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ORIGINAL PAPER

Photocatalytic inactivation and removal of algae with TiO_2-coated materials

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Abstract The capabilities of TiO_2-coated materials for the inactivation and removal of algae were investigated. As supports for TiO_2, non-woven fabric and Ni foam were chosen. To evaluate the ability of noble metal cocatalyst additions to facilitate the photocatalytic algal inhibition of TiO_2-coated materials, Pd nanoparticles were deposited on non-woven fabric-supported TiO_2 by photoelectrochemical deposition. The fabric-supported Pd/TiO_2 showed higher inhibition activity for algal growth compared to the fabric-supported TiO_2 without Pd. In addition, Ni foam-supported TiO_2 also showed high inhibition activity, both in laboratory-scale tests and open-air tests. Therefore, TiO_2-coated materials with suitable coating methods such as the use of cocatalysts or large surface area can substantially inhibit algal growth. The ability of the TiO_2-coated materials to inhibit algae correlated well with their activity for the photocatalytic decolorization of methylene blue, suggesting a nonspecific mechanism in the breakdown of cellular structures.

Keywords TiO_2 photocatalyst · Photoelectrochemical deposition · Photocatalytic inactivation · Algae

1 Introduction

Algae often form dense growths in fresh water that make fishing, swimming, and other recreational uses nearly impossible. *Anabaena*, a typical blue-green algae with beadlike or barrel-like cells and interspersed enlarged spores, has frequently been observed in lakes, ponds, and aquaria. Total coverage of the water surface with algae can restrict sunlight penetration and limit the production of oxygen and food items necessary for fish growth. Traditionally, physical and chemical treatment methods have been applied to the removal of algae from the water surface [1–3]. However, because of the high costs and the significant risk of environmental damage of these techniques, the development of more economical and ecologically favorable methods has attracted increasing attention.

Recently, the strong oxidation ability of TiO_2 photocatalysts has received growing attention [4–7]. TiO_2 nanoparticles in suspension generate hydroxyl radicals and superoxide ions by solar light irradiation. These are highly reactive with organic compounds and microorganisms. Moreover, the photocatalytic activity of TiO_2 can be improved by adding small amounts of other catalytic substances, or cocatalysts, to the light-absorbing particle surface [8]. However, the difficulty of the separation of TiO_2 nanoparticles from suspension after reaction and the aggregation of suspended TiO_2 nanoparticles have hampered practical applications of TiO_2 photocatalysts. In order to resolve these problems, many approaches have been taken to immobilize TiO_2 photocatalysts on various

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supports, such as ceramic foam [9], metal foam [10], and zeolite [11], among others.

In the present work, we examined the possibilities for the application of TiO_2-coated materials in the inactivation and removal of algae. A non-woven fabric and a Ni foam were chosen as supports for their low cost and light weight. The TiO_2-coated materials were allowed to float on the surface of an algal growth culture, and the resulting inhibition activity for algal growth was measured. Moreover, the examination of the efficacy of noble metal cocatalyst additions to facilitate photocatalytic algae inhibition of TiO_2-coated materials was also an objective of this research.

2 Experimental

2.1 Preparation of TiO_2-coated materials

Non-woven fabric with TiO_2 was made by Japan Vilene Co., Ltd., using P25 TiO_2 (Evonik Industries) with a loading level of TiO_2 of 6 g m^{-2}. The surface morphology of the non-woven fabric-supported TiO_2 was examined by scanning electron microscopy (SEM; JSM-5400 microscope, JEOL). The crystalline structure of TiO_2 was investigated by X-ray diffractometry (XRD; RINT 1500, Rigaku).

Pd cocatalyst modification of fabric-supported TiO_2 was performed according to a published photoelectrochemical deposition procedure [12]. A piece of non-woven fabric/TiO_2 (25 cm^2) was immersed into 15 mL of palladium standard aqueous solution (as palladium (II) chloride, 1,000 mg L^{-1}, Wako) with 1 mL of methanol as an oxidizable sacrificial agent and irradiated with 2.5 mW cm^{-2} of UV light. For UV irradiation, we used 10-W black-light lamps (FL10BLB, TOSHIBA) with a peak wavelength of 365 nm. The photoelectrochemical deposition procedure was carried out in a sealed polyethylene bag. The end point of the photoelectrochemical deposition was determined as the time at which the color difference of the non-woven fabric/TiO_2 (vs. the initial color) saturated, as measured by a Color Reader (CR-10, Konica Minolta) through the sealed polyethylene bag. After photoelectrochemical deposition, the non-woven fabric was washed with Milli-Q water and air-dried. The metallic state of the Pd cocatalyst was confirmed by XRD.

Ni foam-supported TiO_2 was prepared by a dip-coating method [10, 13]. Ni foam with an average pore size of 0.5 mm and surface area of 7,500 m^2 m^{-3} (CELMET™, Sumitomo Electric Toyama Co., Ltd.) was heated in air at 550 °C for 3 h to oxidize the surface. A TiO_2 anatase sol (TKD-701, TAYCA), which was diluted with 2-propanol at a concentration of 12.5 wt%, was used for dip-coating, and the oxidized Ni-foam was withdrawn at a rate of 0.5 mm s^{-1} and was calcined at 550 °C for 3 h. The Ni foam-supported TiO_2 was washed by sonication in Milli-Q water, dried, and dip-coated again in 25 wt% TiO_2 anatase sol at a 0.5 mm s^{-1} withdrawal speed, and finally calcined at 550 °C for 3 h. The surface morphology and the crystalline structure of TiO_2 of the Ni foam were examined by SEM and XRD, respectively.

2.2 Photocatalytic activity of TiO_2-coated materials

The photocatalytic activities of TiO_2-coated materials were evaluated by the photocatalytic degradation of methylene blue [14]. A piece of TiO_2-coated material (25 cm^2) was floated on the surface of 0.3 L of 0.1 mM methylene blue solution. The irradiation was started after equilibrium between dissolved and adsorbed methylene blue was reached. The TiO_2-coated materials were irradiated with 2.0 mW cm^{-2} of UV light. The concentration of dissolved methylene blue as a function of irradiation time was measured with a UV–visible spectrophotometer (2450, Shimadzu).

2.3 Algal growth inhibition test

The inhibition ability of the TiO_2-coated materials was assessed using *Anabaena flos-aquae* (NIES-1668, National Institute for Environmental Studies). The axenic cultures of the strain were incubated in a small volume of sterile MA medium and maintained at 20 °C under 2,000 Lx of visible light and 0.3 mW cm^{-2} of UV light with a 12/12-h light/dark cycle [15]. The cultures were grown under these conditions until there was sufficient material to use as an inoculum for a large-scale MA medium. Then, the cultures were resuspended in 3 L of fresh MA medium and separated to sterile 0.3 L beakers. A piece of TiO_2-coated material (25 cm^2) was floated on the surface of the culture. The algal growth under the same conditions was confirmed by a total organic carbon (TOC) analyzer (TOC-V_{CSH}, Shimadzu), analyzing 5 mL aliquots of culture media. TOC values represent the average of three measurements, which is validated by the apparatus only if the standard deviation is less than 2%. Optical microscope images of non-woven fabric materials before and after being used for algal growth testing were obtained with a digital microscope (VHX-1100S, Keyence).

3 Results and discussion

3.1 Characterization of TiO_2-coated materials

The SEM images of the Ni foam before and after sintering the TiO_2 are shown in Fig. 1a and b, showing that the TiO_2 films were made up of spherical particles, and the particle

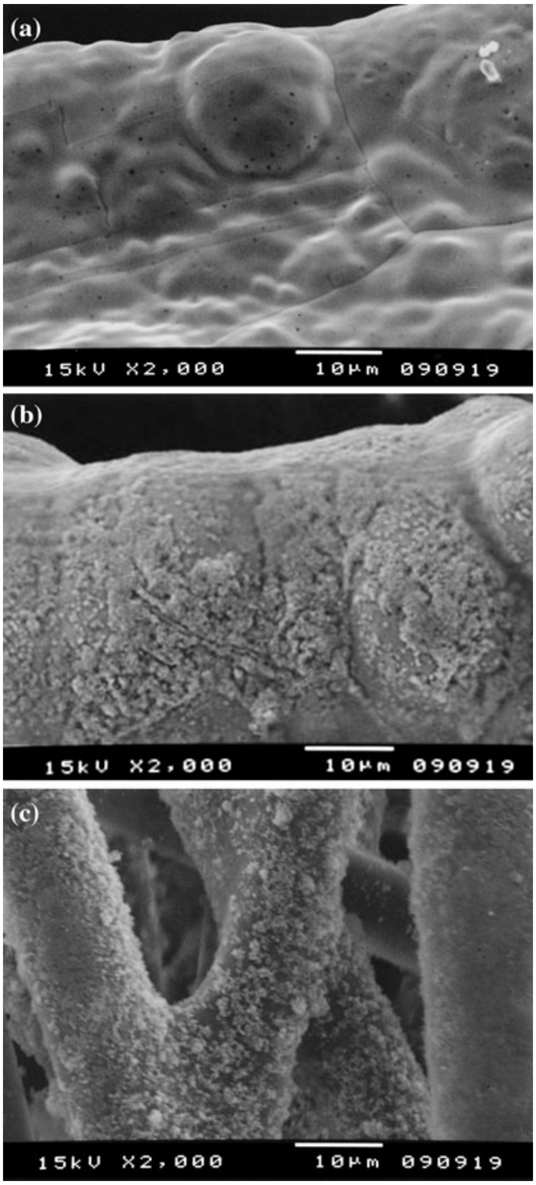

Fig. 1 SEM images of **a** Ni foam, **b** Ni foam-supported TiO_2, and **c** non-woven fabric-supported TiO_2

sizes of TiO_2 in the films were about 1 μm. This is larger than the particle size in suspension. In the sol-gel coating method for immobilization of TiO_2, the repeated calcination treatment of the TiO_2 films results in the growth and aggregation of the particles. Thus, a similar process is likely to be occurring in the present procedure. The SEM image of the fabric-supported TiO_2 shows spherical particles with sizes similar to those for the Ni-supported TiO_2 sample (Fig. 1c).

The XRD patterns of the Ni foam before and after loading and sintering TiO_2 are shown in Figs. 2a and b. The diffraction peaks of TiO_2 (anatase) and NiO can be observed in Fig. 2b. This indicates that the Ni foam surface was oxidized by calcination at high temperature, and it successfully immobilized the TiO_2 particles, as reported in the sol-gel coating method [10]. The XRD patterns of non-woven fabric without and with TiO_2 are shown in Fig. 2c and d. The diffraction peaks of TiO_2 (anatase) in Fig. 2d indicate that P25 TiO_2 particles were successfully immobilized on the surface of the fabric.

The white color of the non-woven fabric/TiO_2 was converted to black by the photoelectrochemical deposition of Pd. After 15 min of photoelectrochemical deposition, the ΔE*ab value, which is a theoretically calculated value of the color deviation based on the CIE L*a*b* color system, saturated at 45. The XRD patterns of the fabric/TiO_2 before and after photoelectrochemical deposition of Pd are shown in Figs. 2d and e. The diffraction peaks of Pd in Fig. 2e indicate that the Pd nanoparticles were successfully immobilized onto the surface of the fabric/TiO_2.

3.2 Photocatalytic activity

The efficacy for improvement of photocatalytic activity by various noble metal cocatalysts has already been demonstrated. Asano [16] reported that Pd/TiO_2 powders yielded the highest rates for methylene blue decolorization. Thus, Pd

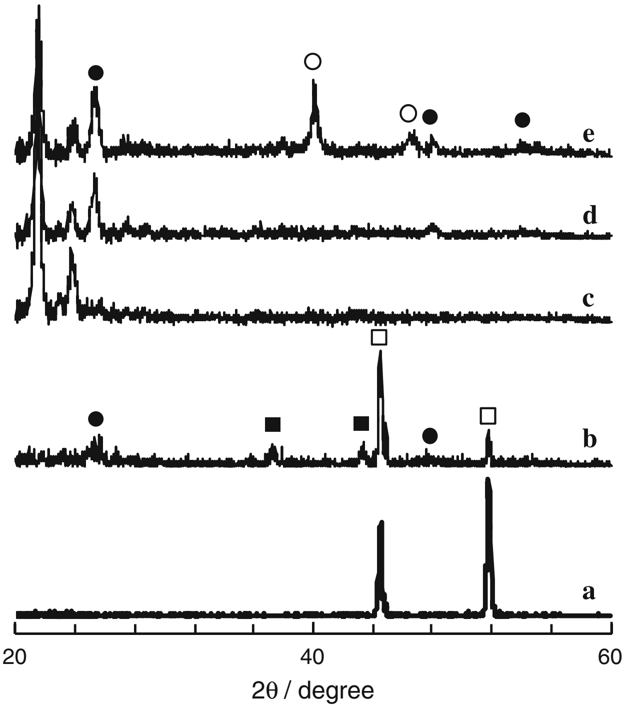

Fig. 2 XRD patterns of (*a*) Ni foam, (*b*) Ni foam/TiO_2, (*c*) non-woven fabric, (*d*) non-woven fabric/TiO_2, and (*e*) non-woven fabric/Pd/TiO_2 (*filled circles*: anatase TiO_2; *open circles*: Pd; *filled squares*: NiO; *open squares*: Ni)

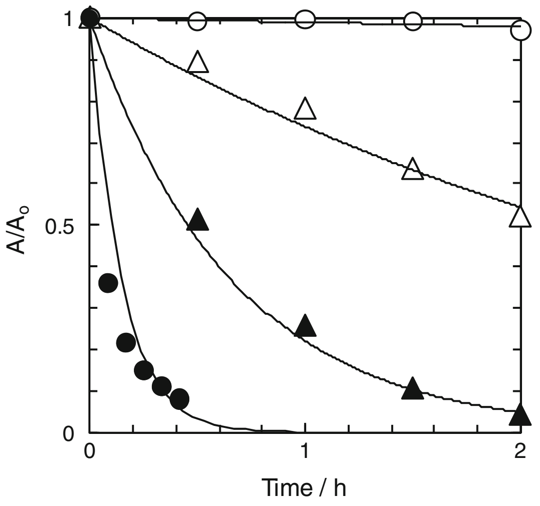

Fig. 3 Kinetics of decolorization of methylene blue (*open circles*: blank; *open triangles*: non-woven fabric/TiO_2; *filled triangles*: non-woven fabric/Pd/TiO_2; *filled circles*: Ni foam/TiO_2). Experimental conditions: sample volume = 0.3 L, UV irradiation intensity = 2.0 mW cm^{-2}

cocatalyst was used for the modification of fabric/TiO_2. To determine whether the TiO_2-coated samples were active, they were initially screened with a 0.1 mM methylene blue solution. Methylene blue decolorization by each photocatalyst is shown in Fig. 3. In all cases, photolysis in the presence of a photocatalyst resulted in net methylene blue decolorization. Photolysis in the absence of photocatalyst produced negligible methylene blue decolorization. The pseudo-first order rate constants for decolorization, k_1, are summarized in Table 1. It was observed that Pd modification of TiO_2 on non-woven fabric did indeed improve the photocatalytic activity. The k_1 of methylene blue decolorization increased by a factor of 5 compared to that for the fabric/TiO_2 without Pd. We found that, under dark conditions, there was negligible methylene blue decolorization by the fabric/Pd/TiO_2. Thus, the result is due to an enhancement of photocatalytic activity. Interestingly, the Ni foam/TiO_2 showed the highest decolorization rate and the highest amount of methylene blue adsorption (data not shown). Hu et al. [10] reported that the surface area of Ni foam was increased by oxidization, and a large amount of TiO_2 particles could be sintered onto the surface. Thus, the large surface area of the Ni foam/TiO_2 resulted in the highest decolorization rate in the present research.

Table 1 Pseudo-first order rate constants (k_1) for photocatalytic methylene blue decomposition by TiO_2-coated materials

TiO_2-coated materials	k_1/h^{-1}
Blank	0.0
Non-woven fabric/TiO_2	0.3
Non-woven fabric/Pd/TiO_2	1.5
Ni foam/TiO_2	6.8

3.3 Algal growth inhibition test

Figure 4 shows the incubation-time dependence of ΔTOC in culture medium containing algae with/without TiO_2-coated materials. After 18 days culture under these conditions without TiO_2-coated materials (blank, open circles), the medium showed a ΔTOC value of 170 mg L^{-1} and a deep green color. Almost the same result was obtained in the culture with the fabric/TiO_2 (open triangles), and the color of the fabric turned a deep green (Fig. 5a, b). Algae can grow on various surfaces such as acrylic substrates, cement, and fabric materials [17]. Thus, the fabric/TiO_2 was not able to inhibit the algal growth, notwithstanding its water purification ability, shown in Fig. 3 and Table 1.

Interestingly, after 18 days culture with the fabric/Pd/TiO_2 (filled triangles), the medium showed a 60 mg L^{-1} ΔTOC and a light green color, and the color of the fabric/Pd/TiO_2 itself was not changed (Figs. 5c, d). Asano and Matsukawa [12] reported that Pd/TiO_2 powder is effective in decreasing both COD and algae in river water, and the purification ability of Pd/TiO_2 was superior to that of TiO_2. They concluded that the photocatalytic decomposition rate of algae may exceed the growth rate of algae. Similar trends were reported by Clovis et al. [17] for glucose decomposition and algae inhibition experiments using cocatalyst-modified TiO_2. The cell walls of plant organisms, including

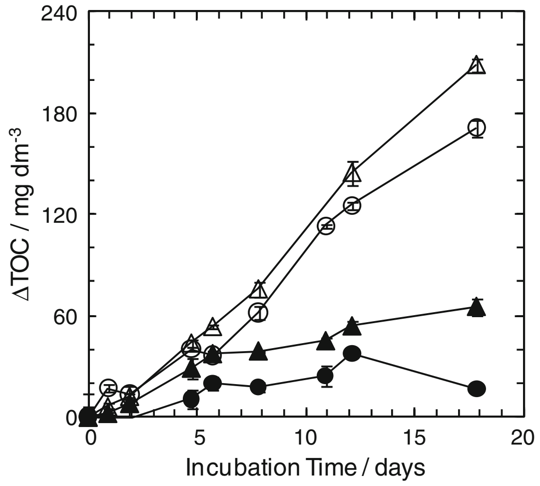

Fig. 4 Incubation-time dependence of ΔTOC in culture medium containing algae with/without TiO_2-coated materials (*open circles*: blank; *open triangles*: non-woven fabric/TiO_2; *filled triangles*: non-woven fabric/Pd/TiO_2; *filled circles*: Ni foam/TiO_2). Experimental conditions: sample volume = 0.3 L, area of TiO_2-coated materials = 25 cm^2, light intensity = 2.0 mW cm^{-2} of UV and 2,000 Lx of visible light (12-h light/12-h dark), water temperature = 20 °C

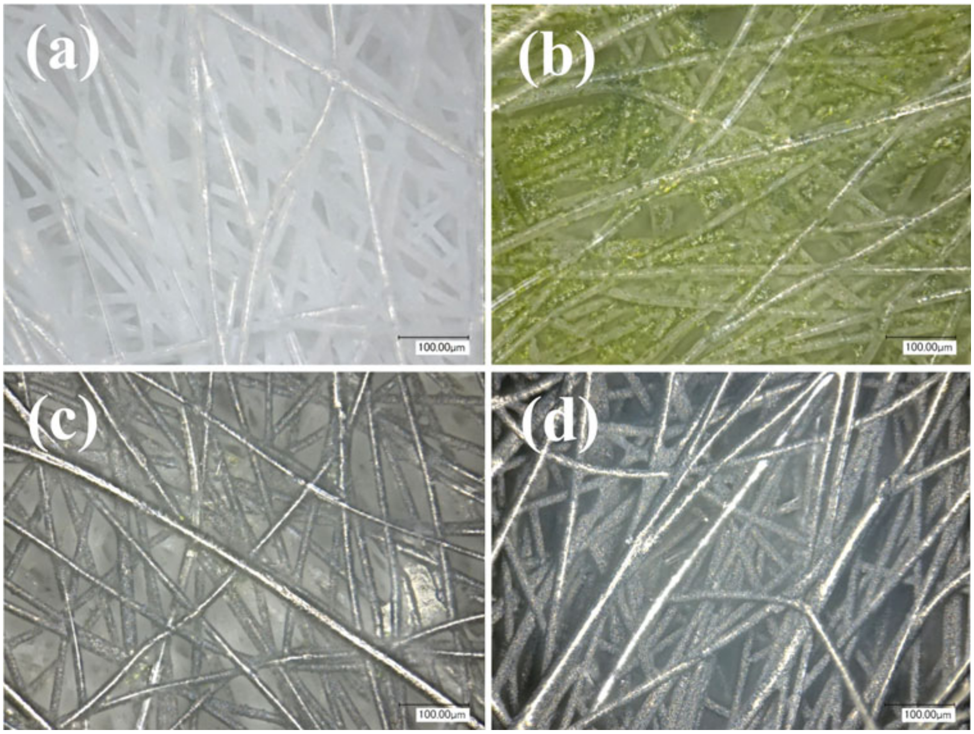

Fig. 5 The optical microscope images of **a** non-woven fabric/TiO_2 before use for algal growth testing, **b** non-woven fabric/TiO_2 after use for algal growth testing, **c** non-woven fabric/Pd/TiO_2 before use for algal growth testing, and **d** non-woven fabric/Pd/TiO_2 after use for algal growth testing. Experimental conditions were the same as those in Fig. 4

algae, are made largely of cellulose, so that one might expect comparable photocatalytic behavior. There is also a report by Huang et al. [18] who irradiated *E. coli* in the presence of TiO_2 and calculated the rate of production of malondialdehyde due to lipid membrane peroxidation. Consistent with these references, a similar cocatalyst effect may be occurring in the fabric/Pd/TiO_2 in the present research.

After 18 days culture with the Ni foam/TiO_2 (filled circles), the medium showed the smallest value, 20 mg L^{-1} ΔTOC, and a slightly green color. Algae can also grow on metal surfaces such as iron, copper, and steel [19]. However, as shown in the methylene blue decolorization experiment, the large surface area of Ni foam/TiO_2 generated high activity for photocatalytic water purification. Therefore, the high photocatalytic decomposition rate of algae may exceed the growth rate of algae. To confirm the practicality of the usage of the Ni foam/TiO_2 for algal growth inhibition, a large scale culture was set up in the open air under sunlight. The cultures were resuspended in 20 L of fresh MA medium and separated to a 10 L tank. A sheet of Ni foam/TiO_2 (600 cm^2) was floated on the surface of the culture. During algal growth, the temperature, UV light intensity, and visible light intensity were 22–25 °C, 0–0.3 mW cm^{-2} and 0–7,000 Lx, respectively. The photographs of the cultures are shown in Fig. 6. At 19 days, the blank culture became deep green in color and opaque (Fig. 6c, left). On the other hand, the culture with the Ni foam/TiO_2 showed a light green color (Fig. 6c, right). In particular, the culture near the Ni foam/TiO_2 had almost no color and was transparent (Fig. 6d, right). This result indicates the possibility of effective usage of the Ni foam/TiO_2 for algal growth inhibition.

4 Conclusion

Anatase TiO_2 particles were successfully immobilized onto the surface of Ni foam substrates. Pd nanoparticles were also successfully immobilized onto non-woven fabric-supported TiO_2 by photoelectrochemical deposition. The TiO_2-coated materials displayed high activities in the photocatalytic decolorization of methylene blue under ultraviolet irradiation. In particular, the Ni foam-supported TiO_2 showed the highest decolorization rate in the present research.

The inhibition of algal growth was not achieved with the non-woven fabric-supported TiO_2. However, the fabric-supported Pd/TiO_2 showed high inhibition activity for algal growth. This may be due to a cocatalyst effect of Pd in the fabric/Pd/TiO_2. Ni foam/TiO_2 also showed the high inhibition activity both in laboratory-scale testing and open-air testing. Therefore, the TiO_2-coated materials with appropriate coating methods such as the use of co-catalysts or large surface area can substantially inhibit algal growth.

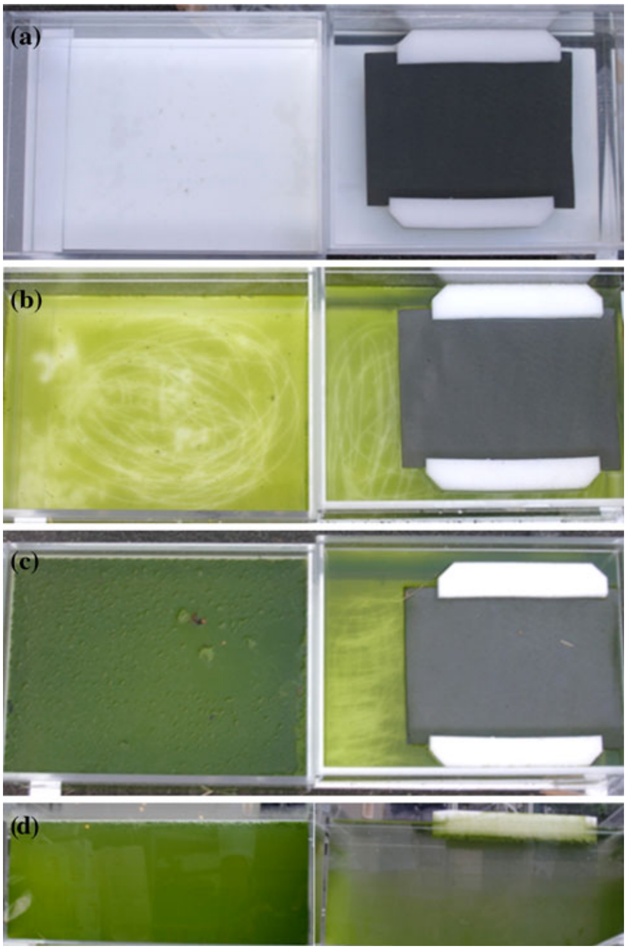

Fig. 6 Photographs of algal growth in an open-air tank without and with Ni foam/TiO_2 at **a** 1 day, **b** 10 days, **c** 19 days, and **d** side view at 19 days (sample volume: 10 L; area of Ni foam/TiO_2: 600 cm^2; light source: sunlight (0–0.3 mW cm^{-2} of UV and 0–7,000 Lx of visible light); water temperature: 22–25 °C)

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