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TiO_2 as a photocatalyst for control of the aquatic invasive alga, *Cladophora*, under natural and artificial light

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Abstract

Cladophora, a nuisance and invasive, filamentous algae (Chlorophyta), massively accumulates along the shores of the lower Great Lakes each summer causing great economic damage and compromising recreational opportunity and perhaps public health. In vitro experiments showed that Cladophora samples were physically and biologically degraded when subjected to TiO_2-mediated photocatalysis. For the most successful photocatalytic process, TiO_2 was immobilized on a glass surface and used in combination with either sunlight or artificial UV light. The loss of vital algal pigments was monitored using UV–vis spectrophotometry, and cell structural changes were determined by microscopic observation. Cladophora, in the presence of TiO_2-covered glass beads, experienced a loss of chloroplast pigments after 2 h of UV lamp light irradiation. In a separate experiment, sunlight exposure over 4 days (~24 h) resulted in the complete oxidative degradation of the green chloroplast pigments, verified by the UV spectra of the algal extracts. These results suggest that TiO_2, mobilized on sunlit silicates may be useful in controlling growth and survival of this alga in the Great Lakes, thus mitigating many of the economic, aesthetic ecological impacts of this invasive alga.

Keywords: Photocatalysis; Phycotoxicity; *Cladophora*; Water quality; TiO_2

1. Introduction

Cladophora (Chlorophyta: Cladophoraceae) grows along the shorelines of Lake Michigan. Unfortunately, the alga has proliferated to an unsightly, malodorous and unhealthy extent over the past 5–10 years, especially where surfaces such as rocks and boulders are present [1]. The Lake Michigan shorelines are tourist attractions in Indiana, Illinois, Wisconsin and Michigan and the overabundant algae leads to negative economic, ecological and health consequences [2]. The algae can interfere with swimming, boating and fishing. Upon decay, that alga is unsightly and highly malodorous. Property values are devalued because of the massive piles of decaying algae along private shorelines. Recently, it has been reported that bacteria (e.g. *E. coli*, enterococci, *Campylobacter*, *Salmonella*) reside and grow in the algae; therefore, excessive amounts of *Cladophora* pose a potential public health threat [3–6]. These detrimental conditions are not unique to the Great Lakes and have been reported in the Baltic Sea [7].

Investigations into the cause(s) of the algal overgrowth continue, and environmentally benign solutions are being developed and tested on various algae and bacteria [8–10]. Control strategies have been largely unsuccessful and the invasive *Cladophora* species continue to broaden. In many cases, large massive algal mats accumulate around popular beachfronts and nearshore waters compromising recreational and developmental use of property. The ecological consequences of these large mats are unclear. Boulder and rock surfaces appear to be the primary initial colonization substrate, but later in the summer strands become detached and accumulate along coves and beachfronts. Attempts to remove the mats by dredging, bulldozing and compositing have largely been unsuccessful. Removal of

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coastal infrastructure (e.g. breakwaters, groins, debris and artificial reefs) and shoreline hardening (revetments) would help reduce algal colonization, but this option is culturally undesirable and impractical. Perhaps another strategy would be the use of material that discourages *Cladophora* growth in high risk area. One approach might be the use of a substance that adheres to siliceous material (e.g. sand/concrete, granite, quartz), since most shoreline infrastructure contain silicates, and affects the growth of the algae. The photocatalyst, titanium dioxide (TiO_2), oxidizes a multitude of organically based materials and was chosen for this study.

Photocatalysis is an environmentally sound, advanced oxidation process (AOP) that utilizes a semiconductor material such as titanium dioxide, TiO_2, in conjunction with sunlight UV energy to promote the formation of oxidative species or oxidative sites. TiO_2-photocatalysis has been studied extensively over the past few decades as an advanced oxidative process in the destruction of environmental contaminants [11–18]. It is one of several advanced oxidation methods that has been shown to successfully degrade a wide variety of organic contaminants completely to carbon dioxide and water [19–22]. Surface holes of the TiO_2 and the hydroxyl radical ($^{\bullet}OH$) constitute the main oxidation species, which are formed from the light-induced promotion of the valence electrons. Oxidation takes place at, or very near, the surface of the photocatalyst, which makes clear the requirement for surface contact. Accordingly, the surface area of the photocatalyst is an important factor in the efficiency of the oxidation process.

Advantages of TiO_2 in natural surroundings overgrown with *Cladophora* include its non-toxic nature and its ability to utilize sunlight. As a photocatalyst, TiO_2 is activated by wavelengths of UV light at or below 387 nm, which allows for the use of a small portion of the sun's energy in the oxidative transformations. While TiO_2 is safe to humans, it is effective as a bactericide. Several recent investigations have reported the ability of TiO_2, in combination with UV light, to kill various bacteria [9,23–26]. More recently reported is the ability of TiO_2-photocatalysis to inhibit the growth of the filamentous algae, *Oedogonium*, and to break down microcystins, cyclic heptapeptides produced by certain freshwater cyanobacteria [8,27].

We report on the use of the photocatalyst TiO_2 in conjunction with either natural sunlight or UV lamp light to successfully oxidize and damage the cells and cellular components of *Cladophora*. This process may ultimately prevent the establishment and survival of *Cladophora* along vulnerable freshwater shorelines.

2. Experimental

2.1. Materials

Both Degussa TiO_2 (P-25) and laboratory synthesized colloidal TiO_2, prepared from titanium isopropoxide (Aldrich, 97%) were utilized.

Degussa TiO_2 was coated onto 5 mm glass beads in the following manner. A 0.5 g TiO_2/L solution was prepared and mixed ultrasonically with the glass beads for 1 h, followed by drying at 110 °C. This was repeated three times followed by a final heating (300 °C) for several hours. When these beads were utilized in the experiments, especially those that involved the mixing of the components, some of the TiO_2 slowly washed off the beads and into the water. Therefore, colloidal TiO_2, which is known to adhere much more effectively to glass, was synthesized using titanium isopropoxide [28].

Briefly, glacial acetic acid (80 mL) was mixed with 250 mL of deionized water in a 1 L round bottom flask. The solution was set in an ice bath and stirred for a few minutes. Ten milliliters of 2-propanol was mixed with 37 mL of titanium isopropoxide in a dropping or separatory funnel. This solution was added to the acid solution slowly with stirring. The cloudy white mixture was then transferred to a 600 mL beaker and set in an oil bath, where it was stirred vigorously at approximately 85 °C. The solution volume after 3 h of stirring was about 200 mL, and the colloidal solution was milky white. This solution was subjected to high pressure and temperature for several hours and then used to coat the glass beads. A final high temperature annealing was done with the coated beads at about 300 °C for 3–4 h. The TiO_2 appears transparent after it is coated on the beads and heated at high temperatures.

2.2. Photocatalytic experiments

The indoor laboratory photocatalytic set-up utilized a medium pressure, 450 W Hg vapor lamp (Ace Glass). The lamp was set in the well of the photochemical glassware. A nickel sulfate hexahydrate (Sigma–Aldrich, A.C.S. reagent grade) filter solution was circulated through the photochemical glassware and through an ice-water cooling system. The green solution filtered out most of the chlorophyll *a* absorption wavelengths (350–440 and 600–800 nm) and the cooling system maintained the lamp environment at temperatures between 25 and 35 °C. In all of the UV lamp experiments, the bases of glass crystallization dishes were covered with either uncoated glass beads or TiO_2-covered glass beads. A liquid volume of 25–40 mL, either deionized water or lake water, was added to each crystallization dish. A fresh, damp algae sample of approximately 0.2 g was then placed on the beads. The crystallization dishes were set on a platform rocker for gentle mixing of the algae and beads. The distance between the crystallization dishes and the lamp varied from 3 to 8 cm as the platform rocked. The samples of the algae were irradiated over the indicated period of time, from 15 min to several hours.

The experiments which were conducted outside for sunlight utilization involved the use of 1-L beakers with glass beads or TiO_2-covered glass beads. Enough deionized or lake water was added to cover the algae fully and measured amounts of fresh, damp *Cladophora* were placed into the beakers. The beakers were set out in natural sunlight for various recorded times and agitated every 15–20 min. Water was added when necessary to keep the water level fairly constant. These outdoor experiments were performed during the months of May–July on days of ample sunlight.

For the photocatalysis experiments using suspended TiO_2, 0.015 g of Degussa TiO_2 was added to the crystallization dishes.

The suspended TiO_2 was removed from solution using 0.2 μm nylon filters.

2.3. Algae collections

All collections were taken at the rock breakwater area in Portage Indiana [6]. *Cladophora* samples were collected from wading depths approximately 20–40 cm below the surface. Cladophora were collected using sterile techniques since microbiological analyses were concurrently done (reported elsewhere). Samples were put in sterile bags, iced and returned to the laboratory. Refrigerated samples (4 °C) were maintained in the dark and analyzed within 3 days to avoid further decomposition.

2.4. Algae extractions and absorption measurements

All extractions were performed using a 90% acetone solvent. A Perkin-Elmer Lambda 35 UV–vis spectrophotometer was used to record absorption spectra. Algae samples from the photocatalysis and photolysis experiments were dried in a dark, warm oven, approximately 65 °C, overnight. The dried, massed algae samples were added to centrifuge tubes and heated with the 90% acetone in 50 °C water bath for 30 min in the dark, with occasional stirring. One milliliter of each extract was diluted to 25 mL using deionized water and the absorption spectra were recorded. In the extraction procedures, some of the chlorophyll *a*, the most abundant pigment in the algae cells, is likely degraded to pheophytin *a*, but all the extractions of natural algae samples were performed in the same way to allow for small procedural effects. The small differences in extract absorption spectra are likely due to slight variations in the amounts of the different pigments.

3. Results and discussion

3.1. Photocatalysis and photolysis of algal extracts

Sampling of algae began in May 2005 and continued throughout the growth season. All of the *Cladophora* samples were collected off granite breakwaters, which provides siliceous surface environment that supports growth. Fig. 1 depicts a typical area of growth for the algae along the southern Lake Michigan shorelines and reveals the intense green color of this type of algae. Initial experiments were performed to decipher the vulnerability of the algal pigments to sunlight (photolysis) and to sunlight with TiO_2 (photocatalysis). Fresh *Cladophora* extracts were prepared, as described in Section 2. The green extract solutions were set out in the sun and monitored by UV–vis spectrophotometry every 10 min, for 1 h. Fig. 2 shows the UV–vis spectra of the original solution, the extract solution without TiO_2 and the extract solution containing the TiO_2 after 10 min of sunlight exposure. Both the direct sunlight and the combination of TiO_2 and sunlight affected the exposed algal pigments in the extract solutions. While a visible loss of color was noted in both cases, the solution containing the TiO_2 decolorized much faster. Fig. 3 illustrates the overall decrease in the solutions' visible absorption at 415 nm, with and without TiO_2, over 60 min.

Fig. 1. Photograph of algae growth along the rocks and near the shore of Lake Michigan in Portage, IN.

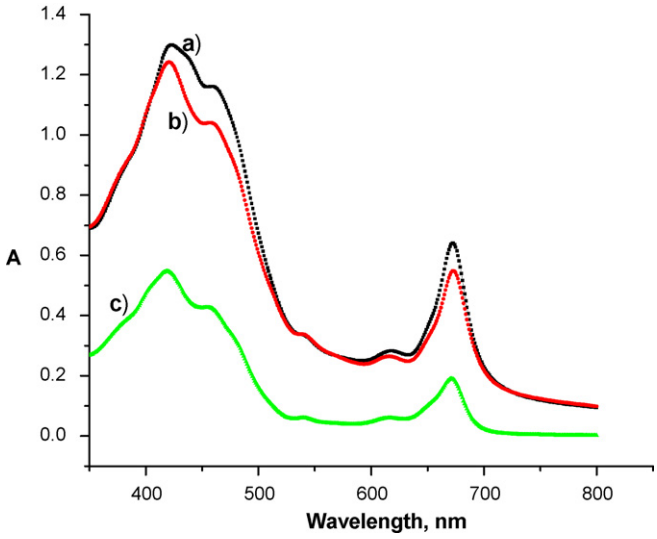

Fig. 2. UV–vis spectra of (a) *Cladophora* extract solution, (b) *Cladophora* extract solution exposed to sunlight for 10 min and (c) *Cladophora* extract solution with suspended TiO_2 (then, filtered out) exposed to sunlight for 10 min.

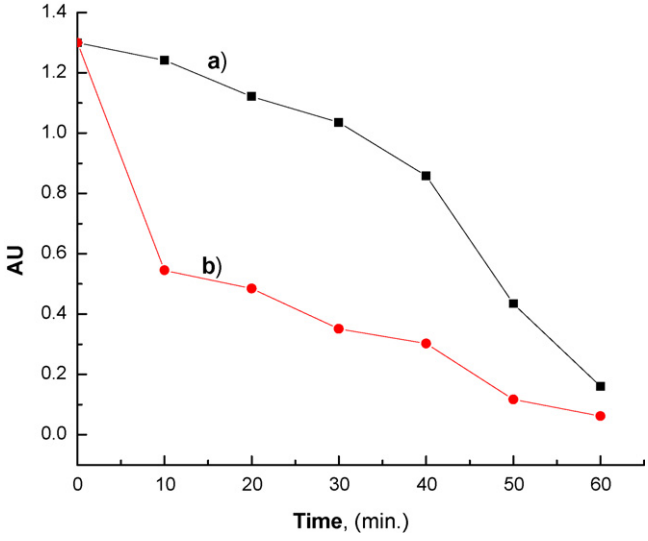

Fig. 3. Change in visible absorption of the *Cladophora* extract solutions (prepared from freshly collected *Cladophora* using 90% acetone) over 60 min of sunlight exposure, monitored at 415 nm: (a) without TiO_2 and (b) with TiO_2.

Suspended, powder TiO_2 was utilized in the aforementioned experiments, and was removed prior to UV–vis absorption examination. The suspended powder is not practical for control of algae using photocatalytic TiO_2 treatment since it would quickly become diluted in large bodies of water or would interfere with light penetration. Given that *Cladophora* grows extensively on surfaces along the Great Lakes, the logical application of TiO_2 would be to incorporate it on a surface. Also, utilization of bound TiO_2 would minimize the attention of the possible toxicological issues associated with suspended TiO_2 particles [29].

The effectiveness of immobilized TiO_2 for the degradation of isolated algal pigments was then investigated. TiO_2-covered glass beads were used in place of suspended TiO_2 in experiments with the algal extract solutions; the control extract solution contained glass beads. Once again, sunlight degraded the chloroplast pigments and the loss in color was faster when the sun was aided by TiO_2. When the results were plotted, the same kinetic behaviors shown in Fig. 3 were observed. The experiment was repeated using actual lake (Lake Michigan) water. The extract solutions made from lake water decolorized at essentially the same rate as the solutions made with deionized water. The naturally dissolved substances (e.g. ions, minerals, and other organic matter) of the lake water did not affect the sunlight-induced breakdown of the algal pigments.

Without the protection provided by the cell's structure, the green algal pigments absorb specific wavelengths of sunlight and go through photo-induced changes that lead to decolorization. No color changes take place in the absence of sunlight, with or without TiO_2. While both photolysis and photocatalysis function to decolorize the extract solutions, the photocatalytic pathway (presence of the TiO_2) leads to a faster degradation of the pigments with different kinetic behavior. Many colored compounds, namely industrial dyes, have been oxidatively decolorized using TiO_2 photocatalysis and display pseudo-first order exponential decay kinetics [30–37]. Fig. 3 (curve), representing the TiO_2-induced changes, demonstrates a pseudo-first order decay, which suggests an oxidative, $^{\bullet}OH$-mediated degradation mechanism. This behavior is different from the photolytic decolorization that follows a nearly linear change.

The fast decomposition of the exposed chloroplast pigments by either photolysis or photocatalysis indicates an extreme susceptibility when the cell membrane and cell wall are compromised. Therefore, the loss of chloroplast pigments in the algae was used as a means to follow the degradation of the *Cladophora* cells. Without the green pigments, photosynthesis cannot take place and the cell's viability is lost.

3.2. Fresh algae and sunlight photocatalysis

Fresh samples of *Cladophora* were utilized in experiments with TiO_2-covered beads and with glass beads (control). Beakers containing the algae samples were set out in the natural sunlight for several (~6 h) hours each day, over which time the photocatalytic action of the TiO_2 became apparent. Fig. 4 shows the algae after the 4th and final day of treatment. The control sample (sunlight, untreated glass beads) remained well pigmented, while degradation of the pigments in algae exposed

Fig. 4. *Cladophora* samples after 4 days of sunlight exposure (~6 h/day) with TiO_2-covered glass beads (left) and glass beads (right) in deionized water.

to the TiO_2-covered glass beads was evident on day 1. By day 4, the chlorophyll content appeared essentially lost, as the algae was fragmented and brown. Spectrophotometric analyses confirmed the loss of the pigments at the completion of the experiment. Fig. 5 displays the UV–vis spectra of the extracts from the samples shown in Fig. 4. In Fig. 5(a), control alga extracts demonstrate maximum absorption values around 420 and 670 nm, consistent with the UV–vis spectra of fresh algae extracts.

Normal sunlight exposure did not affect *Cladophora* chlorophyll pigments, as expected [4]. Algal cells contain a large amount of green pigment in the chloroplasts of the cells. The complete loss of spectral features on the UV–vis spectrum in Fig. 5(b) is attributed to the degradation of algal pigment components such as chlorophyll *a*, chlorophyll *b* and pheophytin *a* by TiO_2-promoted oxidation. The apparent change in color from green to brown in the photocatalyzed algal samples points to a damaging oxidative process taking place at the TiO_2 surfaces that eventually leads to the degradation of the chlorophylls and other pigments, consistent with the data collected by Hong et al. [38]. Therefore, natural sunlight and TiO_2 coated glass beads

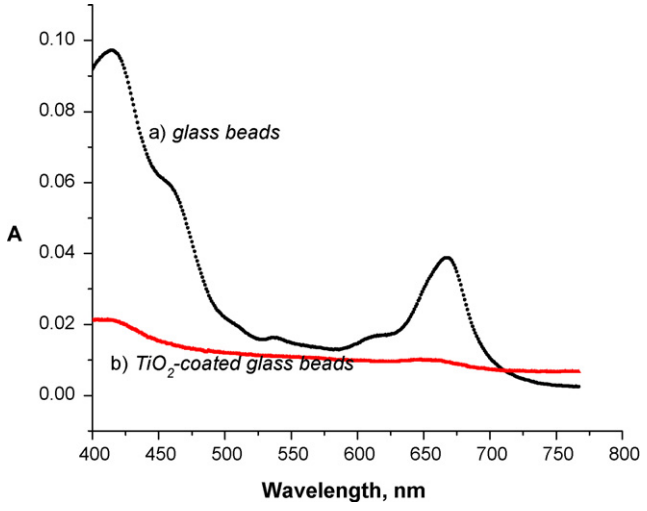

Fig. 5. UV–vis spectra of *Cladophora* samples after 4 days of daylight sun exposure and in the presence of (a) glass beads and deionized water and (b) TiO_2-covered glass beads and deionized water. Ninety percent acetone was used to remove the pigments from the samples.

appear to directly affect algal pigments of intact *Cladophora* species collected from the southern Lake Michigan shoreline.

3.3. Fresh algae and UV lamp photocatalysis

As mentioned earlier, the practical approach to affecting the growth of *Cladophora* does not involve suspended TiO_2 particles. But, since the powder TiO_2 affords the greatest amount of surface area for photocatalytic activity, experiments were carried out to investigate the effects of the greater surface area. Powder Degussa TiO_2 was added to a crystallization dish containing deionized water and fresh algae. A blank experiment was conducted with just the fresh algae and deionized water. The mixtures were subjected to the laboratory UV lamp for several hours. The algae that contained the TiO_2 turned milky green-white in color, mainly due to the presence of the white powder TiO_2. The green color did not slowly convert to brown as it did in the experiment that utilized TiO_2-covered glass beads. After 4 h of irradiation, samples of the algae were analyzed with a microscope at 100 and 400× magnification. Living and non-living particles, such as diatoms, debris, and protists appeared to adhere to the polar TiO_2 particles. These substances were likely impeding the contact necessary between the TiO_2 and the algae.

Since suspended TiO_2 is not an effective catalyst in water solutions containing living algae, the photocatalyst was only used in an immobilized form, on glass beads, for the remainder of the study. Degussa TiO_2 does adhere to glass, but not completely. Some slowly washes off into the aqueous solutions, and eventually the TiO_2-covered glass beads can lose their photocatalytic activity. Colloidal TiO_2 can be synthesized and permanently mounted on glass surfaces [28]. The immobilized TiO_2 is not engulfed by other materials and makes contact with the algae, which is a necessary aspect of the photocatalytic process.

Colloidal TiO_2 was synthesized as described in Section 2. The colloidal TiO_2-covered beads offered similar or better results than the Degussa TiO_2-covered beads in the photocatalytic breakdown of *Cladophora*. Using the UV lamp, photocatalytic experiments were carried out with a shaker to offer movement that mimics natural water environments and also to provide a mixing of the algae and the TiO_2 surfaces. Although the algae samples were checked every 15 or 30 min, a visible change was not noted until after 1 h of irradiation. The algae sample in the presence of the TiO_2-covered beads appeared fragmented after 1 h of light exposure, while the control sample did not visibly change in appearance.

3.4. Microscopic analyses of Cladophora

After 2 h of UV lamp irradiation, each sample was studied under magnifications of 100, 200 and 400×. The algae subjected to the TiO_2 beads appeared damaged to the unaided eye and under magnification. Fig. 6 shows photographs of the algae samples that were exposed to 2 h of UV lamp irradiation. Photomicrograph (A) shows the algal sample exposed to the TiO_2-covered glass beads and photomicrograph (B) shows the control algal sample, which was irradiated in the presence of uncoated glass beads.

The photographs clearly display a difference in the algal cells. Many of the cells that were exposed to both TiO_2 and UV light showed signs of damage to the reticulated chloroplast network. This corresponds well to the work of Hong et al. [38] who investigated the photocatalytic damage to *Chroococcus* sp. algae. In contrast, the algae exposed to UV light and uncovered glass beads appeared healthy to the unaided eye and under microscopic examination. The magnified photographs of the TiO_2-exposed samples revealed areas of algal cells that lost pigmentation. In contrast, the glass bead algal cells appear to be completely filled with chloroplast pigments. The photographs of the TiO_2-exposed algae suggest that, in the photocatalytic oxidation process, the cell wall and cell membrane undergo changes that lead to the loss of cell pigments; this was also verified by the UV–vis absorption spectra shown in Fig. 5. In addition, the results of the algal extract experiments indicate that if the green pigments in the chloroplasts are exposed to sunlight or TiO_2/sunlight, they are extremely susceptible to photocatalytic degradation.

3.5. Postulated mechanism of photocatalytic degradation of Cladophora

The mechanism of degradation begins with photocatalytic action by the oxidative species of TiO_2 on the protective cell

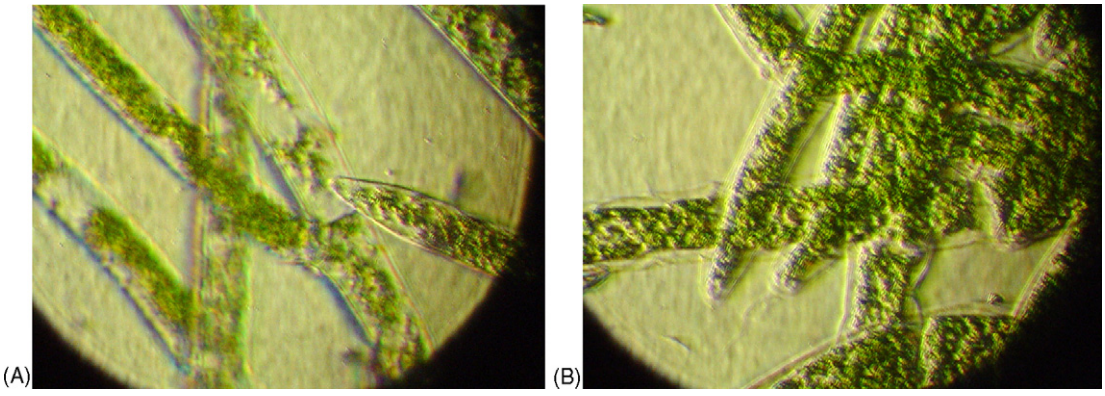

Fig. 6. Photomicrographs (100×) of algae samples after 2 h of UV lamp exposure: (A) TiO_2 beads, and (B) glass beads. Both algae samples were suspended in deionized water.

structures of *Cladophora*: the cell wall, the cell membrane and the organelle membranes. These must be disturbed before the chlorophyll and other pigments are oxidatively transformed by the action of the TiO_2 photocatalyst. The protective wall and membranes of the cell undergo radical-induced changes. Alterations in color, in the form of chlorophyll degradation, do not take place readily, since the catalyst must first affect the cell's protective structures. The delay in the visible color change corresponds to a mechanistic pathway that involves changes in the cell wall, cell membrane and other membrane structures prior to oxidation of pigments. This preliminary explanation of the mechanistic pathway is in agreement with other TiO_2 studies reported with different algal species [8,38]. Many aspects of the oxidative mechanism are currently being studied in our laboratories to better understand the photocatalytic action of TiO_2 on *Cladophora*.

4. Conclusions

Our studies show that the nontoxic photocatalyst TiO_2 very readily breaks down the chloroplast pigments of algae extract solutions and successfully damages the problematic alga, *Cladophora*, in the presence of sunlight or a filtered UV lamp. Furthermore, we established that for effective oxidative degradation of the living organism, the photocatalyst must be immobilized on a surface. Our choice was glass beads, which simulates material used in the development of shoreline infrastructure yet also encourages algal growth. The TiO_2-covered glass beads maintained their photocatalytic activity after several uses. Microscope images and UV absorption spectra clearly demonstrated severe cellular changes and breakdown of the chloroplast pigments. The experimental evidence in this study provides encouragement for use of the TiO_2 photocatalytic approach to control harmful algal blooms. Since the green *Cladophora* grows most abundantly along the rock surfaces of the shoreline, the integration of a TiO_2 covered surface along these rocks may eventually be incorporated into a strategic plan for controlling this widespread and important environmental problem.

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References

[1] V. Harris, Lakeshore Technical College, 2005.
[2] V. Harris, Great Lakes WATER Institute, University of Wisconsin-Milwaukee, 2004.
[3] M.N. Byappanahalli, D.A. Shively, M.B. Nevers, M.J. Sadowsky, R.L. Whitman, FEMS Microbiol. Ecol. 46 (2003) 203–211.
[4] R.L. Whitman, D.A. Shively, H. Pawlik, M.B. Nevers, M.N. Byappanahalli, Appl. Environ. Microbiol. 69 (2003) 4714–4719.
[5] O.A. Olapade, M.M. Depas, E.T. Jensen, S.L. McLellan, Appl. Environ. Microbiol. 72 (2006).
[6] S. Ishii, T. Yan, D.A. Shively, M.N. Byappanahalli, R.L. Whitman, M.J. Sadowsky, Appl. Environ. Microbiol. 72 (2006) 4545–4553.
[7] A. Lehvo, S. Back, Aquat. Conserv.: Mar. Freshw. Ecosyst. 11 (2001) 11–18.
[8] C.A. Linkous, G.J. Carter, D.B. Locuson, A.J. Ouellette, D.K. Slattery, L.A. Smitha, Environ. Sci. Technol. 34 (2000) 4754–4758.
[9] P.-C. Maness, S. Smolinski, D.M. Blake, Z. Huang, E.J. Wolfrum, W.A. Jacoby, Appl. Environ. Microbiol. 65 (1999) 4094–4098.
[10] J.D. Boylan, J.E. Morris, Lake Reservoir Manage. 19 (2003) 265–271.
[11] A. Agüera, M. Mezcua, D. Hernando, J. Vial, A.R. Fernández-Alba, Environ. Sci. Technol. 35 (2001) 4359–4366.
[12] M.E. Calvo, R.J. Candal, S.A. Bilmes, Environ. Sci. Technol. 35 (2001) 4132–4138.
[13] J. Cunningham, G. Al-Sayyed, S. Srijaranai, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Aquatic and Surface Photochemistry, Lewis Publishers, 1994.
[14] Z. Ding, G.Q. Lu, P.F. Greenfield, J. Phys. Chem. B 104 (2000) 4815–4820.
[15] K.A. Gray, U. Stafford, M.S. Dieckmann, P.V. Kamat, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier Publishing, Amsterdam, 1993.
[16] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, Blanco, J. Appl. Catal. B: Environ. 17 (1998) 15–23.
[17] S.-A. Lee, K.-H. Choo, C.-H. Lee, H.-I. Lee, T. Hyeon, W. Choi, H.-H. Kwon, Ind. Eng. Chem. Res. 40 (2001) 1712–1719.
[18] X. Li, J.W. Cubbage, W.S. Jenks, J. Photochem. Photobiol. A: Chem. 143 (2001) 69–85.
[19] M. Kaneko, I. Okura (Eds.), Photocatalysis: Science and Technology, Springer-Verlag, New York, 2002.
[20] D.F. Ollis, N. Serpone, E. Pelizzetti, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989.
[21] J. Peller, O. Wiest, P.V. Kamat, Environ. Sci. Technol. 37 (2003) 1926–1932.
[22] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341–357.
[23] K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Environ. Sci. Technol. 32 (1998) 726–728.
[24] P.S.M. Dunlop, J.A. Byrne, N. Manga, B.R. Eggins, J. Photochem. Photobiol. A: Chem. 148 (2002) 355–363.
[25] Y.-S. Choi, B.-W. Kim, J. Chem. Technol. Biotechnol. 75 (2000) 1145–1150.
[26] W.A. Jacoby, P.-C. Maness, E.J. Wolfrum, D.M. Blake, J.A. Fennell, Environ. Sci. Technol. 32 (1998) 2650–2653.
[27] I. Liu, L.A. Lawton, P.K. Robertson, J. Environ. Sci. Technol. 37 (2003) 3214–3219.
[28] V. Subramanian, E. Wolf, P.V. Kamat, J. Phys. Chem. B 105 (2001) 11439–11446.
[29] A. Nel, T. Xia, L. Madler, N. Li, Science 311 (2006) 622–627.
[30] N.L. Stock, J. Peller, K. Vinodgopal, P.V. Kamat, Environ. Sci. Technol. 34 (2000) 1747–1750.
[31] C. Nasr, K. Vinodgopal, L. Fisher, S. Hotchandani, A.K. Chattopadhyay, P.V. Kamat, J. Phys. Chem. 100 (1996) 8436–8442.
[32] K. Vinodgopal, P.V. Kamat, Environ. Sci. Technol. 29 (1995) 841–845.
[33] K. Vinodgopal, I. Bedja, P.V. Kamat, Chem. Mater. 8 (1996) 2180–2187.
[34] S. Horikoshi, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 1357–1366.
[35] C. Chen, W. Zhao, J. Li, J. Zhao, H. Hidaka, N. Serpone, Environ. Sci. Technol. 36 (2002) 3604–3611.
[36] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, Environ. Sci. Technol. 32 (1998) 2394–2400.
[37] G. Liu, T. Wu, J. Zhao, H. Hidaka, N. Serpone, Environ. Sci. Technol. 33 (1999) 2081–2087.
[38] J. Hong, H. Ma, M. Otaki, J. Biosci. Bioeng. 99 (2005) 592–597.