Preparation and Photocatalytic Performance of TiO_2 Immobilized on Fiberglass Cloth

Deqiang Chen and Yiqun Chen

***Abstract*—In this study, the TiO_2 immobilized on fiberglass cloth was prepared to improve the photocatalytic activity of TiO_2 and overcome the difficulty of reuse through painting followed by sol-gel process. The morphology and microstructure of TiO_2 loaded on FGC were characterized via XRD and SEM, respectively. The result revealed that 1) the crystalline structure of immobilized TiO_2 was nearly unchanged compared with pure P25 nanoparticles. 2) The TiO_2 loaded on FGC had larger specific surface area than that of P25. 3) The TiO_2/FGC system displayed remarkable photocatalytic activity on decomposition of MC-LR.**

***Index Terms*—TiO_2, fiberglass cloth, MC-LR, photocatalytic performance.**

I. Introduction

Nano-titanium dioxide (TiO_2) is considered as one of the most promising photocatalyst for environmental remediation due to its physicochemical properties such as thermal and chemical stability, relatively high photocatalytic activity, low-toxicity, and low cost [1]-[3]. However, there are some obstacles, including the difficulty in seperating the suspended TiO_2 from the liquid-solid photocatalytic system and the low quantum yield of TiO_2 under the radiation of sunlight, impeding the large-scale application of TiO_2 photocatalysis in water and air remediation [4], [5]. The immobilization of TiO_2 onto solid materials (glass plates, ceramic membranes, etc.) makes it easy to be recycled but the consequent problem is the considerable reduction of photocatalytic activity than that of suspension system due to the decrease of effective surface area of photocatalyst [6]-[9].

Human activities such as the agricultural and industrial development, which contribute to eutrophication, water pollution and climate change, have led to an increasing occurrence of prolonged and intense harmful blooms of cyanobacteria around the world in recent years [10]. Cyanobacteria are a photosynthetic -prokaryotic group that is among the most ancient organisms on earth [11]-[13]. They can release various metabolites such as taste and odor compounds, anti-microbials, and also problematic toxins known as cyanobacterial toxins or cyanotoxins [14]-[16]. The cyclic hepatotoxic peptides microcystins (MCs) are among the most important and by far themost studied cyanotoxins. This group of toxins can be produced by by a number of cyanobacteria genera such as Microcystis, Anabaena, Plankothrix and Nostoc had been proved to be acute hepatotoxicity [17], [18]. Though MCs mainly inhibit the serine/threonine phosphatases (PP1 and PP2A), they may also promote tumor formation, induce apoptosis, and present long-term chronic toxic effects on wildlife, domestic animals and humans [19]-[22].

MCs are extremely stable in natural aquatic environments, being resistant to various natural elimination processes including chemical oxidation by naturally generated reactive oxygen species and biological transformation by other microorganisms [23]-[26]. Consequently, the presence of MCs in source water presents a significant threat to the ecosystemintegrity and human health [10], [27].

MCs is a group of monocyclic heptapeptides with many different isomerides and among which Microcystin-LR(MC-LR) possesses the most toxic effect [28], [29]. As a result, a guideline value of $1\ \mu gL^{-1}$ for MC-LR in drinking water has been issued by the World Health Organization [30]. In general, MC-LR exhibits a stable property against physicochemical and biological factors such as temperature, sunlight and enzymes [31]-[33]. It was been proved difficult to remove MC-LR from drinking water by conventional water treatment techniques due to their stable physical and chemical properties[34]. Advanced oxidation processes (AOPs) including chlorination, ozonation, hydrogen peroxide disinfection and photocatalysis have been proved efficient to remove MC-LR [35]-[37], but the cost of continuous input of expensive chemical reagents is prohibitive. On the other hand, the use of chemical methods to remove the MC-LR may result the secondary contamination of drinking water. As the presence of MCs in water environment has a potential hazard to human health, it's urgent to find effective methods to eliminate it and make sure the safety of drinking water.

Fiberglass cloth (FGC) is one kind of performance outstanding inorganic nonmetallic material with flexibility, corrosion resistance and easy to handle [38]. It was proved the photocatalyst of TiO_2 immobilized fiberglass cloth exhibited photocatalytic activity in photodecomposition of organic pollutants [39]-[42]. However, there are fewer studies on the photocatalytic degradation of MCs in a liquid phase using TiO_2 immobilized onto FGC. In this study, the TiO_2 immobilized FGC was introduced which was expected to effectively improve the removal rate of MCs in aqueous phase and deal with the problem of recycle.

II. Experimental

A. Preparation of TiO_2 Immobilized On Fiberglass Cloth

Pristine FGC was heat-treated in an electric furnace at 500 ℃ with ramping rate of 5 ℃/min for 2 h before

Manuscript received March 31, 2015; revised July 21, 2015.

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immobilization of the catalysts to ensure complete removal of any organic residuals and then cut into pieces of equal size.

The TiO_2 catalysts loaded on FGC included TiO_2 suspension and TiO_2 sol. TiO_2 suspension was obtained by dispersing TiO_2 (P25) nanoparticles (80% anatase + 20% rutile, purchased from Degussa) (2g) in deionized water (150ml) and agtitating for 10 minutes. TiO_2 sol was prepared as follows: tetrabutyl orthotitanate (TBOT) (85ml), triethanolamine (15ml) and ethanol (400ml) were mixed and agitated for 1.5h. A solution included deionized water (9ml) and ethanol (50ml) had its pH value adjusted to 3 by nitric acid (1M) was subsequently added to the above mixture and kept stirring for 1h at ambient temperature. The resultant light yellow and transparent sol was obtained and aged for 24h from light.

The immobilization was done by two steps: 1) the TiO_2 suspension was painted on FGC pieces uniformly and heating at 200℃ with ramping rate of 2℃/min for 2 h. 2) the TiO_2 coated FGC was sequently submerged into prepared TiO_2 sol and extracted at a speed of 10 cm/min and then calcined at 450℃ for 1 h with the heating rate of 2℃ /min.

B. Characterization of Catalysts

XRD patterns of the catalyst-immobilized on FGC samples were obtained by the X-ray diffractometer (XTRA/3KW, ARL, Switzerland). The crystallite size of each phase was determined from line broadening of the respective X-ray spectral peaks using the Scherrer's formula. The microstructure of TiO_2 immobilized on FGC was observed by a scanning electron microscope (SEM, Hitachi-3400N, Japan).

C. Photocatalytic Testing

A 250 W high pressure mercury lamp with dominant wavelength of 365 nm were used as the UV light source for photocatalytic reaction. The photocatalytic activity of the photocatalyst was assessed by decomposition of Microcystin-LR (MC-LR). 0.8 g of photocatalysts was dispersed into 500 ml water solution containing 50 μg MC-LR, and then the mixture was stirred constantly under the light with a distance of 25 cm. The reaction solution was sampled every 30 min. The samples was filtered by acetate cellulose films of 0.45 μm and enriched by C18 solid phase extraction column. The concentration of MC-LR was measured by a high performance liquid chromatograph (HPLC, Waters).

III. Results and Discussion

A. X-ray Diffraction (XRD)

The XRD patterns of commercial titanium dioxide (P25) and TiO_2 immobilized on FGC were presented in Fig. 1. Clearly, both materials exhibit the similar XRD patterns. As shown in Fig.1, the series of strong peaks at 2θ of 25.2, 37.8 and 38.5 were respectively corresponding to the (101), (004) and (112) crystal planes of anatase phase, and the peak at 2θ of 27.4 was corresponding to the (110) crystal plane of rutile phase as well. These signals were indicative of the dominant anatase phase in both catalysts which was generally recognized with higher photocatalytic activity than rutile form.

According to the Scherrer formula [43], the mean particles of P25 and TiO_2 loaded on FGC were respectively calculated to be 21nm and 16nm. The results indicated the catalysts immobilized on FGC had larger specific surface area than that of P25 which was conducive to photocatalytic performance.

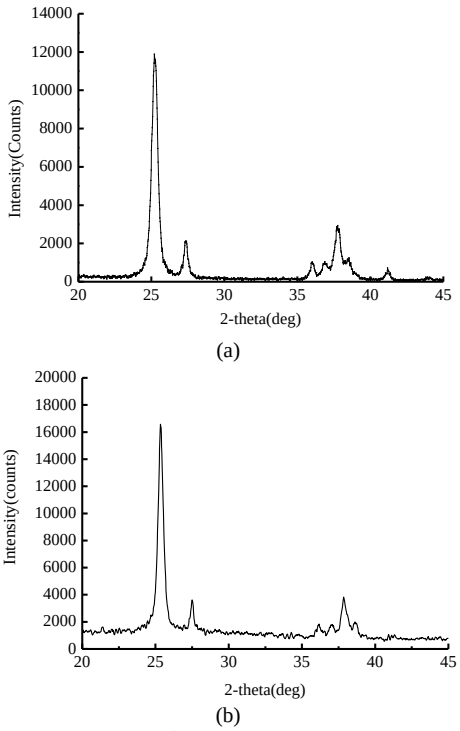

Fig. 1. a) XRD patterns of P25 and b) TiO_2 immobilized on FGC.

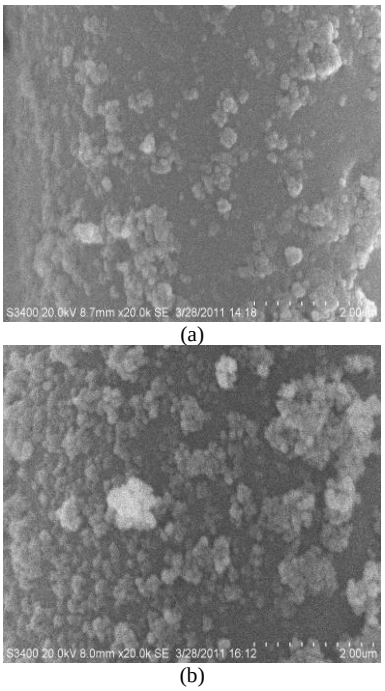

Fig. 2. TEM image of TiO_2 loading on FGC a) by painting & sol-gel method and b) by painting twice.

B. Scanning Electron Microscopy (SEM)

Fig. 2 was the SEM images of TiO_2 loaded on FGC by two patterns. As showed in both images, the TiO_2

nanoparticles distributed evenly on the FGC with regular structure. Furthermore, it was apparently the pattern of painting twice result in more TiO_2 particles loading on FGC compared to the pattern of painting followed by sol-gel process, which indicated the painting was more effectively way to immobilize TiO_2 onto FGC than sol-gel method. According to the TEM image, the average particle size of TiO_2 particles was about 15 nm which was in concordance with the results calculated from XRD spectra.

C. Photocatalytic Performance of TiO_2 Immobilized FGC

The decompositions of MC-LR in different reactive systems were illustrated in Fig. 3. MC-LR was almost not degraded by single TiO_2 and UV in 3h, but its removal rate was up to 68% by TiO_2 immobilized on FGC under UV light. Obviously, the immobilization on FGC improved the photocatalytic performance of TiO_2. According the result above mentioned, the loading of TiO_2 on FGC could increase specific surface area of the composite, thus offering more photocatalytic reaction centers and improving the photoactivity of catalysts.

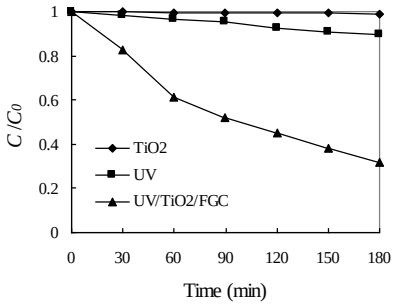

Fig. 3. Decompositions of MC-LR by TiO_2, UV and UV/TiO_2/FGC.

IV. Conclusions

The results showed that the TiO_2 immobilized on FGC would not alter its crystal phase composition. The TiO_2 loaded on FGC had larger specific surface area than that of P25 which was conducive to photocatalytic performance. The TiO_2/FGC system can be efficiently used for the degradation of MC-LR.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No. 51309081), Fundamental Research Funds for the Central Universities (2010B05314) and A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions..

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