increased adsorption and decomposition of MC-LR onto N-TiO$_2$ due to electrical attraction.

The effect of the number of coating layers was also examined, as shown in Figure 5. When the number of coating layers increased from 1 to 3, MC-LR decomposition almost doubled. Above 3, the number of coating layers did not affect the reactivity significantly. In general, multiple coatings bring more TiO$_2$ loading to the film, resulting in high reactivity. However, the disproportional increase in the reactivity could be explained by the porous structure of inner TiO$_2$ layers becoming more collapsed during the repeated calcination processes and thus less available for subsequent chemical reaction (Choi et al. 2006). In addition, a reaction rate-limiting factor might be the low intensity of the visible light used in this study (3.52 mW/cm$^2$), rather than TiO$_2$ loading.

**On-site decomposition of MC-LR under solar radiation**

The previous experiments were conducted under laboratory conditions employing MC-LR in pure water and artificial visible light. Subsequently, a field test was undertaken to evaluate whether the TiO$_2$ film can be activated under solar radiation and thus MC-LR in a real water matrix can be decomposed, as shown in Figure 6. TOC in the lake water, representing NOM as a competing component for TiO$_2$, was very high at 15.5 mg/L and solar intensity was at 1.55 mW/cm$^2$. The concentration of MC-LR used in this study was 0.1 mg/L, which is much higher than 0.087 mg/L, the average of maximum detection of MCs in eight major lakes in the USA (USEPA 2015). MC-LR was not decomposed at all under solar radiation in the absence of TiO$_2$ and control TiO$_2$ was also unable to decompose MC-LR under solar radiation. Only N-TiO$_2$ showed significant reactivity under solar radiation to decompose MC-LR. Around 47% of MC-LR was decomposed after 4 hr exposure of N-TiO$_2$ to solar radiation. The result is significant, considering the low solar intensity, the high initial MC-LR concentration, and even the presence of NOM.

**CONCLUSIONS**

The overall goal of this study was to develop a new sustainable approach to decompose biological toxins, if feasible, on-site and in real-time with minimal effort, fewer chemicals, and low energy inputs. A high efficiency N-TiO$_2$ photocatalytic film immobilized onto a glass substrate was fabricated via integrated materials synthesis processing. The N-TiO$_2$ film was characterized with a highly porous,
anatase crystal, transparent, and nitrogen-doped nature. All the results proved the dual role of DEA surfactant as a nitrogen-doping source and a pore-directing agent. N-TiO₂ prepared with DEA at 450–500 °C exhibited fast decomposition of MC-LR under visible light due to its compromised properties with respect to surface area, crystal phase, and nitrogen content. N-TiO₂ film was able to successfully decompose MC-LR in a lake containing high NOM under solar radiation. This study implies the high potential of the N-TiO₂ film for on-site and real-time decomposition of organic contaminants in water by using sustainable solar energy.

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