

Preparation of mesoporous ammonium phosphotungstate/silica catalyst and study on the degradation performance of chlorothalonil

Wei Tan, Yifei Zhang, Tianli Wang, Lei Liu, Junxiu Ye, Min Yang and Hongbin Wang

ABSTRACT

Chlorothalonil is widely used to control fungal diseases and it is usually detected in the environment. Phototransformation is an important process to remove chlorothalonil from the aquatic environment. The mesoporous ammonium phosphotungstate/silica catalyst ($\text{NH}_4\text{PW}/\text{SiO}_2$) was synthesized from cetyl trimethyl ammonium bromide (CTAB) and tetraethoxysilane (TEOS) as raw materials by adding insoluble ammonium phosphotungstate into the alkaline alcohol–water system by the sol-gel method. The structure of $\text{NH}_4\text{PW}/\text{SiO}_2$ was characterized by X-ray diffractometry (XRD), Brunauer–Emmett–Teller (BET) and Fourier transform infrared spectroscopy (FT-IR). The photocatalytic activity of $\text{NH}_4\text{PW}/\text{SiO}_2$ was evaluated by using the organic pesticide chlorothalonil as a model reactant. The result indicated that when the dosage of $\text{NH}_4\text{PW}/\text{SiO}_2$ is 0.02 g, the illumination is 180 min, the concentration of chlorothalonil is 5 mg/L, pH = 5, the degradation effect is better, and the degradation rate reaches 83.23%. The results contributed to the understanding of chlorothalonil phototransformation and the potential of mesoporous SiO_2 to effectively enhance the photocatalytic activity of NH_4PW (64.16%) to reduce aquatic toxicity and pollution by chlorothalonil.

Key words | chlorothalonil, mesoporous ammonium phosphotungstate, photocatalyst, silicon dioxide

HIGHLIGHTS

- The prepared mesoporous material ammonium phosphotungstate/silica ($\text{NH}_4\text{PW}/\text{SiO}_2$) effectively improves the catalytic degradation activity of ammonium phosphotungstate photocatalyst.
- $\text{NH}_4\text{PW}/\text{SiO}_2$ was used for the degradation of organic pesticide chlorothalonil, and four factors affecting the degradation performance (different quality, different degradation time, different chlorothalonil concentration and different pH) were discussed separately.
- The mechanism of kinetics of photocatalytic degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$ was studied.

INTRODUCTION

Pesticide is an essential means of production for modern agricultural production. The use of a large number of pesticides not only guarantees agricultural production and income, but also causes a large number of environmental problems (Zinatloo-Ajabshir *et al.* 2020), such as the

Lipton tea pollution incident in 2012, the pesticide pollution accident in Guangzhou on the Pearl river (de Souza *et al.* 2017; Prabavathi *et al.* 2020), the pesticide fish-poisoning incident in Shien, Hubei, etc. Water pollution caused by pesticides has attracted widespread attention. Reducing or

Wei Tan[†]
Yifei Zhang[†]
Lei Liu
Junxiu Ye
Min Yang

Hongbin Wang (corresponding author)
School of Chemistry and Environment,
Yunnan Minzu University,
Kunming, Yunnan, 650500,
China
E-mail: wanghb2152@126.com

Tianli Wang
Kunming Chenggong District Environmental
Monitoring Station,
Kunming, Yunnan, 650500,
China

[†]These authors contributed equally to this work.

eliminating the hazards of pesticides and secondary pollution is also an important direction of environmental chemistry research at this stage. Chlorothalonil is a widely used substitutive benzene fungicide (Huang *et al.* 2019; Lv *et al.* 2020), not only used in agriculture to prevent and control diseases of vegetables, melons and fruits, peanuts, rice, wheat and other crops, but also used in industry for mildew-proof coatings and additives (Lu *et al.* 2005). Chlorothalonil is a low-toxicity fungicide. Its annual production in China exceeds 8,000 t (He *et al.* 2018), the solubility in water is 0.9 mg/L, and its half-life in water is 8–9 days. Under normal conditions, chlorothalonil powder acute transoral LD50 in both rats and rabbits was greater than 10,000 mg/kg, and rats with acute inhalation LD50 > 4.7 mg/L. However, some studies have shown that the harm of chlorothalonil to the environment should not be underestimated. For example, Tang Mingde and others found that chlorothalonil can induce cell mutation and sister chromatid exchange in mouse bone marrow lymphocytes (Tang & Yi 1985). Córdova Juárez *et al.* (2010) found that chlorothalonil can cause genetic mutations in aquatic organisms, amphibians and plant cells. Wang *et al.* (1986) found that chlorothalonil has sensitive effects on the human body, and skin contact can cause contact dermatitis. Mozzachio *et al.* (2008) explored the relationship between chlorothalonil and colon, lung, and prostate cancers (Meng *et al.* 2019). The United States Environmental Protection Agency (USEPA) has listed chlorothalonil as one of the possible inducements of human cancer, and it is a potential threat to environmental and food safety (Lawruk *et al.* 1995; He *et al.* 2018). It is imperative to eliminate the harm of residual chlorothalonil in the water environment to the environment and human body.

In the water environment, the degradation pathway of chlorothalonil is mainly biodegradation, hydrolysis and photochemical degradation (Zhang *et al.* 2017). Caux *et al.* (1996) studied the degradation of chlorothalonil in a simulated marine environment, and the results showed that the half-life of chlorothalonil degradation in seawater was 8–9 days; Li *et al.* (2004) studied the influence of several factors on the hydrolysis of chlorothalonil and the results showed pH has a significant effect on the hydrolysis of chlorothalonil. The hydrolysis half-life of chlorothalonil in distilled water is 117.46d, while the hydrolysis half-life of

chlorothalonil in groundwater and Chaohu Lake water is 58.24d and 56.8d, respectively. Although biodegradation is environmentally protective, it has a long degradation period. Hydrolysis is greatly affected by pH and the temperature of the water body. Photochemical degradation has the best effect, but its efficiency is greatly affected by photosensitizers (Zhang & Wang 2018). Therefore, choosing a suitable photocatalyst is the key to degrading chlorothalonil in a water body (Wang *et al.* 2015; Li *et al.* 2019), the compound being a kind of polynuclear inorganic polymer compound containing an oxygen bridge. It is composed of heteropoly anions, cations (including metal cations, protons and other organic cations) and crystal water or organic molecules (Zhao 2008). Its unique structure and spectral properties make it suitable for becoming an efficient photocatalyst (Chen *et al.* 2011; Bayal *et al.* 2017). With regard to the synthesis and application of heteropoly acid photocatalysts (Chen *et al.* 2014; Shaban *et al.* 2017), scholars at home and abroad have carried out relevant research in this field, such as Friesen *et al.* (1999), who showed that CsCl and $H_3PW_{12}O_{40}$ react to generate $Cs_3PW_{12}O_{40}$, and $Cs_3PW_{12}O_{40}$ can rapidly degrade *N*-methylpyrrolidone under 254 nm ultraviolet light exposure. However, traditional heteropoly acid photocatalysts have a strong water solubility, are easily soluble in water and oxygen-containing organic solvents, have low reuse efficiency and small specific surface area and are difficult to recycle and reuse. Therefore, the preparation of water-insoluble photodegradation catalysts for organic pesticides has great theoretical and practical significance (Li *et al.* 2004, 2014; Chang *et al.* 2017).

EXPERIMENTAL

Instruments and reagents

D/max-38 X-ray Diffractometer (incident light source is $CuK\alpha$ target, incident wavelength $\lambda = 0.154$ nm, voltage 40 kV, current 40 mA). Nicolet10 Fourier Infrared Spectrometer (resolution 4 cm^{-1} , wavenumber range 4,000–400 cm^{-1} , KBr tableting method), QUANTA 200 Electron Microscope, UV-2550 Spectrophotometer (with diffuse reflection measuring device – integrating sphere, measuring wavelength 200–900 nm, calcium sulfate as reference), XPA

Photochemical Reaction Instrument (light source is 100 W mercury lamp, Trace 1300 Gas Chromatograph (ECD detector, TR-5 column). Phosphotungstic acid, ammonium chloride and ethyl acetate are analytically pure. Florisil Solid Phase Extraction Column (500 mg/6 mL), chlorothalonil purity 98.2%, is provided by the National Pesticide Quality Supervision and Inspection Center.

Preparation of $\text{NH}_4\text{PW}/\text{SiO}_2$

Firstly, a certain amount of CTAB was dissolved in distilled water and stirred to be clarified in a constant temperature water bath at 40 °C. Then, anhydrous ethanol was added and stirred for 10 min. Secondly, the ammonia water was added drop by drop and stirred for 10 min. TEOS was added until the solution turned into opalescent turbidities ($n_{\text{ethanol}}: n_{\text{TEOS}}: n_{\text{CTAB}} = 60:2.5:1$). The stirring continued for 2 h. Finally, ammonium phosphotungstate prepared by reflux adsorption was added to the solution and stirred for 2 h. After washing the white sediment with distilled water until Cl-free, it was first dried at 105 °C, then dried overnight at 70 °C in vacuum. Finally, the $\text{NH}_4\text{PW}/\text{SiO}_2$ composite material was obtained by forging and burning at 500 °C in a Muffle furnace for 3 h.

Structural characterization of $\text{NH}_4\text{PW}/\text{SiO}_2$

The $\text{NH}_4\text{PW}/\text{SiO}_2$ was characterized by D/max-38 X-ray diffractometer (the incident light source was $\text{CuK}\alpha$ target, the incident wavelength was $\lambda = 0.154$ nm, the voltage was 40 kV, the current was 40 mA, the scanning rate was 0.095°/min, the measuring range was $2\theta = 0.5^\circ - 8^\circ$), NOVA 2000 specific surface tester (under 7 K condition, N_2 was used as adsorbent; degassing conditions: degassing stage, heating rate 10 °C/min, final temperature 90 °C, sample degassed at 363 K for 3 h before analysis), NICOLET IS10 Fourier infrared spectrometer (KBr tableting test, resolution 4 cm^{-1} , scanning range 4,000 cm^{-1} –400 cm^{-1}).

Photocatalytic activity analysis

The photocatalytic activity of $\text{NH}_4\text{PW}/\text{SiO}_2$ was carried out on an XPA-7 photochemical reactor, using a 100W mercury lamp as light source. Chlorothalonil was detected according

to the literature method (Wang et al. 2014). The retention time of chlorothalonil was 2.28 min and the detection limit was 0.0035 mg/L.

RESULTS AND DISCUSSION

Characterization of $\text{NH}_4\text{PW}/\text{SiO}_2$

BET analysis

The N_2 adsorption–desorption experiments were carried out on mesoporous SiO_2 and $\text{NH}_4\text{PW}/\text{SiO}_2$. The adsorption–desorption isotherms of SiO_2 and $\text{NH}_4\text{PW}/\text{SiO}_2$ were obtained as shown in Figure 1. As can be seen from the figure, there are obvious hysteresis loops caused by capillary condensation in the range of relative pressure of 0.25–1.0, belonging to the class IV Langmuir adsorption–desorption isotherm, and belonging to the isotherm peculiar to the adsorption of porous substances by a multi-molecular layer. This indicates that the prepared sample is a typical mesoporous material. The hysteresis loop shape on the desorption branch is between H_2 and H_3 , which also indicates the existence of mesopore structure in the catalyst (Chen et al. 2006; Cao et al. 2008). Table 1 shows the Brunauer–Emmett–Teller (BET) analysis of SiO_2 and $\text{NH}_4\text{PW}/\text{SiO}_2$. As shown in Table 1, the mesoporous $\text{NH}_4\text{PW}/\text{SiO}_2$ has a pore diameter of 2.93 nm, a specific surface area of 1,368.15 m^2/g , and a pore volume of 1 cm^3/g . Compared

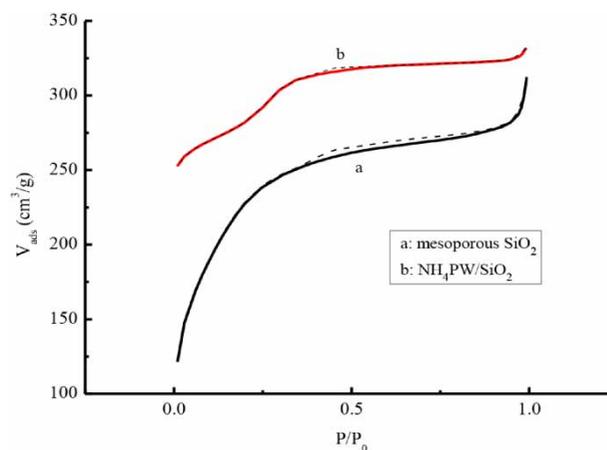


Figure 1 | Adsorption–desorption isotherm curve of mesoporous SiO_2 , $\text{NH}_4\text{PW}/\text{SiO}_2$.

Table 1 | BET analysis of SiO₂ and NH₄PW/SiO₂

Sample name	Specific surface area (m ² /g)	Aperture (nm)	Pore volume (cm ³ /g)
SiO ₂	840.32	2.12	0.44
NH ₄ PW/SiO ₂	1,368.15	2.93	1.00

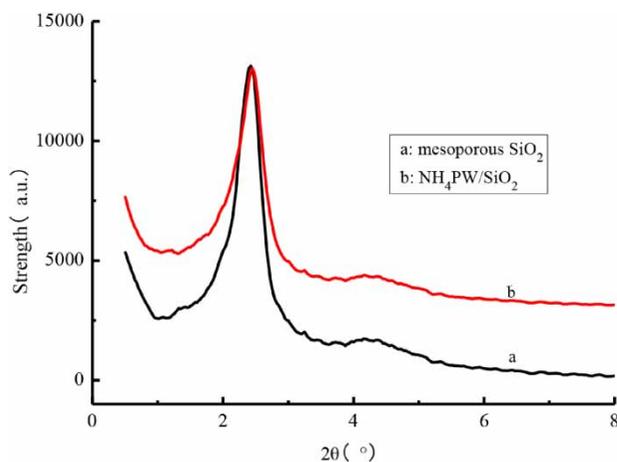
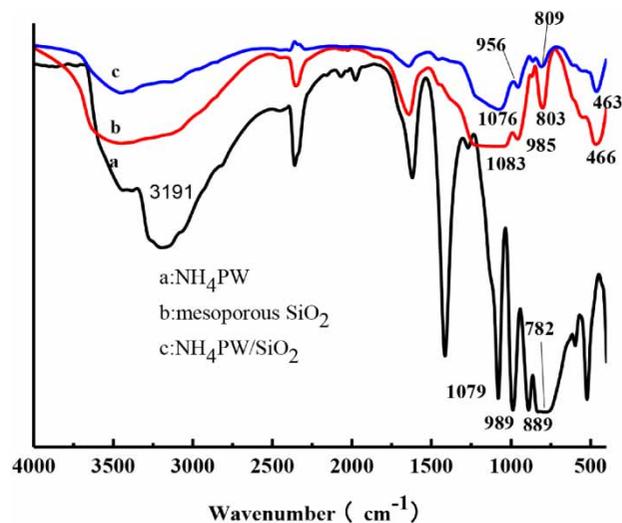
with mesoporous SiO₂, there is no law that the specific surface area decreases and the pore diameter becomes lower after loading. It indicates that the mesoporous structure of silica is not destroyed after the ammonium phosphotungstate loading.

XRD analysis

As shown in Figure 2, it can be seen that both have strong diffraction peaks in the range of $2\theta = 2^\circ - 3^\circ$, and there is still one diffraction peak in the range of $4^\circ - 6^\circ$, corresponding to the characteristic crystal face peaks (200) and (210). This shows that both mesoporous SiO₂ and mesoporous NH₄PW/SiO₂ have mesoporous structures, and also shows that the introduction of ammonium phosphotungstate does not destroy the mesoporous structure, but weakens the crystallinity of SiO₂.

IR analysis

IR characterization of NH₄PW/SiO₂ is shown in Figure 3. As can be seen from the figure, there is a strong O-H contraction vibration peak at 3,191 cm⁻¹, which may be

**Figure 2** | XRD spectrum of mesoporous SiO₂, NH₄PW/SiO₂.**Figure 3** | IR spectrum of NH₄PW, mesoporous SiO₂ and NH₄PW/SiO₂.

related to the presence of bound water inside the material. After SiO₂ is loaded with ammonium phosphotungstate, phosphotungstic acid is at 1,079 cm⁻¹ (P-O); 989 cm⁻¹ (W=O); 889 cm⁻¹ (W-Oc-W). The characteristic absorption peak of 782 cm⁻¹ (W-Oc-W) is still obvious. The characteristic peaks of SiO₂ are as follows: 466 cm⁻¹ is the stretching vibration absorption peak of the Si-O-Si bond. The bending vibration absorption peak of the Si-O-Si bond is 803 cm⁻¹ and 953 cm⁻¹ is the stretching vibration absorption peak of Si-O in silanol. The asymmetric vibration absorption peak of the Si-O-Si bond in siloxane is 1,062 cm⁻¹ (Yang 2010). At 1,076 cm⁻¹, there is also a broad peak formed by the overlapping 1,079 cm⁻¹ peak of phosphotungstic acid and 1,062 cm⁻¹ peak of SiO₂, which also shows that the heteropoly acid interacts with the carrier, but does not destroy the Keggin structure of phosphotungstate and the mesoporous structure of SiO₂.

Study on degradation performance

Influence of NH₄PW/SiO₂ dosage on degradation effect

The effect of different dosages of NH₄PW/SiO₂ on the degradation of chlorothalonil is shown in Figure 4. As can be seen from the figure, when the dosage of NH₄PW/SiO₂ is 0.02 g, the degradation effect is the best, the degradation rate reaches 82.55%, and the degradation rate of NH₄PW

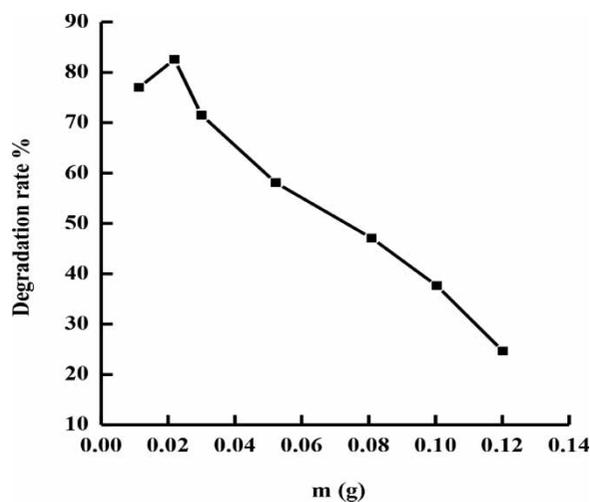


Figure 4 | Effect of different masses of $\text{NH}_4\text{PW}/\text{SiO}_2$ on the degradation of chlorothalonil.

(64.76%) is 17.79%. When the amount of $\text{NH}_4\text{PW}/\text{SiO}_2$ exceeds the optimum amount, the degradation rate decreases. This may be because the turbidity of the solution will affect the photocatalytic effect. When the amount of the catalyst is large, the turbidity of the suspension increases, the light transmittance decreases, and eventually the degradation effect is lowered.

Effect of different degradation time

In [Figure 5](#), the degradation effect becomes better with the increase of the degradation time within 0–120 min. When the degradation time is 120 min, $\text{NH}_4\text{PW}/\text{SiO}_2$ has the best degradation effect on chlorothalonil, with the degradation rate reaching 68.53%. It may be due to the recombination of some electrons and holes as time increases, the electron transfer rate decreases, and the degradation rate of chlorothalonil decreases.

Selection of initial concentration of chlorothalonil

[Figure 6](#) is a graph showing the effect of different chlorothalonil concentrations on the degradation rate of $\text{NH}_4\text{PW}/\text{SiO}_2$. From the graph, it can be seen that with the increase of chlorothalonil concentration, the degradation rate of $\text{NH}_4\text{PW}/\text{SiO}_2$ decreases. This is because the larger chlorothalonil concentration affects the transmittance of light, so that the absorption of light by the photocatalyst is

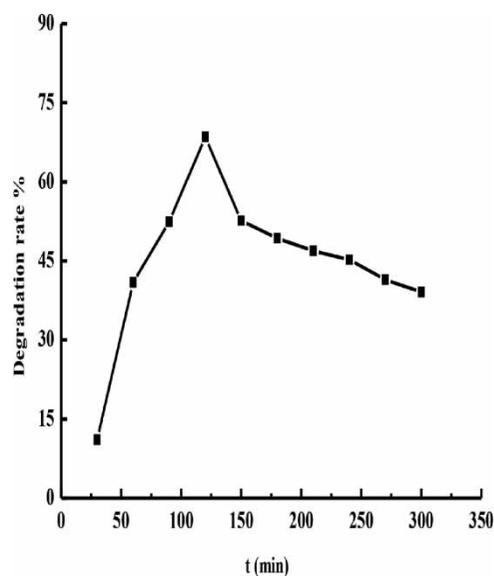


Figure 5 | Effect of degradation time on degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$.

lowered, and thus the degradation rate is lowered. In the following experiments, the concentration of chlorothalonil was selected at 5 mg/L.

Effect of pH

The effect of different pH on chlorothalonil degradation by $\text{NH}_4\text{PW}/\text{SiO}_2$ is shown in [Figure 7](#). From [Figure 7](#), $\text{NH}_4\text{PW}/\text{SiO}_2$ has the best degradation effect on

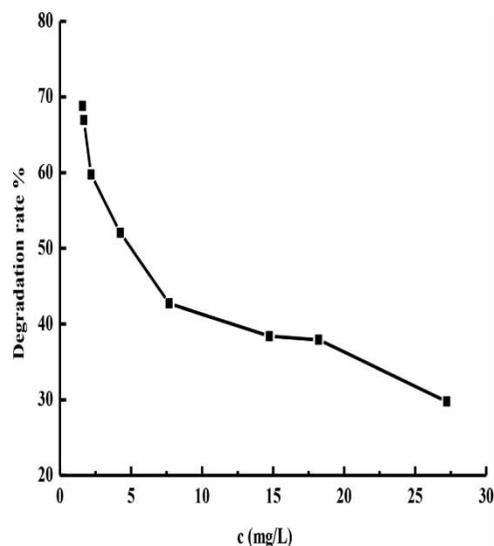


Figure 6 | Effect of different initial concentrations of chlorothalonil on the degradation rate of $\text{NH}_4\text{PW}/\text{SiO}_2$.

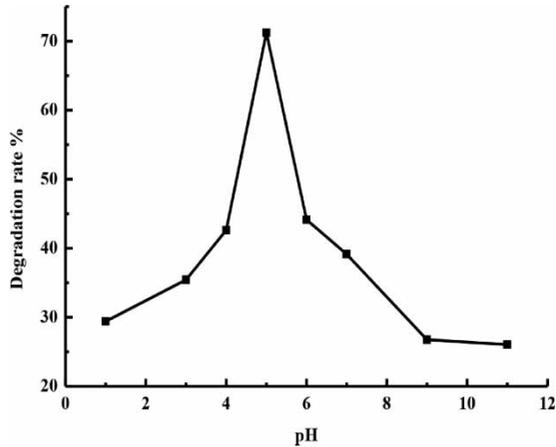


Figure 7 | Effect of different pH on the degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$.

chlorothalonil when the pH is about 5, with the degradation rate reaching 71.21% respectively. The degradation effect is not good in chlorothalonil solution with low or high pH, which may be due to different pH values affecting the structure of mesoporous silicon dioxide, the stability of $\text{NH}_4\text{PW}/\text{SiO}_2$ and the dispersibility in chlorothalonil solution, thus affecting their degradation effect.

Comparison of degradation effects before and after NH_4PW loading SiO_2

The degradation effects of NH_4PW and $\text{NH}_4\text{PW}/\text{SiO}_2$ are shown in Figure 8. As can be seen from Figure 8, the removal rate of chlorothalonil by SiO_2 loaded with NH_4PW is obviously increased compared with that before

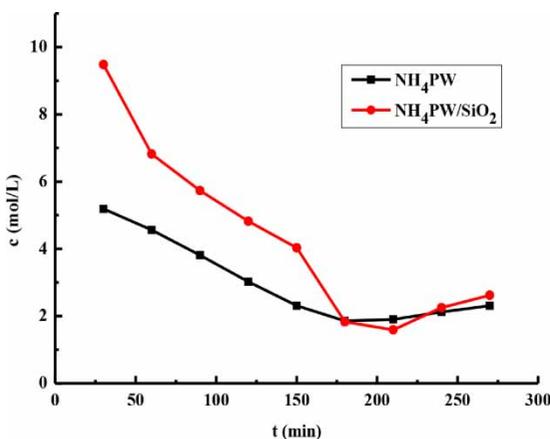


Figure 8 | Study on the degradation of chlorothalonil by NH_4PW and $\text{NH}_4\text{PW}/\text{SiO}_2$.

loading, with the removal rate increasing from 64.16% to 83.23%.

Comparison of chlorothalonil degradation methods

Table 2 shows the comparison of the degradation effect of chlorothalonil in different methods. It can be seen that the mesoporous material $\text{NH}_4\text{PW}/\text{SiO}_2$ has the best degradation effect on chlorothalonil, and the removal rate can reach 83.23%. By preparing the mesoporous material $\text{NH}_4\text{PW}/\text{SiO}_2$, the degradation activity of the photocatalyst is effectively improved. Therefore, the photocatalytic degradation of chlorothalonil by the mesoporous material $\text{NH}_4\text{PW}/\text{SiO}_2$ is of great significance.

Changes in COD_{Cr} value

The changes of COD_{Cr} before and after chlorothalonil degradation are shown in Table 3. From the data in Table 3, it can be seen that SiO_2 loaded with NH_4PW can more effectively remove chlorothalonil from aqueous solution, and the COD change value is 22.74, which is 10.76 higher than for NH_4PW (11.98).

Study on degradation kinetics

According to the photocatalytic degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$, the degradation process is fitted by

Table 2 | Comparison of different methods to degrade chlorothalonil

References	Degradation rate of chlorothalonil
Chang et al. (2017)	60.40%
Wang et al. (2015)	71.88%
Li et al. (2014)	73.62%
This article	83.23%

Table 3 | COD_{Cr} values of chlorothalonil degraded before and after SiO_2 loading NH_4PW

COD _{Cr} (mg/L)	NH_4PW	$\text{NH}_4\text{PW}/\text{SiO}_2$
Before degradation	30.27	55.00
After degradation	18.29	32.26
Change value	11.98	22.74

Table 4 | Parameters of quasi-first-order, second-order kinetic models and intraparticle diffusion model for the degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$

First-order kinetic model			Secondary dynamics model			Intraparticle diffusion model	
k_1 (min^{-1})	Q_e (mg/g)	R	k_2 (g/(kg·mg·min))	Q_e (mg/g)	R	k_3 (g/(kg·min ^{0.5}))	R
0.02556	9.213	0.9882	0.007619	8.937	0.9879	1.785	0.8594
Fitting equation	$\lg(Q_e - Q) = -0.0111t + 0.9644$		$t/Q = 0.1119t + 1.644$			$Q = 1.785t^{0.5} - 0.9963$	

pseudo-first-order and second-order kinetic models and intraparticle diffusion models. The fitting parameters are shown in Table 3. It can be seen from the data in Table 4 that the degradation of chlorothalonil by $\text{NH}_4\text{PW}/\text{SiO}_2$ is more in line with the first-order kinetic model. The correlation coefficient of the linear equation fitted by the first-order kinetic model was 0.9882, and the calculated Q_e value of $\text{NH}_4\text{PW}/\text{SiO}_2$ to chlorothalonil was 9.213 mg/g, which was close to the actual value (9.431 mg/g).

Analysis of degradation products

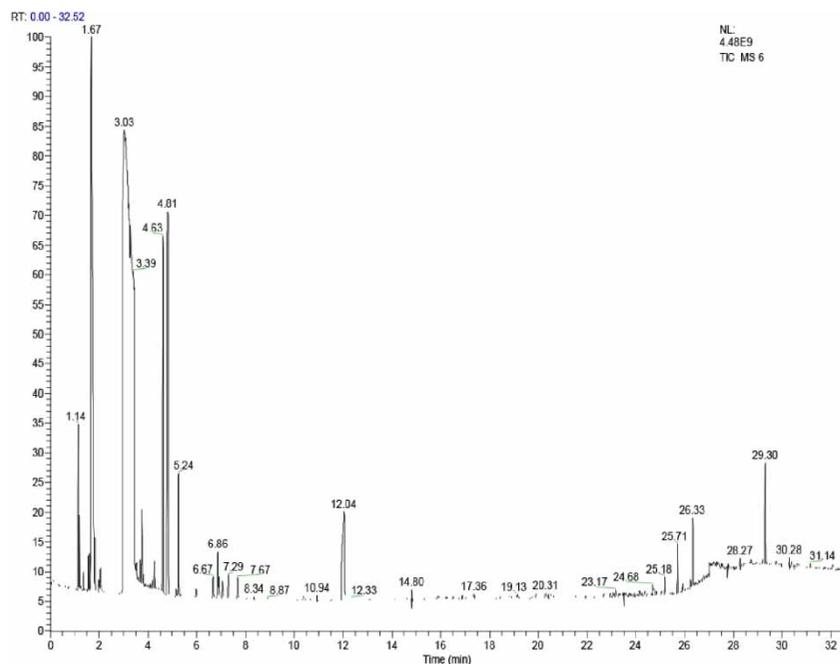
GC-MS analysis

The degraded water samples were extracted three times with 5 mL of chloroform, ethyl acetate, toluene and n-hexane,

respectively, and the organic phases were combined. After evaporation by a rotary evaporator, the samples were fixed in volume with 1 mL of toluene and analyzed by gas chromatography–mass spectrometry (GC-MS). The results are shown in Figure 9. The peak of the intermediate product appeared at $t = 7.68$ min and was identified as 1,2,3-trimethylbenzene by mass spectrometry.

IC analysis

The solution before and after degradation was centrifuged, and the supernatant was taken for IC analysis. As a result, the ion chromatogram before and after degradation was obtained as shown in Figure 10. It can be seen from the spectrum that the concentration of Cl^- and NO_3^- changed before and after NH_4PW loading SiO_2 , Cl^- increased from

**Figure 9** | GC-MS analysis of the product.

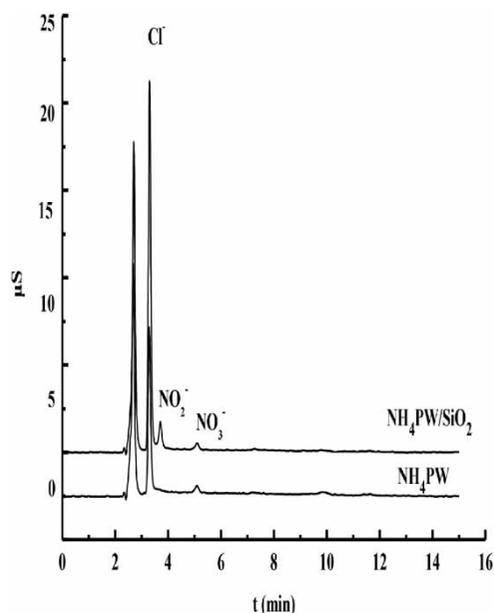


Figure 10 | Ion chromatogram of degradation products.

3.80 mg/L before loading to 17.16 mg/L, and NO_3^- from 0.5237 mg/L before loading. Increased to 0.6147 mg/L, with the formation of NO_2^- after the load, the concentration is 4.1221 mg/L. It can be seen that the photocatalytic degradation activity of NH_4PW is increased by the load, which is consistent with the conclusions drawn from the performance. The degradation activity of chlorothalonil after SiO_2 loading NH_4PW is improved, mainly due to the large specific area of SiO_2 and porous channels, which is beneficial to the adsorption of chlorothalonil to its surface, and finally improves the photocatalytic degradation performance.

Degradation mechanism analysis

According to the analysis of chlorothalonil degradation products, it is preliminarily concluded that $\text{NH}_4\text{PW}/\text{SiO}_2$ photocatalytic degradation of chlorothalonil is a surface photocatalytic reaction caused by $\cdot\text{OH}$ attack. When ultraviolet light is irradiated onto the surface of the photocatalyst, an electron-hole pair will be generated on the surface thereof, and OH^- and H_2O adsorbed on the surface of the catalyst by oxidation of the hole will form $\cdot\text{OH}$, thereby promoting oxidation of chlorothalonil. However, the increase of the chlorothalonil degradation activity of SiO_2 loaded with NH_4PW is due to the fact that mesoporous SiO_2 can adsorb

chlorothalonil to its surface by using its large specific area and pore channel characteristics, thus increasing the contact surface between $\cdot\text{OH}$ and chlorothalonil and finally improving the photocatalytic degradation performance.

CONCLUSIONS

Non-water-soluble ammonium phosphotungstate was added to an alkaline alcohol water system by using cetyltrimethylammonium bromide and ethyl orthosilicate as raw materials, and mesoporous phosphorus was synthesized by one-step synthesis by the sol-gel method. Ammonium tungstate/silica photocatalyst ($\text{NH}_4\text{PW}/\text{SiO}_2$): BET and XRD analysis show that the prepared $\text{NH}_4\text{PW}/\text{SiO}_2$ is a mesoporous material. IR characterization indicated that the SiO_2 supported NH_4PW retained the Keggin structure of phosphotungstic acid and preserved the mesoporous structure of SiO_2 . When the amount of $\text{NH}_4\text{PW}/\text{SiO}_2$ was 0.02 g, the light was 180 min, the concentration of chlorothalonil was 5 mg/L, and the $\text{pH} = 5$, the degradation rate of $\text{NH}_4\text{PW}/\text{SiO}_2$ to chlorothalonil reached 83.23%, and the degradation kinetics conformed to the first-order kinetic equation. Mesoporous SiO_2 effectively enhanced the photocatalytic activity of NH_4PW (64.16%). Therefore, $\text{NH}_4\text{PW}/\text{SiO}_2$ is an excellent photocatalyst, which not only makes up for the shortcomings of difficult recovery and low efficiency of phosphotungstate, but also can be used in water environment remediation and the chemical industry.

ACKNOWLEDGEMENTS

This work was funded by the Yunnan Provincial Department of Education YMU-DEAKIN International Functional Materials Related Laboratory (2017ZZX087), China University Students Innovation and Entrepreneurship Training Program (2018JWC-DC-30).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 29 June 2020; accepted in revised form 22 September 2020. Available online 12 October 2020