Preparation of mesoporous TiO$_2$ with enhanced photocatalytic activity towards tannery wastewater degradation

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ABSTRACT

Ordered mesoporous TiO$_2$ materials are successfully synthesized via a sol-gel route using butyl titanate as a precursor and sodium dodecyl benzene sulfonate surfactants as soft templates. The as-prepared TiO$_2$ samples possess a relatively high surface area of 40.03 m$^2$/g and the center of pore diameter distribution of 13.04 nm. They exhibit excellent photocatalytic activity towards degradation of organic pollutants in tannery wastewater under UV-light and natural sunlight irradiation. The effect of the catalyst dosage, the pH value of the solution and the concentration of H$_2$O$_2$ are discussed in detail. This work would pave an avenue for purifying various industrial wastewaters through an advanced photocatalytic oxidation process.

Key words | nanomaterials, photodegradation, porosity, tannery wastewater, TiO$_2$

INTRODUCTION

The leather industry was considered as one of the most polluting industries because a series of stable and nondegradable products were produced in leather tanning processes (Haydar & Aziz 2009; Dixit et al. 2015; Abdel-Shafy et al. 2016; Chen et al. 2016; Elabbas et al. 2016). The low biodegradability of such chemicals resulted in serious environmental and technological problems. Conventional treatment methods, including coagulation and biological oxidation, could not achieve a complete decomposition of these contaminants in leather wastewater (Thankappan et al. 2015; Abdalh & WalidSayedAbdelhalim 2016; Gungor et al. 2016; Hashem et al. 2016; Jiang et al. 2016). Therefore, an alternative method, such as advanced oxidation process (AOP), probably will become a representative strategy in the near future (Oturan & Aaron 2014; Asghar et al. 2015).

Photocatalytic oxidation, as an efficient and economical AOP, aimed at mineralizing the organic contaminant into water, carbon dioxide and inorganic salts (Qu & Duan 2013; Wang et al. 2014). Among numerous photocatalytic materials, mesoporous TiO$_2$ with an interpenetrated and regular mesopore system has attracted extensive attention because of its prominent characteristics of low cost, high specific surface areas, good chemical stability and environmental benignity (Qiu et al. 2014; Zhou et al. 2014). Guo’s group has adopted mesoporous TiO$_2$ microspheres for photocatalytic degradation of bisphenol A in aqueous suspension by high performance liquid chromatography-mass spectrometry, and an excellent photocatalytic activity was obtained (Guo et al. 2010). Ahirwar et al. reported a modified sol-gel route to synthesize mesoporous TiO$_2$ catalyst, and the catalyst showed an outstanding photocatalytic activity towards the degradation of indigo carmine in the presence of visible light (Ahirwar et al. 2016). Thus, the mesoporous TiO$_2$ materials were expected to exhibit excellent photocatalytic activity towards the degradation of contaminants in tannery wastewater.

Herein, we successfully synthesized mesoporous TiO$_2$ through a facile sol-gel strategy. The mesoporous TiO$_2$ products were utilized to degrade tannery wastewater under the irradiation of 365 nm UV-light and natural sunlight.

EXPERIMENTAL

Chemicals

All chemicals were of analytical grade and used as received without further purification. Distilled water...
was used throughout the experiment. The tannery wastewater was collected from Tianjin Fusheng Leather Co., Ltd. The wastewater samples were collected from the equalization tank of a treatment plant designed to treat 2,500 m³/d of tannery wastewater generated from about 128 tanneries. First, the raw tannery wastewater was pre-treated. Conventional coagulants were adopted for the amendment of suspended solids and precipitation of chromium. Then, the pre-treated wastewater was sequentially used as feed to the sequencing batch reactor. The average chemical compositions of raw effluent and pre-treated effluent were measured according to Standard Methods (1995) (APHA, AWWA, WEF 1995; Ganesh et al. 2006).

Preparation of mesoporous TiO₂

Mesoporous TiO₂ photocatalyst was synthesized via a sol-gel method. In a typical synthesis, 10 g of butyl titanate and a certain amount of sodium dodecyl benzene sulfonate were dissolved in 20 mL of ethanol under stirring at room temperature. Then, a homogeneous mixture containing 1 mL of H₂O₂, 10 mL of ethanol and 0.5 mL of hydrochloric acid was added to the above solution. A transparent yellow sol solution was formed. The sol was aged at room temperature for 2 days to acquire homogeneous solution. Then, the gel was formed by placing the sol-containing solution into an oven kept at 80 °C for 6 h. Subsequently, the gel was dried overnight at 80 °C to eliminate the solvent, which was mainly the distilled water used for the preparation of surfactant aqueous solution. After drying, the xerogel (dried sample) was obtained. The dried samples were heated to 500 °C at a rate of 8 °C min⁻¹ and calcined for 4 h. The calcination was aimed at removing surfactant and achieving a certain degree of crystallinity. The mesoporous TiO₂ sample was prepared via the sol-gel method.

Characterization

Scanning electron microscopy (SEM) was carried out on a Hitachi SU-1510 microscope. Transmission electron microscopy (TEM) was performed on a JEOL 100-CX microscope. X-ray diffractometry (XRD) was examined on Rigaku 97D/max-2500 with Cu Kα radiation (λ = 0.15406 nm) with a continuous scanning mode at the scanning rate of 6 °C min⁻¹. N₂ adsorption-desorption isotherms were recorded on Quantachrome autosorb. The surface area is calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined by the Barrett–Joyner–Halenda (BJH) approach.

Photocatalytic activity

The photocatalytic activity of mesoporous TiO₂ was evaluated by the degradation of organic pollutants in the diluted tannery wastewater under UV irradiation of 365 nm from a 150 W UV light lamp (Supporting Information Table S1, available with the online version of this paper). The photocatalysis reaction was carried out in a Pyrex-glass photocatalytic reactor of cylindrical shape. The volume of the reactor was 500 mL with an actual size that was 10 cm in diameter and 7 cm in height. The distance from the irradiation source to the solution was about 15 cm. To avoid the fast evaporation of the tannery wastewater under the 150 W UV lamp, the reaction temperature was controlled by a circulation condensate device. First, mesoporous TiO₂ was dispersed in 200 mL of wastewater (initial chemical oxygen demand (COD): 170 mg/L). Then, the solution was continuously stirred for 60 min in the dark to ensure the establishment of an adsorption-desorption equilibrium between the photocatalysts and the pollutants (Supporting Information Figure S1, available with the online version of this paper). After that, the solution was exposed to UV irradiation under magnetic stirring. At a certain time, the suspension was taken out and centrifuged to remove the photocatalysts. The filtrates were diluted multiple times to determine the color. COD was measured using the dichromate method to evaluate the degradation effect.

The COD and chroma value of tannery wastewater were measured by the potassium dichromate method and the dilution method, respectively (Drolc et al. 2003).

Tannery wastewater chroma was tested through adopting the dilution multiple method. First, the tannery wastewater was diluted with distilled water into diluted samples with different multiple concentrations. Then, they were sequentially transferred into colorimetric tubes (50 mL) and diluted to volume. The colorimetric tubes were compared with distilled water on a white background until the chroma of diluted wastewater coincided with the distilled water. The dilution multiple was the chroma value of the corresponding wastewater sample.

The COD of tannery wastewater was determined by the potassium dichromate method, according to the standardized method ISO 6060 (Thomas & Mazas 1986; ISO 6060 1989). The COD result was corrected through taking into account the hydrogen peroxide perturbation (Talinli & Anderson 1992; Kang et al. 1999).
RESULTS AND DISCUSSION

Characterization of mesoporous TiO$_2$

The mesoporous TiO$_2$ is synthesized through a facile sol-gel method. The SEM image (Figure 1(a)) shows that the as-prepared mesoporous TiO$_2$ samples are in large quantities and composed of stacked nanoparticles. The TEM image (Figure 1(b)) clearly displays the size of stacked TiO$_2$ nanoparticles about 500 nm and the mesoporous structure of the samples. The typical XRD pattern (Figure 1(c)) identifies the products as a highly crystalline anatase phase of TiO$_2$ (JCPDS no. 21-1272). No additional peak of impurities is observed, demonstrating the high purity of the resulting TiO$_2$ samples. Figure 1(d) displays the N$_2$ adsorption/desorption isotherm and the BJH pore size distribution plot of mesoporous TiO$_2$. The shape of the isotherm coincides with a typical IV type isotherm according to the International Union of Pure and Applied Chemistry classification, indicating the presence of mesopores (Zhao et al. 2014). The pore size is about 13.04 nm judging from the BJH pore size distribution obtained from the isotherm. The surface area of the mesoporous TiO$_2$ determined by the BET method is 40.03 m$^2$/g.

Photocatalytic performance

Control experiments show that the photodegradation efficiency of the tannery wastewater is highly dependent on the catalyst dosage, the pH value of the solution, and the concentration of H$_2$O$_2$. Figure 2(a) shows that the removal of color and COD is affected by the dosage of mesoporous TiO$_2$. As the dosage of TiO$_2$ changes from 0.5 g/L to 1 g/L, the photocatalytic efficiency increases (see details in Supporting Information Figure S2, available with the online version of this paper), while further increasing the dosage of TiO$_2$ to 3 g/L leads to a decreased photocatalytic rate. It suggests that a TiO$_2$ dosage of 1 g/L is optimal in such a system. This is mainly due to the fact that mesoporous TiO$_2$ with a high dosage tends to agglomerate, resulting in less surface exposure and light absorption (Gogate & Pandit 2004; Ghaly et al. 2011). Figure 2(b) discusses the influence of pH value on the removal efficiency of color and COD. pH 2.5 is observed to give the highest photocatalytic activity, which is in accordance with the previous research (Gogate & Pandit 2004). This pH-dependent effect may be involved in the following aspects. When the pH of the solution is above 6.3, both the titanium surface and pollutants in wastewater are negatively charged; thus, the adsorption of
pollutants on TiO$_2$ is repulsive. At lower pH, the pollutants and hydroxyl radicals can contact each other well, thus promoting the photocatalytic performance (Konstantinou & Albanis 2004). As shown in Figure 2(c), the oxidizing agent H$_2$O$_2$ has an important impact on the photocatalytic activity towards the degradation of the organic compounds (Dionysiou et al. 2004). The activity is significantly improved with the concentration of H$_2$O$_2$ increasing from 0 to 3.5%, while further increasing the concentration of H$_2$O$_2$ to 4.0% leads to a decreased performance, thus determining an optimal H$_2$O$_2$ concentration of 3.5%. Under UV-light irradiation, the mesoporous TiO$_2$ catalyst is activated to generate long-lived electron-hole pairs, including conduction band electrons (e$^-$) and valence band holes (h$^+$). On one hand, H$_2$O$_2$ can act as an electron acceptor to capture the reductive photogenerated electron (e$^-$), which prevents the recombination of photogenerated carriers (Equations (1) and (2)). On the other hand, the photolysis of H$_2$O$_2$ can also produce higher amounts of OH· radicals (Equation (3)) (Dionysiou et al. 2004; Sauer et al. 2006). The OH· radicals exert a noticeable positive influence on oxidizing the organic molecule to form small molecule products.

\[
\text{TiO}_2(\text{e}^-) + \text{H}_2\text{O}_2 \rightarrow \text{TiO}_2(\text{h}^+) + \text{HO}^+ + \text{OH}^- \quad (1)
\]

\[
\text{H}_2\text{O}_2(\text{e}^-) + \text{e}^-_{\text{CB}} \rightarrow \text{HO}^+ + \text{OH}^- \quad (2)
\]

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH}^- \quad (3)
\]

But, at higher concentrations, H$_2$O$_2$ may compete with the organic contaminants for adsorption at catalytic active sites (Bandala et al. 2002). Competitive adsorption by H$_2$O$_2$ also leads to a reduction in the degradation rates. Moreover, at higher concentrations, H$_2$O$_2$ itself acts as an effective OH$^-$ scavenger (Equation (4)) (Dionysiou et al. 2004; Sauer et al. 2006). The oxidation potential of OH$_2^-$ is much lower than that of OH$^-$; thus, excessive H$_2$O$_2$ can lower the degradation efficiency, and an optimal concentration must be considered for each kind of wastewater.

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{OH}_2^- + \text{H}_2\text{O} \quad (4)
\]

According to the control experiments above, we confirm the optimum reaction conditions with the catalyst dosage of 1 g/L, the pH value of 2.5, and the H$_2$O$_2$ concentration of 3.5%. In the optimum conditions, the catalyst possesses a color and COD degradation rate of 100% and 60%. It shows a better photoactivity than that of the commercial P25 (Figure 3(a)). The enhanced photocatalytic performance is mainly attributed to the relatively large surface area and pore volume. The ordered mesopore structure is convenient for the mass transport of the organic pollutants. Therefore, the mesoporous structure plays a crucial role in determining the photoactivity. The durability of the mesoporous TiO$_2$ is evaluated by reusing the catalyst for five runs towards the decomposition of organic pollutants in tannery wastewater under the same conditions. The catalyst almost affords the same photocatalytic activity as the initial one, demonstrating its excellent photocatalytic stability (Figure 3(b)). Furthermore, the mesoporous TiO$_2$ photocatalysts also possess superior catalytic performance under natural sunlight (see details in Supporting Information Figure S3, available with the online version of this paper).

**CONCLUSIONS**

In summary, ordered mesoporous TiO$_2$ is successfully prepared via a sol-gel route. The as-obtained TiO$_2$ samples exhibit excellent photocatalytic activity towards the
degradation of organic pollutants in tannery wastewater. Control experiments show that the photodegradation efficiency of tannery wastewater is highly dependent on the catalyst dosage, the pH value of the solution and the concentration of H₂O₂. This work would provide an avenue for industrial wastewater degradation under natural light.

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