Photocatalytic degradation of sulfamonomethoxine in aqueous phase using PW$_{12}$/TiO$_2$ composites under UV lights

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Abstract. A composite catalyst with phosphotungstic acid and TiO$_2$ has been synthesized by sol-gel method. The phase, structure, morphology and optical properties were explored by the X-ray diffraction (XRD), electron microscopy (SEM) and ultraviolet-visible diffuse reflectance (UV-Vis DRS). The effects of calcilation temperature, calcilation time and the doping ratio of phosphotungstic acid on the catalytic performance of the composite catalyst were investigated for sulfamonomethoxine (SMM) degradation. Results showed that the TiO$_2$ in the sample had an anatase type and had a large specific surface area and a better catalytic performance when compared with the pure TiO$_2$. When Recycling tests with calcination temperature of 500 degree centigrade, calcination time of 2h and PW$_{12}$/TiO$_2$ doping ratio of 0.35, the degradation of SMM in water phase was high by photo catalytic treatment of PW$_{12}$/TiO$_2$ composites under UV lights. With UV radiation for 30 min, the degradation efficiency of SMM can up to 90% and the synthesized catalyst had a high recovery.

1. Introduction

As a significant scientific discovery, antibiotics have been widely used in the diseases prevention and control of human, live stocks and aquatic animals, as well as in animal feed [1]. However, in recent years, the abuse of antibiotics has become a common phenomenon in recent years. Large amount of antibiotics enter into water bodies, with low doze exposure but persistent pollution, will cause terrible impacts on aquatic ecosystems in long term [2]. Therefore, developing treatment technologies for pharmaceuticals are urgently required. Sulfonamides (SAs) are widely used in antimicrobial spectrum and are cheap and easy to obtain, and therefore they become one of the most widely used antibiotic drugs, with high detection rates in surface water, drinking water and sewage [3,4].

Sulfamonomethoxine (SMM) is the most representative sulfa drug and has been detected in the effluent of aquaculture ponds, in sewage sludge from wastewater treatment plants, and in manure from livestock farming, or even in drinking water. Hence, it is important to develop efficient ways of SMM degradation in water bodies.

Photocatalytic oxidation process, using the strong reduction/oxidation electron-hole pairs which generated by semiconductor catalyst in light excitation, can effectively degrade organic pollutants. Therefore, it has broad application prospects in water treatment [3,4]. Researchers have conducted lots of studies on the Photocatalytic technology based on TiO$_2$ due to its low cost, strong stability and free secondary pollution [5-7]. However, narrow ranges of spectral response and low quantum efficiency have limited the practicability and industrialization of Photocatalytic technology. The development of novel photo-catalyst with high catalytic activity for organic pollutants degradation is a hot issue.
Report showed that phosphotungstic acid (H$_3$PO$_4$W$_{12}$xH$_2$O, abbreviated as PW$_{12}$) doped Titanium dioxide (TiO$_2$) for ninocomposite films fabrication could effectively degrade the methyl orange under ultraviolet (UV) irradiation [8]. Therefore, this paper took TiO$_2$ as matrix, and used PW$_{12}$ by doping modification for preparation composite catalyst (PW$_{12}$/TiO$_2$). The degradation efficiency of SMM by the composite catalyst with UV light was studied. The structure of composite catalyst and the impact of preparation conditions on its catalyst light properties were considered.

2. Materials and methods
SMM with a high purity more than 99% was commercial procurement. PW$_{12}$ and butyl titanate, absoluted ethyl alcohol, galcial acetic acid and triethanolamine were used for preparation of composite catalyst, and all of which were analytically pure. Ultra-pure water was made in our laboratory.

The composite catalyst was prepared by sol-gel method, which was used extensively among all the methods for doping TiO$_2$-based materials [9]. The preparation procedure of catalyst preparation was referred to Zhao et al [7]. In this paper, the calcination temperature (400-600 centi degree), calcination time (1to 4 hours) and the amount of doped phosphotungstic acid (the mass ratio of PW$_{12}$ and TiO$_2$ with the range of 0 to 0.55) were considered according to related references [7,9].

X-ray diffraction patterns of PW$_{12}$/TiO$_2$ were recorded on XRD-7000s ray diffractometer (Japan Shimadzu co. LTD). The shape and size of the catalyst were observed by VEGA 3 SBH high resolution scanning electron microscope (Czech TESCAN Company). Diffuse reflectance spectrums was measured by Cary 500 UV-DRS (USA Varian Company).

The degradation of SMM was happened in ultraviolet light catalysis device. The photocatalytic degradation reaction device was mainly composed of light source, catalyst, the origin fluid, quartz reactor. Around the reactor was dark, light source fixed in the centre of the reactor of quartz in the condenser pipe, the origin fluid placed in a quartz tube with a length of 30 cm long and a diameter of 2.5 cm. The light source was located in the same horizontal plane, with a distance of 9 cm. Aeration rubber hose ventilation is about 2.5 L/min. A certain amount of PW$_{12}$/TiO$_2$ photocatalyst and 50 mL of SMM solution with a concentration of 10mg/L were mixed in the reactor, aerated for 30 min and avoided light to ensure the adsorption equilibrium of the catalyst. And then, when the light source was opened and the time was recorded, the water samples were sampled at 5 min intervals. After the high speed centrifugation, the supernatant was removed by a 0.25 m filter membrane, the concentration of SMM was determined by high performance liquid chromatography (HPLC, PE Company), and the degradation rate was calculated.

Each degradation test was carried out in triplicate for averaged results.

3. Results and discussion
3.1. Characterizations of composite catalyst

![Figure 1. XRD patterns of different catalysts.](image-url)
3.1.1. XRD patterns of catalyst. XRD patterns of composite catalyst were shown, as seen in figure 1. Comparing to pure TiO$_2$, the peak of 20 values of 25.4, 37.8, 48.1, 53.9, 55.2 and 62.8 can be indexed as the anatase type diffractions of (101), (112), (200), (105), (211) and (204), respectively. The characteristic peak of PW$_{12}$ was not found in the spectrogram, possibly because the PW$_{12}$ had been evenly doped in TiO$_2$, and W had replaced the Ti into the skeleton of TiO$_2$. The diffraction peak of PW$_{12}$/TiO$_2$ became weak and peak width became wide, indicating that the PW$_{12}$ doping inhibited the crystallization of TiO$_2$.

3.1.2. SEM image analysis. SEM images of TiO$_2$ and PW$_{12}$/TiO$_2$ were shown in figure 2. Clearly, the addition of PW$_{12}$ in TiO$_2$ resulted in irregular microporous structure in the surface of catalyst, which was significantly increased the surface area and therefore enhanced the photo-catalytic activity.

![SEM images of different catalysts](image)

Figure 2. SEM images of different catalysts.

3.1.3. UV-visible diffuse reflection spectrum. Figure 3 showed the UV-visible diffuse reflection spectrum of TiO$_2$ and PW$_{12}$/TiO$_2$. By comparing its spectral curve, PW$_{12}$/TiO$_2$ had obvious absorption in the ultraviolet region of 200-400 nm. The absorption band had a significant red-shift. Energy gap of PW$_{12}$/TiO$_2$ was lower than that of TiO$_2$. The result was that after combined with PW$_{12}$, a new hybrid orbital was formed and the energy level became lower, and the electrons became easily transition.

![UV-Vis absorbance spectra and bandgap energy](image)

Figure 3. UV-Vis absorbance spectra and bandgap energy of different catalysts. (a) UV-Vis absorbance spectra and (b) band gap energy spectra.

3.2. Effect of catalyst preparation conditions on photocatalytic degradation of SMM
Catalyst preparation conditions greatly affected the photo-catalytic activity, and then affected the degradation of SMM. Therefore, calcinations temperature, time and the doping ratio of PW$_{12}$/TiO$_2$ were considered in our studies. The effects of the conditions on Photocatalytic degradation of SMM were shown in figure 4.

![Figure 4](image_url)

**Figure 4.** Effect of calcination temperature on photocatalytic degradation of SMM.

3.2.1. *Effect of calcination temperature on photocatalytic degradation of SMM.* Temperature was important parameters in catalyst preparation. It was seen that the PW$_{12}$/TiO$_2$ with heat treatment of 500 degree centigrade for 2 h had a well photo-catalytic activity that the SMM degradation was high. Temperature higher or lower than 500 degree centigrade, the SMM degradation decreased.

3.2.2. *Effect of calcination time on photocatalytic degradation of SMM.* Calcination time of 2 h for preparing PW$_{12}$/TiO$_2$ showed a high photocatalytic activity of catalyst that the SMM degradation was up to 90% with 30 minutes UV irradiation, as shown in figure 5. Short calcination time might cause the incomplete crystallization of TiO$_2$, and long time resulted in golden red stone type.

![Figure 5](image_url)

**Figure 5.** Effect of calcination time on photocatalytic degradation of SMM.

3.2.3. *Effect of doping ratio of PW$_{12}$ on photocatalytic degradation of SMM.* The doping of PW$_{12}$ had great influence on the photocatalytic activity of catalyst, as shown in figure 6. Results showed that when the mass ratio of PW$_{12}$ and TiO$_2$ was less than 0.35, the photocatalytic activity of SMM degradation increased with the increasing of PW$_{12}$ doping. When the ratio was larger than 0.35, the photo-catalytic activity of the composite catalyst decreased. It may be that the doping of PW$_{12}$
changed the surface acidity of TiO$_2$, and therefore improved the surface activity level. However, doping too much PW$_{12}$ might bring large amount of negative ion of PW$_{12}$O$_{40}^{3-}$, causing the decrease of sol-stability of TiO$_2$. The agglomeration of particles was intensified, and the effective surface area of TiO$_2$ reduced.

![Figure 6](image6.png)

**Figure 6.** Effect of mass ratio of PW$_{12}$ and TiO$_2$ on photocatalytic degradation of SMM.

3.3. *Stability of composite catalyst*

In order to study the stability of the composite catalyst, recycling tests of PW$_{12}$/TiO$_2$ with temperature of 500 degree centigrade, calcinations time of 2 h and the PW$_{12}$/TiO$_2$ doping ratio of 0.35 were conducted, as seen in figure 7. Four times of recycling tests were conducted. And the tests were in the same SMM degradation conditions. The results showed that after 4 times recycling, the degradation of SMM by PW$_{12}$/TiO$_2$ with UV lights was up to 90%. This result meant that the composite catalyst with UV lights had stable photocatalytic activity and good recycling performance, which was a promising catalyst for organic matters degradation in aqueous phase.

![Figure 7](image7.png)

**Figure 7.** Effect of using frequency on photocatalytic activities of PW$_{12}$/TiO$_2$.

4. **Conclusion**

A photocatalytic method was investigated for SMM degradation. Catalyst of TiO$_2$ doped by PW$_{12}$ greatly enhanced the photocatalytic activity and stability. Characterizations results showed that the composite catalyst had large specific surface and anatase types, which greatly enhanced the performance of SMM degradation. The SMM degradation was affected by the preparation conditions
of composite catalyst.

**Acknowledgments**

Financial supports from the National Science Foundation of China (Grants Nos. 51709224 and 21077037) are gratefully acknowledged.

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