Photocatalytic Degradation of Methylene Blue Using TiO$_2$ Impregnated Diatomite

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Nano-TiO$_2$ showed a good catalytic activity, but it is easy to agglomerate, resulting in the reduction or even complete loss of photocatalytic activity. The dispersion of TiO$_2$ particles on porous materials was a potential solution to this problem. Diatomite has high specific surface and absorbability because of its particular shell structure. Thus, TiO$_2$/diatomite composite, prepared by loading TiO$_2$ on the surface of diatomite, was a good photocatalyst, through absorbing organic compounds with diatomite and degrading them with TiO$_2$. Scanning electron microscopy (SEM), energy dispersive spectrum (EDS), X-ray diffraction (XRD), chemical analysis, and Fourier transform infrared spectrometry (FTIR) indicated that TiO$_2$ was impregnated well on the surface of diatomite. Furthermore, TiO$_2$/diatomite was more active than nano-TiO$_2$ for the degradation of methylene blue (MB) in solution. MB at concentrations of 15 and 35 ppm can be completely degraded in 20 and 40 min, respectively.

1. Introduction

With the progression of global industrialization, environmental pollution becomes a more serious issue and, thus, has received considerable attention. The treatment of colored wastewaters produced by the textile industry has recently been heavily researched. Titanium dioxide (TiO$_2$) is an established $n$-type semiconductor used as a photocatalyst to decompose pollutants in water and air as well as produce self-cleaning materials [1,2]. In recent years, TiO$_2$ has been widely investigated and used because of its nontoxicity, chemical inertness, high photocatalytic activity, and low cost. TiO$_2$ has a significant degradation effect as a good photocatalyst of organic and inorganic pollutants in the air and water, which has a broad prospect of application [3].

The photocatalytic activity of TiO$_2$ is influenced by its crystal structure, particle size, specific surface area, and porosity. Ultrafine powders of TiO$_2$ show a good catalytic activity. However, agglomeration often takes place, resulting in reduction or even complete loss of photocatalytic activity. The dispersion of TiO$_2$ particles on porous materials is a potential solution to this problem. Porous materials impregnated with TiO$_2$ show high thermal stability and larger pore sizes that afford better incorporation of the species without diffusion problems and increased specific surface area [4]. In order to facilitate its recycling and reuse, considerable efforts have been made to load TiO$_2$ particles on various substrates, such as mica, graphite, glass, diatoms stone, fly-ash, and attapulgite [5, 6]. Diatomite is an important nonmetallic resource with nontoxic and good chemical stability. Diatomite has high specific surface and absorbability because of its particular shell structure [7]. It could serve as an effective substrate for TiO$_2$ impregnation. This study presents the preparation and characterization of TiO$_2$-supported diatomite and its photodegradation of methylene blue (MB) in solution.

2. Experimental

2.1. Materials. Diatomite was supplied by Changbai Mountain, Ltd., Jilin Province, China. The medium diameter of diatomite powder, $d_{50}$, is 34 $\mu$m, and the specific surface is
10 m$^2$/g. Its SiO$_2$ content was 87%, with other elements, such as Al, Fe, Ca, K, Mg, and Na. Tetrabutyl titanate was obtained from commercially available.

2.2. Preparation of TiO$_2$/Diatomite Composite. Tetrabutyl titanate was dissolved by ethanol and the solution was gradually added to diatomite. The mixture was stirred for 2 h by magnetic stirrers and then dried in the oven at 80°C. Finally, the dried mixture was further heated to 550°C for about 2 h, before it was cooled naturally. The specific surface of TiO$_2$/diatomite composite is 32 m$^2$/g.

2.3. Characterization. The particle size of diatomite powder was measured by a laser particle analyzer Mastersizer 2000. The morphologies of pure diatomite and TiO$_2$/diatomite composite were examined by scanning electron microscopy (SEM). X-ray diffraction analysis was performed using a D5000 Diffractometer (Siemens) with a Ni filter and CuK$_\alpha$ ($\lambda = 1.54$ Å) radiation. The UV-Vis absorbance spectra were recorded using Varian Cary 5000. BET surface area was determined at liquid nitrogen temperature (77.3 K) using QUADRASORB SI-MP.

3. Result and Discussion

3.1. The Microstructure and EDS Analysis of Diatomite and TiO$_2$/Diatomite Composite. Diatomite has porous structure and rough surface after acid treatment (Figure 1(a)). The pore size of diatomite is between 2 and 5 μm. After impregnation, TiO$_2$ particles formed a dense coating on the surface of the orifice, which presents honeycomb with smaller pore (Figure 1(b)). Compared with raw diatomite, Ti element appeared in the EDS analysis of TiO$_2$/diatomite composite, indicating that TiO$_2$ was successfully coated on the surface of diatomite. This result corroborates the high TiO$_2$ content detected by EDS analysis.

3.2. Chemical Analysis and XRD Patterns. Chemical composition analyses showed that the content of TiO$_2$ increased from 0.15 to 8.71% after TiO$_2$ impregnation (Table 1). The result together with that from the EDS analysis indicates that TiO$_2$ was coated on the surface of diatomite successfully. The reflections of TiO$_2$ were characteristics of anatase. Diatomite is made of amorphous SiO$_2$ with only trace amount of quartz. The XRD pattern of TiO$_2$/diatomite composite revealed mixed phases of anatase TiO$_2$ and amorphous SiO$_2$ (Figure 2). The coating of diatomite particles by TiO$_2$ does not cause any change in their peak positions and shapes compared with the pure TiO$_2$ and diatomite. The results of XRD analysis and chemical analysis were consistent with that of SEM analysis totally.

3.3. FTIR Analysis. The FTIR spectrum of TiO$_2$/diatomite composite consists of the characteristic peaks of TiO$_2$ and diatomite (Figure 3). The band at 1089 cm$^{-1}$ was assigned to the asymmetric stretching vibration modes of Si–O–Si bond [8, 9] and the band at 1633 cm$^{-1}$ was attributed to the stretching mode of O–H bonds on the surface of TiO$_2$ [10]. The band at 797 cm$^{-1}$ was assigned to the symmetric stretching vibration modes of Si–O bond and the strong absorption peak at 400–600 cm$^{-1}$ was attributed to the vibration mode of Si–O–Ti and Ti–O–Ti bonds [11].

3.4. Adsorption of MB on Different Catalysts and Characterization of Photocatalytic Activity. TiO$_2$ almost had no adsorption as well as no photocatalyst for MB and the adsorption of TiO$_2$/diatomite on MB was much lower than pure diatomite for MB (Figure 4). The adsorption reached equilibrium after 30 min in dark. Under dark conditions, TiO$_2$/diatomite composite removed more MB in comparison to TiO$_2$ and control, showing almost no activity as well as no photocatalyst for TiO$_2$ and the control (Figure 5), agreeable to the results presented in Figure 4. In the presence of UV, the rate of MB degradation by TiO$_2$/diatomite composite was higher than that by TiO$_2$, attributing to its high surface area and high adsorbability. The MB at concentrations 15 and 35 ppm could be completely degraded after irradiating 20 and 40 min, respectively. The control had the lowest MB self-degradation under UV light. The photoactivity of TiO$_2$ loaded on diatomite was evidently increased because the high surface area of diatomite effectively concentrates MB around the deposited TiO$_2$ and produces high concentrations of organic compounds for the TiO$_2$ photocatalysis. The diatomite might improve the thermal stability of TiO$_2$ and the surface area and preserve a higher content of surface hydroxyl groups [12].

3.5. UV-Vis Absorption Analysis of MB Solution. Two major absorbance peaks of methylene blue were located at 292 and 664 nm, due to benzene ring and heteropolyaromatic linkage (Figure 6). In addition, the aqueous solution of MB molecules exhibited a double-peak feature at 664 and 615 nm, which correspond to monomers and dimers, respectively [13]. Upon irradiation, the peak at 664 nm has a progressively blue shift to shorter wavelength (Figure 6(b)) because of hypsochromic effect [14, 15]. The absorbance of MB solution was about 2.5 a.u. at time zero. In the presence of TiO$_2$, the absorbance of MB remained the same after 30 min (Figure 6(a)), agreeing well with the results in Figure 5, while the absorbance of MB decreased sharply after 30 min in the presence of TiO$_2$/diatomite composite, indicating that TiO$_2$/diatomite composite has good adsorbability (Figure 6(b)). The absorption peak at 615 nm becomes higher than the peak at 664 nm after 30 min, indicating that the degradation rate of monomers is much higher than that of dimers [14]. Besides, a parallel decrease in intensities and slight blue shift of the bands located at 664 nm also could be observed. These are caused by the N-demethylated degradation concomitantly with the degradation of the phenothiazine [16], as shown in Figure 6(a). And MB was degraded completely after irradiating 60 min and 20 min by TiO$_2$ and TiO$_2$/diatomite composite, respectively.

3.6. Mechanism of TiO$_2$ Activation with UV Light and Photosensitized Oxidation for MB and Its Identification of Intermediate Products. The electron and the hole are generated
in the conduction band and in the valence band of TiO$_2$ by UV irradiation, respectively, as shown in (A1) [17]. The positive hole can oxidize hydroxide ions (or water molecule) adsorbed on the surface of TiO$_2$ particles to produce hydroxyl radical [18], as presented in (A2) and (A3) [17]. The electrons of conduction band can react with the oxygen to produce superoxide radical anions (A4) [19]. The superoxide radical anion reacts with a proton to form hydroperoxyl radical (A5):

\[
\begin{align*}
\text{TiO}_2 + h\nu (\text{UV}) &\rightarrow \text{TiO}_2 (e_{\text{CB}}^- + h_{\text{VB}}^+) \quad (A1) \\
\text{TiO}_2 (h_{\text{VB}}^+) + \text{H}_2\text{O} &\rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^- \quad (A2)
\end{align*}
\]

For the mechanism of photosensitized oxidation, in the presence of catalysts the excited state of MB injects an electron into the conduction band (B1). The MB dye is then converted to a cationic dye radical that undergoes degradation to yield products according to (B2) to (B5) [17].

\[
\begin{align*}
\text{TiO}_2 (h_{\text{VB}}^+) + \text{OH}^- &\rightarrow \text{TiO}_2 + \text{OH}^- \quad (A3) \\
\text{TiO}_2 (e_{\text{CB}}^-) + \text{O}_2 &\rightarrow \text{TiO}_2 + \text{O}_2^- \quad (A4) \\
\text{O}_2^- + \text{H}^+ &\rightarrow \text{HO}_2 \quad (A5)
\end{align*}
\]
The hydroxyl radical existing on the surface of diatomite accelerated the degradation of MB (B3):

\[
\begin{align*}
\text{MB}^+ + \text{TiO}_2 & \rightarrow \text{MB}^{++} e^-_{CB} (\text{TiO}_2) \quad \text{(B1)} \\
\text{O}_2 + e^- & \rightarrow \text{O}_2^{--} \quad \text{(B2)} \\
\text{MB}^{++} + \text{OH}^- & \rightarrow \text{MB} + \text{OH}^+ \quad \text{(B3)} \\
\text{MB}^{++} + \text{OH}^- & \rightarrow \text{products} \quad \text{(B4)} \\
\text{MB}^{++} + \text{O}_2^{--} & \rightarrow \text{products} \quad \text{(B5)}
\end{align*}
\]

The typical HPLC chromatograms of MB degraded by TiO$_2$/diatomite under UV light were shown in Figure 7. HPLC analyses showed no degradation products of MB under the condition of adsorption (Figure 7(a)). The decrease in peak height was just caused by adsorption of MB on TiO$_2$/diatomite (Figure 7(b)). However, the adsorption of the dye molecules over the TiO$_2$ surface directly affects the occurrence of electron transfer between the excited dye and TiO$_2$ which further accelerated the degradation rate [20]. In the inserts, peak number 1 represented the retention time of MB, peak number 2 was the self-degradation intermediate metabolite of MB, while peaks number 3 and 4 were further...
degradation products of MB (Figure 7(c)). Peaks number 3 and 4 were further degraded to CO$_2$ completely in addition to further reduction of peak height of peaks number 1 and 2 after UV irradiation for 20 min. These results are in agreement with the results shown in Figures 5 and 6(b). The MB and its progressive degradation products corresponding to the peaks of 1, 2, 3, and 4 were reported in Scheme 1. The OH$^\cdot$ radicals can attack the C–S$^+$=C functional group in MB, which is in direct Coulombic interaction with the surface of TiO$_2$/diatomite. Therefore, the initial step of MB degradation can be ascribed to the cleavage of the bonds of the C–S$^+$=C functional group in MB. The passage from C–S$^+$=C to C–S(=O)=C requires the conservation of the double bond conjugation, which induces the opening of the central aromatic ring containing both heteroatoms, S and N. The origin of H atoms necessary to C–H and N–H bond formation can be proposed from the proton reduction by photo-generated [21].

4. Conclusion

Impregnation of diatomite with TiO$_2$ yielded supported anatase catalyst for MB photodegradation. The diatomite supported anatase catalysts were more active than the nano-TiO$_2$, probably due to the adsorption of MB on diatomite
and the hydroxyl radicals existing on its surface, which accelerated the degradation of MB. At an initial concentration of 15 ppm MB can be completely degraded in 20 min. The results demonstrate that TiO$_2$/diatomite photocatalysis is a good candidate for color removal in wastewater treatment.

**Highlights**

(1) Diatomite has high specific surface and absorbability.

(2) The TiO$_2$/diatomite facilitates the recycling and reuse of TiO$_2$.

(3) TiO$_2$/diatomite adsorbs organic compounds with diatomite and degrades them with TiO$_2$.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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