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APPLICATION OF WASTED SILICA PARTICLES TO TITANIA PHOTOCATALYST SUPPORT FOR WATER PURIFICATION

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ABSTRACT
TiO_2-coated SiO_2 particles were prepared from industrially-wasted SiO_2 particles by an alkoxide method. The TiO_2-coated SiO_2 powder was shaped in pellet form by extrusion molding and sintering, and used to retard the growth of cyanobacteria in water. After natural light and UV irradiation, the decolorization of green cyanobacteria was observed and the amount of cyanobacteria decreased. The TiO_2 coating of wasted SiO_2 powder is useful for the photocatalytic application to water purification.

KEYWORDS
Silica, titania, photocatalyst, water purification, chlorophyll a, cyanobacteria.

INTRODUCTION
TiO_2 photocatalyst is commercially applied for gas purification, decomposition of organic pollutants and so on [1,2]. For gas or water purification, TiO_2 photocatalyst is fabricated by using porous materials and activate carbon fiber as support [3-6]. The authors have reported that SiO_2 support stabilizes anatase phase even after heat treatment to crystallize TiO_2 deposit by an alkoxide method, which leads to improvement of photocatalytic activity [7]. The photocatalyst is needed for water purification, because the heat exchange efficiency decreases when the cyanobacteria grows in the large-scale cooling tower. The air-conditioning machine stops by the proliferation of the cyanobacteria. The breeding environment of legionella is formed by the cyanobacteria and so on. There are several demands of the water purification using the photocatalyst, which will be able to solve their problems. However, when the TiO_2 photocatalyst is soaked in circulation water, it will peel off from the substrate easily. Therefore, the photocatalyst function doesn't have long-term stability when it is used in circulation water. Several researches and development have been attempted to retard the growth of cyanobacteria in water so far[8-13] , but neither a large-scale test nor a real machine test can be seen.
In the present work, the SiO_2-supported TiO_2 photocatalyst was used to retard the growth of cyanobacteria in circulation water. To use the photocatalyst for a long term in circulation water, the TiO_2-coated SiO_2 powder was shaped in pellet form by extrusion molding and sintering. The aim of this work is to clarify the effect of the photocatalyst on retardation of growth of cyanobacteria (chlorophyll a) in the large-scale cooling tower by use of the photocatalyst water purification device and sintering pellet.

EXPERIMENTAL

Samples
Wasted SiO_2 powder was supplied from a semiconductor company. The crystalline phase was quartz and the mean diameter was about 5 μm. TiO_2-coated SiO_2 powder was prepared by hydrolysis of titanium tetraisopropoxide on the surface of wasted SiO_2 powder as described in the previous work [7]. The dried powder was mixed with clay component, and then shaped in pellet form by extrusion molding and

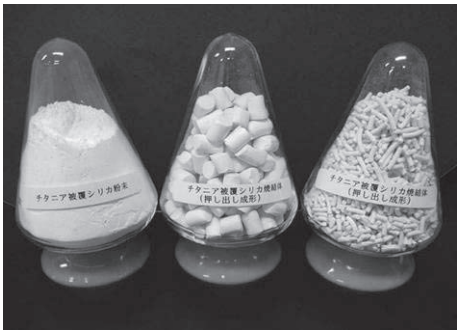

Fig. 1 Photograph of TiO_2-coated SiO_2 powder and pellets (left: powder, center: 5 mmφ, right: 2 mmφ).

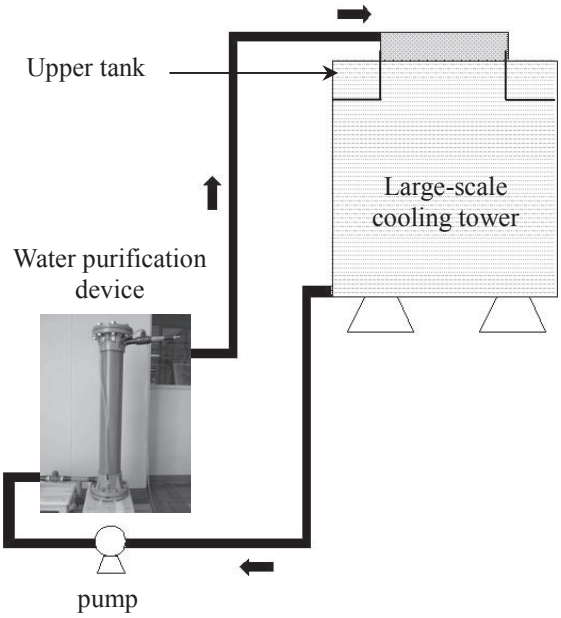

Fig. 2 Flow diagram of photocatalyst water purification system by UV irradiation.

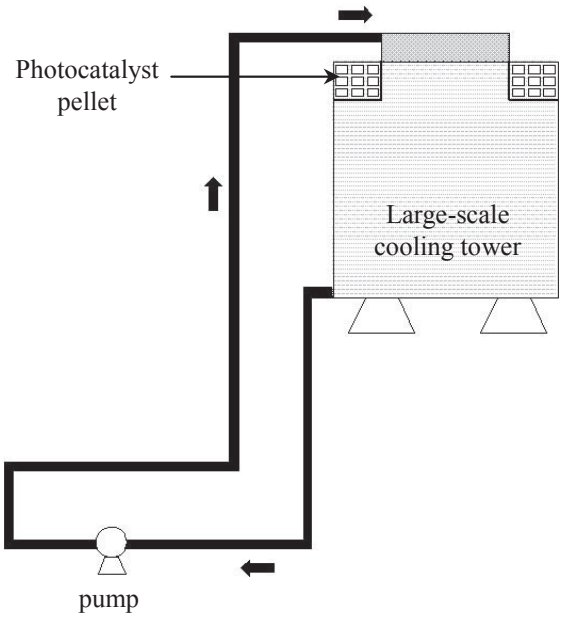

Fig. 3 Flow diagram of water purification system with photocatalyst pellets under natural light.

sintering at 1000°C. Figure 1 shows the photograph of TiO_2-coated SiO_2 powder and pellets. The sintered pellets were not crushed in the circulation water for 6 months.

Water Purification System

The flow diagram of photocatalyst water purification system by UV irradiation is shown in Fig. 2. The size of water purification device is 45 mmφ×1200 mm height. A UV tube with a wavelength of 254 nm was placed inside a quartz glass tube equipped in the center of the device.

The 3 kg of photocatalyst pellets were set up in the water purification device. After water circulation in the purification device, the treated water returned to the large-scale cooling tower. When natural light was used, the 8 kg of photocatalyst pellets were soaked in the upper tank of the large-scale cooling tower. The flow diagram of water purification system with photocatalyst pellets under natural light is shown in Fig. 3.

The whole amount of circulated water was approximately 280L. The flow velocity was 120L/min. The UV light was continuously irradiated for 300 h. The circulated water in the large-scale cooling tower was sampled at every 24 h.

Analysis of Chlorophyll a

A constant amount of circulated water from the large-scale cooling tower was filtrated with a glass fiber filter. The glass fiber filter was put in an agate mortar and ground by a pestle in 90% acetone. The ground powder was moved to a centrifugal glass tube and separated by centrifugation at 3000 rpm for 20 min. To extract the coloring matter enough, the ground powder was left in a refrigerator for 2 h before centrifugation. The amount of extracted chlorophyll a was analyzed with a UV/Vis spectrometer.

RESULTS AND DISCUSSION

Shape of Cyanobacteria

Figure 4 shows an optical photomicrograph of cyanobacteria in circulated water (digital microscope, KEYENCE VHX-100). The shape of cyanobacteria was roundish and fibrous. The size of cyanobacteria grain was approximately 2 μm.

Appearance change of the upper tank

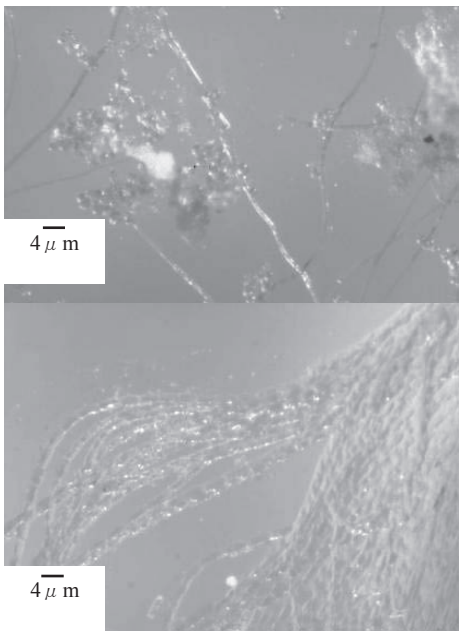

Fig. 4 Optical photomicrograph of cyanobacteria in circulated water.

Figure 5(a) shows an upper tank of the large-scale cooling tower before the photocatalyst pellets were introduced. Cyanobacteria grew in abundance at all over the upper tank. Figure 5(b) shows an upper tank of the large-scale cooling tower after 1.5 months with photocatalyst pellets. The decolorization of green cyanobacteria was observed. Figure 5(c) shows an upper tank of the large-scale cooling tower after 3 months. Compared to the start (Fig.5(a)), the amount of cyanobacteria in circulated water was reduced. It was found that the photocatalyst pellets tended to retard the growth of cyanobacteria in circulated water under natural light.

Effect of Natural Light and UV Light

Figure6 shows the change in the amount of chlorophyll a in circulated water of large-scale cooling tower under natural light irradiation with photocatalyst pellets. The amount of chlorophyll a decreased by about 60% for 14 days, and by about 80% for 50 days or over.

Figure 7 shows the change in the amount of chlorophyll a in circulated water of the large-scale cooling tower under UV light irradiation with photocatalyst pellets. The amount of chlorophyll a decreased by about 80% for 200 h. These experimental results indicate that the amount of chlorophyll a can be reduced in a short time when UV light was used. This may be due to the

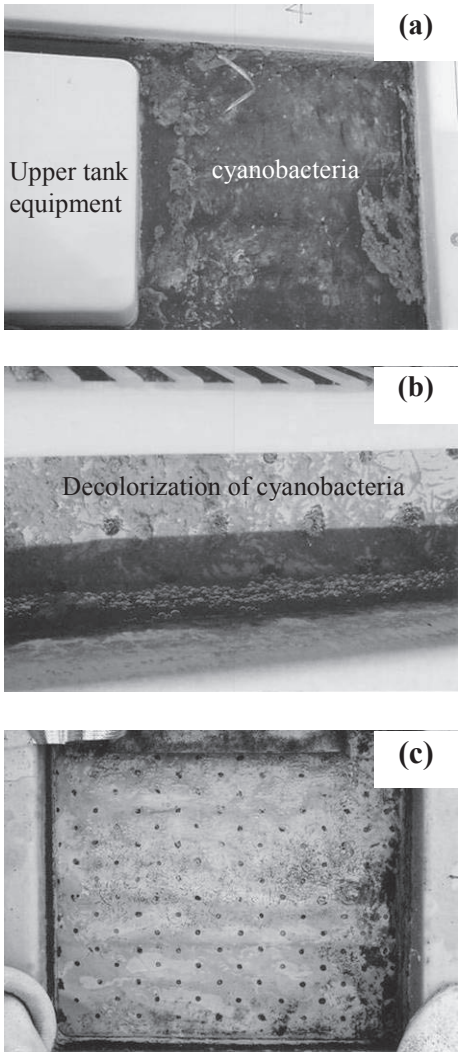

Fig. 5 Photograph of the upper tank of large-scale cooling tower (a) start, (b)1.5months, (c)3months.

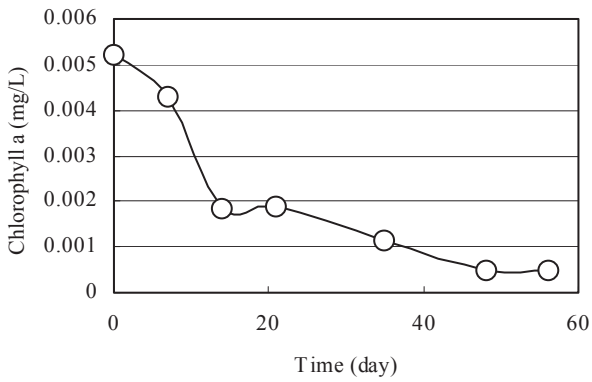

Fig. 6 Analysis result of chlorophyll a (natural light).

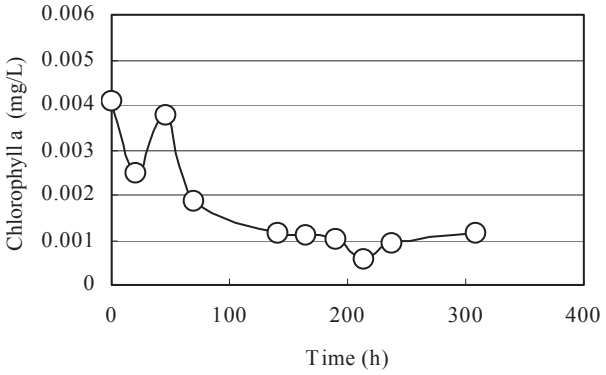

Fig. 7 Analysis result of chlorophyll a (UV light).

increase in high-efficiency OH radicals from TiO_2 with a continuous irradiation of UV light of short wavelength. The amount of chlorophyll a after 200 h little changed because large-scale cooling tower was open system and cyanobacteria might invade from the outside.

CONCLUSIONS

The amount of chlorophyll a in the circulated water of large-scale cooling tower decreased under natural light with photocatalyst pellets. The water purification device decreased the amount of chlorophyll a in a short term under UV light with photocatalyst pellets.

The amount of chlorophyll a did not reach absolutely zero, because this large-scale cooling tower was open system and cyanobacteria might invade from the outside easily.

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