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Preparation, characterization of recyclable ammonia phosphotungstate and degradation of chlorothalonil

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ABSTRACT

In this study, insoluble ammonium phosphotungstate (NH_4PW), which is a photocatalyst, was used to degrade the herbicide chlorothalonil present in aqueous solutions. NH_4PW was prepared by both the immersion method (NH_4PW^1) and the reflux method (NH_4PW^2), and preparing conditions were optimized for degrading chlorothalonil present in aqueous solutions. NH_4PW grain sizes are relatively small and well dispersible, when compared with phosphotungstic acid by scanning electron microscope images, while still maintaining the original Keggin structure as can be seen from the results obtained by X-ray diffraction, UV-visible spectra and Fourier transforming infrared spectrum. The efficiency of NH_4PW prepared by both methods in degrading chlorothalonil was evaluated. The degradation efficiency of NH_4PW^1 and NH_4PW^2 can reach 73.64% and 55.21%, respectively, under the following conditions: 0.05 g of NH_4PW catalysts, 180 min of exposure to UV light and chlorothalonil concentration of 5 mg/L. Moreover, these catalysts showed excellent reproducibility and stability. Catalytic properties did not change significantly when they were calcinated for more than 4 h. Ion chromatographic analysis of the samples further indicated that dissociation occurred in the molecular skeleton of chlorothalonil during the degradation process. The results suggest that ammonium phosphotungstate can be used as a photocatalyst to accelerate the degradation of chlorothalonil present in aqueous solutions and the degradation mechanism of chlorothalonil is discussed in detail in the text.

Keywords: Ammonium phosphotungstate; Chlorothalonil; Degradation; Immersion method; Photocatalysts; Reflux method

1. Introduction

Chlorothalonil has been used widely as a broad-spectrum fungicide and regarded as an effective remedy to control plant diseases in China due to its stability. The main intermediate during its degradation is chlorothalonil-4-hydroxy, which is more toxic than chlorothalonil and does not degrade in the environment easily. Furthermore, the intermediate has potential to leach slowly into soil, groundwater or surface water and cause harm to the ecology of the soil environment [1,2]. Based on the toxicity analysis, chlorothalonil is very toxic to fish and amphibians and the scientific research has shown that chlorothalonil has strong mutagenic effect [3,4].

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At present, chlorothalonil is degraded either microbially or chemically using ozone and photochemicals [5,6]. However, the rate of microbial degradation of chlorothalonil is low and ozone does not degrade it fully. Thus, photochemicals are the best candidates to degrade chlorothalonil by using sunlight and thereby reducing the costs involved in processing. Further, photocatalysts are safe, non-toxic, highly stable and cheap. Due to those factors, synthesis of photocatalysts to degrade various industrial pollutants has become important [7]. Additionally, over the past 20 years, photocatalytic degradation technique has played an important role in the removal of pesticide residues. Strong oxidizing hydroxyl radicals are formed due to photo-induced electron and hole pairs on the surface of photocatalysts convert pesticides completely into H_2O, CO_2, PO_4^{3-} or less toxic smaller organic molecules [8].

The heteropoly compounds with [9] broad absorption band ranging from 200 to 400 nm are highly efficient photocatalysts for the degradation of pollutants due to the ease of operation [10,11]. Phosphotungstic acid (HPW) of Keggin structure, one of the heteropoly compounds, has attracted a lot of attention due to its catalytic properties with different counter ions [12]. But the traditional phosphotungstate suffers from non-reusability ascribed to its high solubility in water. Hence it is necessary to develop novel phosphotungstate which is insoluble in water.

However, the new kinds of water insoluble phosphotungstate catalysts should also possess high catalytic efficiency and overcome the corrosion caused by acid catalytic reaction. More importantly, it still should maintain high catalytic activity during the reuse.

In this study, HPW and ammonium chloride were used as raw materials to produce insoluble ammonium phosphotungstate photocatalysts using the immersion method (NH_4PW^1) and the reflux method (NH_4PW^2). The structure of photocatalysts was characterized and analyzed. The optimal preparation conditions of NH_4PW^1 and NH_4PW^2 for the photocatalytic degradation of the chlorothalonil were investigated. The reuse effect of catalyst was also investigated. The photocatalytic degradation performance and stability of NH_4PW^1 and NH_4PW^2 were assessed while degrading chlorothalonil. In addition, the degradation mechanism of chlorothalonil was also discussed.

2. Experimental setup

2.1. Preparation of photocatalysts

Impregnation method [13,14]: A series of NH_4PW^1 samples were prepared at different experimental conditions. In a typical procedure, certain amounts of HPW and ammonium chloride were dissolved separately in deionized water to prepare aqueous solutions. Then, the excessive ammonium chloride aqueous solution was slowly dropped into HPW aqueous solution at a rate of 1 mL/min, and stirred rapidly until a white precipitation was generated. Stirring continued for 10 h to complete the precipitation. Then the precipitate was centrifuged and washed repeatedly with deionized water until the Cl^- was not detected in the filtrate; the presence of Cl^- was detected by titrating the filtrate with $AgNO_3$ solution. After standing in the freezing dryer for overnight, the precipitate named NH_4PW^1 was calcined under a certain temperature in a muffle furnace for a specific period of time. In this study, different concentrations of HPW and NH_4Cl were used to obtain NH_4PW at different calcination temperatures and roasting times.

Reflux method [15]: Certain amounts of HPW and ammonium chloride solution were mixed in a round bottom flask, and subsequently the whole solution was stirred continuously for 10 h at 80°C. The precipitate was centrifuged and washed repeatedly with deionized water until Cl^- in the filtrate was not detected. At last, the sample (NH_4PW^2) was obtained by firing under a certain temperature and roasting time in muffle furnace.

In order to investigate the effect of molar ratios of ammonium chloride to phosphotungstic on the performance of the photocatalysts, NH_4PW^1 and NH_4PW^2 were prepared at different molar ratios ranging from 1.5:1 to 3.0:1 ($n\mathrm{NH_4}$:$n\mathrm{HPW}$), and roasted under different calcination temperatures (200°C, 300°C, 400°C and 600°C). Under the best molar ratio and roasting temperature (based on the maximum degradation of chlorothalonil by the photocatalysts), the effects of different roasting time (2, 3, 4 and 6 h) of NH_4PW^1 and NH_4PW^2 in the degradation of chlorothalonil were investigated. All the raw materials, including HPW, ammonium chloride and chlorothalonil, were of analytical grade.

2.2. Characterization of photocatalysts

The phase structure, morphology and elemental composition of the as-prepared ammonium phosphotungstate were analyzed by scanning electron microscope (SEM QUANTA200), X-ray diffraction (XRD, RIGAKU) with CuK radiation Kα at 40 kV, and 40 mA over the 2θ range of 5°–70° and IR (NICOLET IS10) for KBr tabletting method, respectively. Impurities were detected by using Shimadzu UV-2550 spectrophotometer (attach diffuse reflection determinator-integrating sphere), using calcium sulfate as reference, and the wavelength of determination was 200–900 nm.

2.3. Photocatalytic degradation experiments

A certain concentration of chlorothalonil solution was divided into two portions: one with a certain amount of photocatalyst and another without photocatalyst. Both samples were put into a photocatalytic apparatus and kept for 4 h under 100 W ultraviolet radiation and were taken out and centrifuged. The chlorothalonil pesticide residue in centrifuged liquid was analysed according to the determination of chlorothalonil pesticide residues by SPE-GC [16]. The percentage degradation of chlorothalonil (D) is used to evaluate the degradation efficiency of the photocatalysts. The percentage degradation of chlorothalonil (D) was computed using the following formula:

$$D = \frac{c_0 - c_t}{c_0} \times 100\% \tag{1}$$

where c_0 (mg/L) and c_t (mg/L) are the concentrations of chlorothalonil in the solution before and after photodegradation, respectively.

2.4. Degradation mechanism

Degradation products were analyzed by using ion chromatography (IC) to explore the mechanism of the degradation of chlorothalonil [17,18]. IC analysis of the test condition was as below: IonPac AS11 (250 mm × 4.0 mm) ion exchange column; IonPac AG11 (50 mm × 4.0 mm) guard column; detector (DS6); suppressor (ASRS-300), current limiter: 13 mA; mobile phase: 7.5 mmol/L NaOH, flow velocity: 0.7 mL/min; injection volume: 25 μL; column temperature: 30 C; following standard curve equations were used to calculate the concentration (Y) of Cl^- and NO_3^- (for Cl^-: $Y = 0.0103C + 0.1393$, $R = 0.9990$; for NO_3^-: $Y = 0.1213C - 0.0101$, $R = 0.9998$; where C is the concentration of Cl^- or NO_3^-).

3. Results and discussion

3.1. SEM analysis

The SEM images of HPW, NH_4PW^1 and NH_4PW^2 are shown in Fig. 1. It is found that the grain size of HPW is larger, irregular shape and lumpy. NH_4PW^1 and NH_4PW^2 grain sizes are relatively small. And they have good dispersibility. NH_4PW^1 grains appear much smaller compared with that of NH_4PW^2. Photocatalytic activity is affected by the size of the particles and the degree of dispersion [19]. The formation of large surface area will lead to more active points on the surface of photocatalyst to be exposed to the pollutants to be degraded.

3.2. XRD analysis

Fig. 2(A) shows that NH_4PW^1 and NH_4PW^2 have some diffraction peaks, and each peak is sharp, which shows the as-prepared samples have good crystallinity [20]. The diffraction peaks of NH_4PW^1 and NH_4PW^2 are in good agreement with standard card (JCPDS NO.50-0305). We can see the characteristic peaks of NH_4PW^1 and NH_4PW^2 at $2\theta = 10.7°$, 11.5°, 26.4° and 36.02°, which belong to 110, 200, 222 and 110 crystal plane diffraction characteristic peaks of ammonium phosphotungstate, and that confirms the formation of ammonium phosphotungstate. HPW, NH_4PW^1 and NH_4PW^2 in $2\theta = 5°–70°$ have strong diffraction peak, and are similar among them compared with the characteristics of diffraction peaks position. The structure of the synthesised photocatalysts did not change from the original HPW after the association of ammonium ions with the anions of HPW, still keeping the original Keggin structure of HPW [21].

3.3. Solid UV-visible diffuse reflection spectra analysis

Fig. 2(B) shows that NH_4PW^1 and NH_4PW^2 have strong absorption band from 200 to 400 nm. The absorption of HPW at 394 nm had moved to 381 nm for NH_4PW^1 and 379 nm for NH_4PW^2. This blue shift will cause the energy gap of these materials to be widened, the potential of conduction band will be more negative and the potential of the valence band will be more anodic. This indicates that these materials can have stronger capability in the redox properties, thereby possess better photocatalytic activity [22].

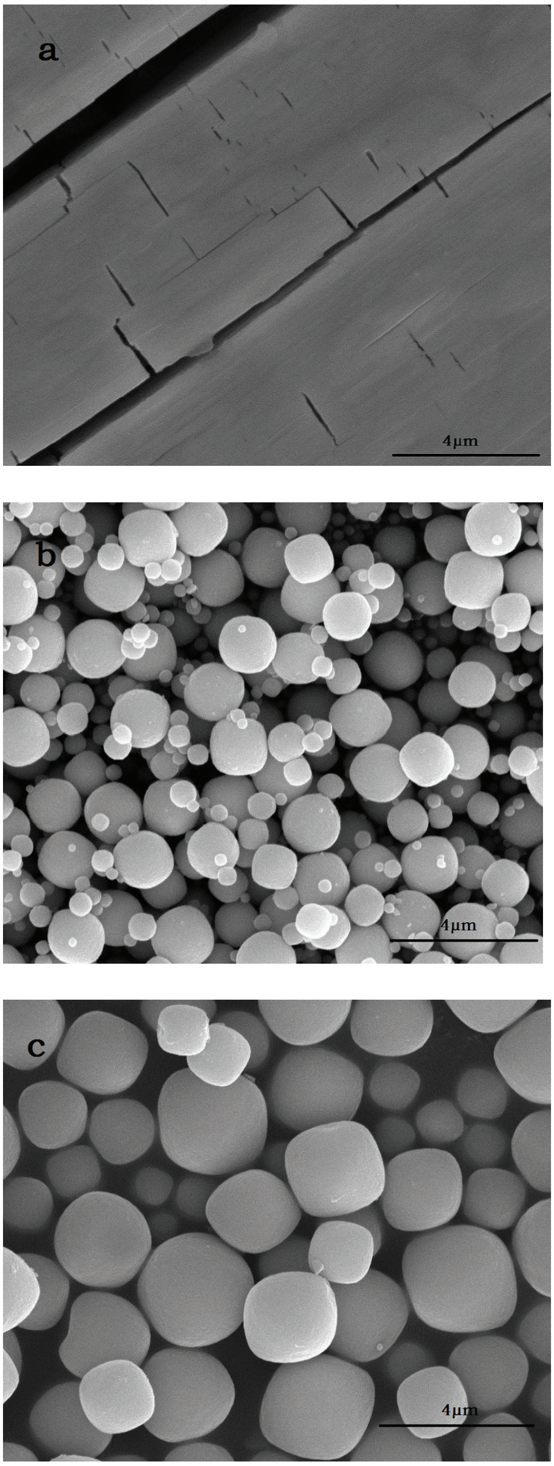

Fig. 1. SEM images of (a) HPW, (b) NH_4PW^1, (c) NH_4PW^2.

3.4. FT-IR analysis

Fourier transforming infrared spectrum (FT-IR) was used to verify the structure of HPW, NH_4PW^1 and NH_4PW^2. It can be seen from Fig. 2(C) that the vibration wave peak less than 1,300 cm^{-1} is the characteristic vibration peak of the anion frame of Keggin. Many absorption peaks of NH_4PW^1 and NH_4PW^2 such as PO_a, $W–O_c$, $W–O_b$ and $W=O_t$ stretching, W=O and

P=O oxygen-bridged vibration peak had no obvious change compared with HPW at 1,400–500 cm^{-1} range. This indicates that the ammonium ions did not enter the HPW anion, consequently did not affect the internal structure of phosphotungstic acid anions. So NH_4PW^1 and NH_4PW^2 can keep the original Keggin structure. Comparing the spectrums of HPW, NH_4PW^1 and NH_4PW^2, the peaks at 1,414 and 3,100 cm^{-1}of NH_4PW^1 and NH_4PW^2 belong to the N–H bending vibration peak and the N–H stretching vibration peak, respectively. This indicates that the HPW has been recombined with NH_4^+ and NH_4PW^1 and NH_4PW^2 had been successfully synthesized [23]. This is consistent with the results obtained from XRD analysis.

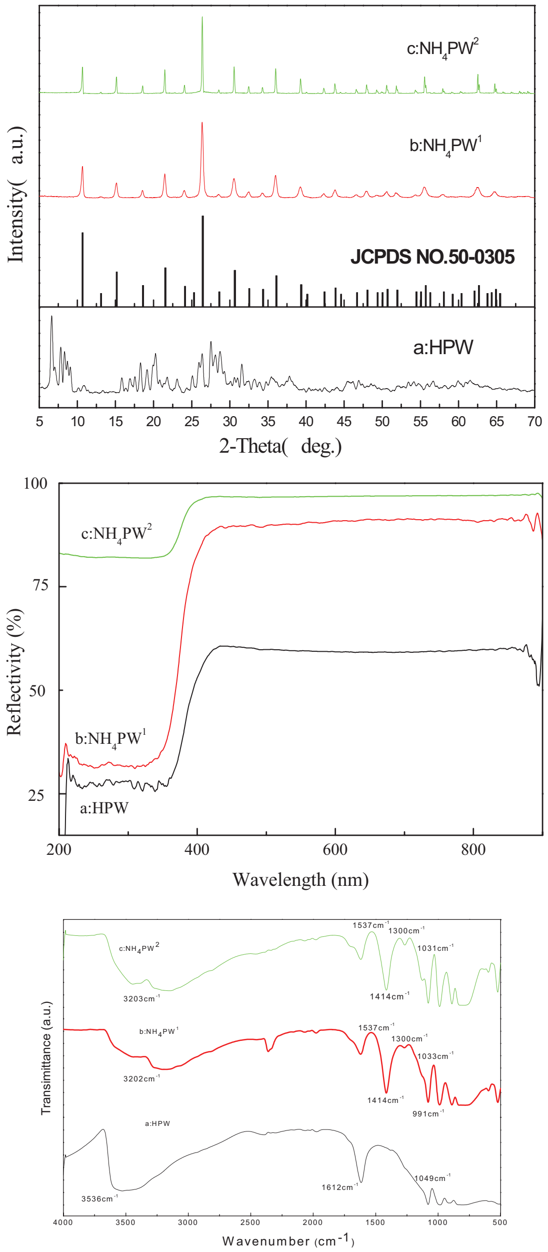

Fig. 2. (A) XRD patterns of modified (a) HPW, (b) NH_4PW^1, (c) NH_4PW^2; (B) UV-visible spectra of modified (a) HPW, (b) NH_4PW^1, (c) NH_4PW^2; (C) FT-IR spectra of modified (a) HPW, (b) NH_4PW^1, (c) NH_4PW^2.

3.5. Optimizing the synthesizing conditions of the photocatalysts

It is necessary to optimize the synthesizing conditions of NH_4PW^1 and NH_4PW^2 in order to get higher productivity and optical property [24,25]. For example, factors such as the molar ratio of ammonium chloride and phosphotungstic acid (nNH_4:nHPW), calcination temperature and calcination time should be optimised. As shown in Figs. 3 and 4(B), the degradation effect of NH_4PW^1 at the molar ratio of 2.0:1 was best (Fig. 3), and the degradation could reach 43.8%. It also shows that the degradation effect of NH_4PW^2 at the molar ratio of 2.5:1 was best, and the degradation rate could reach 51.1%. Further increase in molar ratio decreased the percentage of degradation. As shown in Fig. 4(A), when calcination temperature is 400°C, NH_4PW^1 and NH_4PW^2 have the best degradation efficiency of chlorothalonil, and the degradation efficiencies are 52.2% and 61.2%, respectively. Solid material has not been activated completely at lower temperatures and higher temperatures may have destroyed the structure of HPW or made ammonium HPW to decompose. Fig. 4(B) shows that the calcination time had no obvious effect to the catalytic activity of solid catalyst. In order to save time and energy, we selected 2 and 3 h as the calcination time of NH_4PW^1 and NH_4PW^2, respectively, at 400°C for subsequent experiments.

3.6. Photocatalytic activities

3.6.1. The influence of photocatalyst dosage

Fig. 5(A) shows that the degradation effect is the best when the dosage of NH_4PW^1 is 0.05 g, and the degradation of chlorothalonil can reach 64.8%. While the dosage of NH_4PW^2 is 0.02 g when the degradation effect was at its best and the degradation rate can reach 69.3%. But when more than the desired dosage is applied, the degradation efficiency will decline. Because too much catalyst will increase the surface

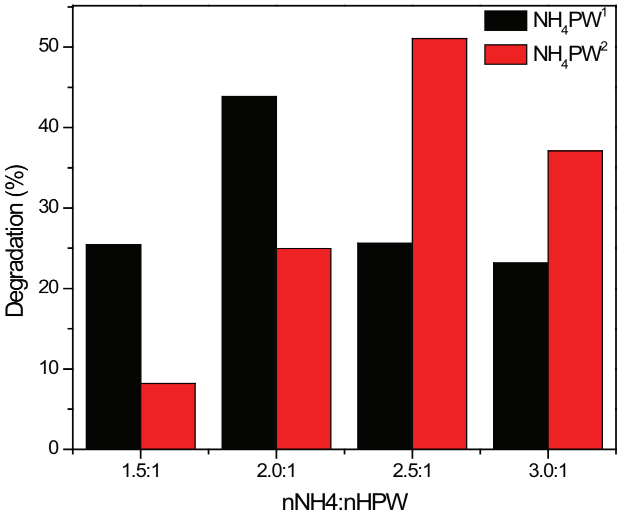

Fig. 3. Effect of molar ratio of the raw materials (nNH_4:nHPW) on the degradation of chlorothalonil (calcination temperature = 400°C; calcination time = 3 h; concentration of chlorothalonil before degradation = 5 mg/L).

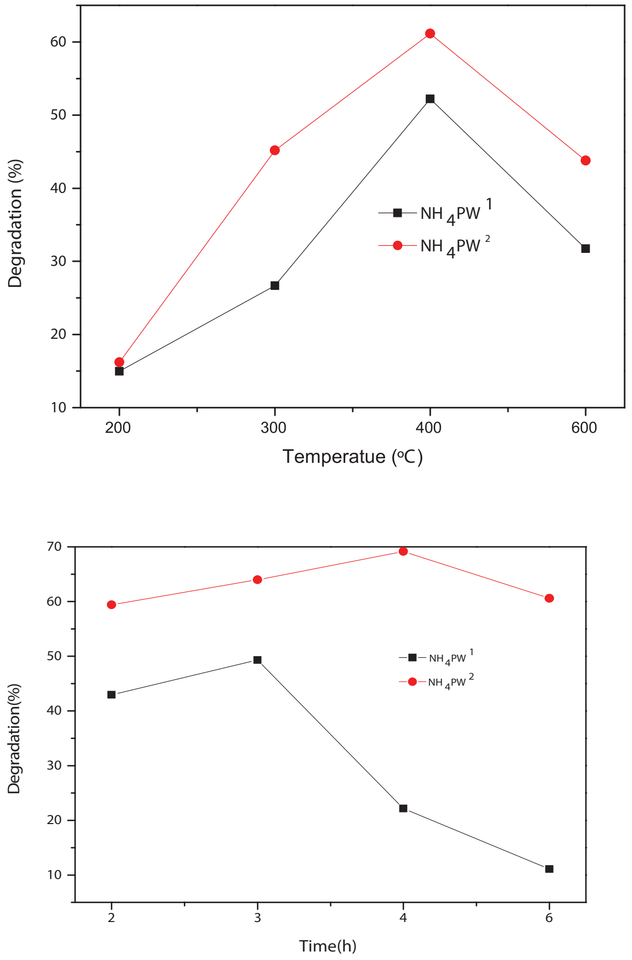

Fig. 4. (A) Effect of calcination temperature on the degradation of chlorothalonil (molar ratio of NH_4:HPW = 2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination time = 3 h; concentration of chlorothalonil before degradation = 5 mg/L). (B) Effect of calcination time on the degradation of chlorothalonil (molar ratio of NH_4:HPW =2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination temperature = 400°C; concentration of chlorothalonil before degradation = 5 mg/L).

acid which will lead to intermediates (by-product) [26] and the intermediates may cover catalytic active center on the surface of the catalyst. This will affect the degradation reaction and eventually lead to lower efficiency of degradation [27,28]. These results were reproducible.

3.6.2. The influence of degradation time

From Fig. 5(B) it can be seen that the degradation efficiency increased when the degradation time was increased until 180 min. When the degradation time was 180 min, the degradation efficiencies of NH_4PW^1 and NH_4PW^2 were 40.7% and 64.1%, respectively. When the degradation time was increased more than 180 min, the photodegradation efficiency decreased. This indicates the utilization rate of light no longer increases and the electron and hole will be composited with the increase in time. So the electron transfer rate is reduced and the degradation efficiency is reduced.

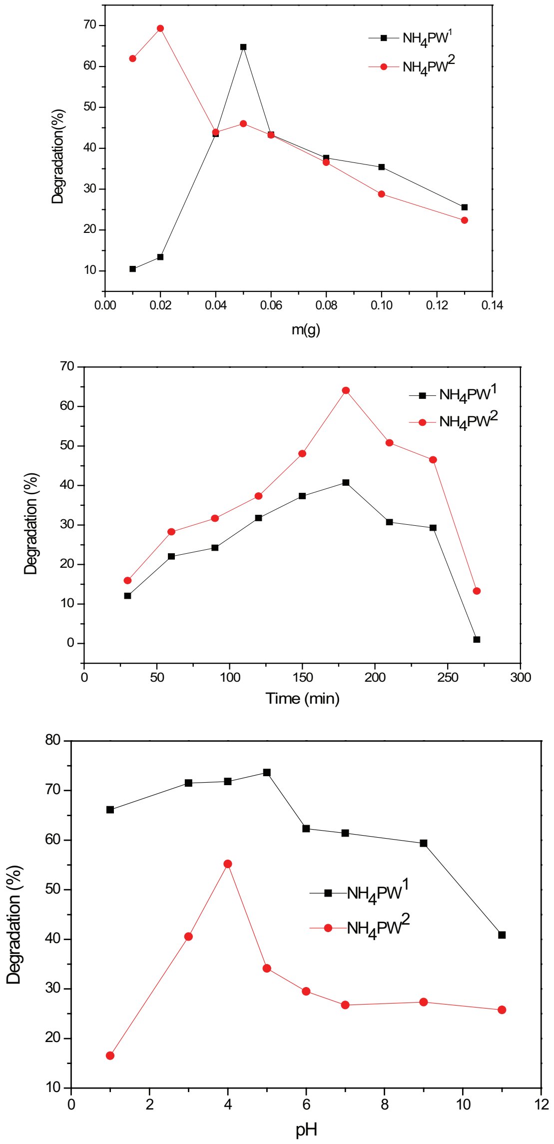

Fig. 5. (A) The influence of ammonium phosphotungstate dosage on the degradation of chlorothalonil (molar ratio of NH_4:HPW = 2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination temperature = 400°C; calcination time = 2 h (NH_4PW^1), 3 h (NH_4PW^2); concentration of chlorothalonil before degradation = 5 mg/L). (B) The influence of different degradation time on the degradation of chlorothalonil (molar ratio of NH_4:HPW = 2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination temperature = 400°C; ammonium phosphotungstate = 0.05 g (NH_4PW^1), 0.02 g (NH_4PW^2); concentration of chlorothalonil before degradation = 5 mg/L). (C) Influence of pH on the degradation of chlorothalonil (molar ratio of NH_4:HPW = 2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination temperature = 400°C; ammonium phosphotungstate = 0.05 g (NH_4PW^1), 0.02 g (NH_4PW^2); degradation time = 180 min; concentration of chlorothalonil before degradation = 5 mg/L).

3.6.3. The influence of pH

As can be seen from Fig. 5(C), when the pH value was 4 and the concentration of chlorothalonil was 5 mg/L, the degradation rate reached 73.6% for NH_4PW^1. When the pH value was 3 and the concentration of chlorothalonil was 5 mg/L, the degradation of chlorothalonil was the highest and reached 55.2% for NH_4PW^2. Either too low or too high pH can affect the stability of NH_4PW^1 and NH_4PW^2, which will impact photocatalytic performance. The destruction of solid structure and the influence on the dispersion of the chlorothalonil solution will affect the degradation [29]. The study further demonstrates that specific surface and the activity of photocatalysts can be increased by decreasing the size of the photocatalytic particles.

3.6.4. Effect of catalyst recycling

As can be seen from Fig. 6, from the first to the fourth cycles, the degradation percentages of chlorothalonil by NH_4PW^1 were 59.7%, 53.8%, 51.7% and 53.8%, respectively, and that of NH_4PW^2 were 44.1%, 40.9%, 36.6% and 40.9%, respectively. The reduction in the efficiency of degradation found to decrease only about 10% after four cycles of reuse of the catalysts synthesized in this study. The traditional HPW photocatalyst has some disadvantages such as higher solubility in water and oxygen-containing organic solvents, low removal efficiency during reuse, smaller specific surface area and difficult to be recycled, which limit the scope of heteropolyacid. But when HPW is combined with the larger radius of NH_4^+ to prepare heteropolyacid that is insoluble in water, not only the corresponding specific surface area was increased to make the product easy to separate but also the repeatability and recyclability in the applications were also improved. Thus, NH_4PW^1 and NH_4PW^2 have good stability and can be reused for several times.

3.7. Study on the mechanism of degradation

The chlorothalonil water samples treated by NH_4PW^1 and NH_4PW^2 were analysed by IC after separating the catalysts by centrifugation. According to Fig. 7, the concentration of Cl^- changed from 0.3 mg/L in the initial chlorothalonil aqueous samples to 3.80 mg/L (when treated with NH_4PW^1) and 7.03 mg/L (when treated with NH_4PW^2); similarly, the concentration of NO_3^- changed from 0.33 to 0.55 mg/L and 0.52 mg/L, respectively. This indicates that NH_4PW^2 is stronger than NH_4PW^1 in converting chlorothalonil to small organic materials and eventually to inorganic ions, such as Cl^-, NO_3^-, CO_2, H_2O and so on, the degradation pathway of chlorothalonil during photocatalysis using NH_4PW^1 and NH_4PW^2 may be as shown in Fig. 8.

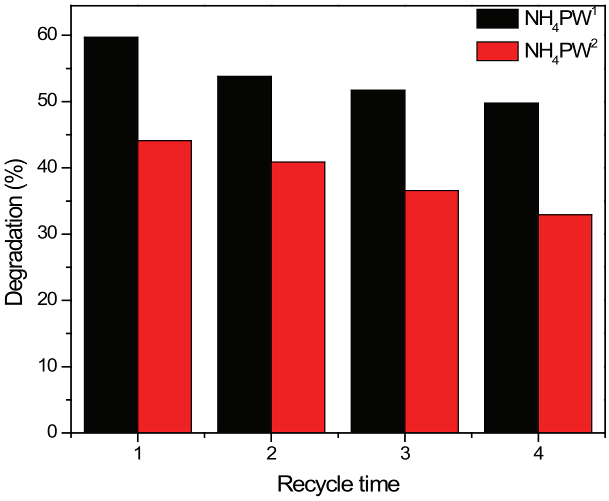

Fig. 6. Effectiveness of the synthesized catalysts on the degradation of chlorothalonil when recycling (molar ratio of NH_4:HPW = 2.0:1 (NH_4PW^1), 2.5:1 (NH_4PW^2); calcination temperature = 400°C; ammonium phosphotungstate = 0.05 g (NH_4PW^1), 0.02 g (NH_4PW^2); degradation time = 180 min; pH = 4 (NH_4PW^1), 3 (NH_4PW^2); concentration of chlorothalonil before degradation = 5 mg/L).

4. Conclusion

In this study, the characterizations of water insoluble photocatalysts NH_4PW^1 and NH_4PW^2 show that ammonium phosphotungstate can be generated with Keggin structure. Molar ratio (nNH$_4$:nHPW) of 2.0:1, calcination time 2 h and calcination temperature 400°C were selected to prepare NH_4PW^1. Molar ratio (nNH$_4$:nHPW) of 2.5:1, calcination time 3 h and calcination temperature 400°C were selected to prepare NH_4PW^2. Degradation efficiency is high when the NH_4PW^1 dosage was 0.05 g, exposure to light for 180 min and the pH value is buffered at 4 when degrading 5 mg/L of chlorothalonil. For NH_4PW^2 the best operating conditions were: dosage = 0.02 g, illumination time = 180 min, pH = 3 (buffered at) when degrading 5 mg/L of chlorothalonil concentration. The experimental data indicated that NH_4PW^1 and NH_4PW^2 have similar properties, but the catalytic performance of NH_4PW^1 is better than that of NH_4PW^2. The best degradation efficiency did not reach 75%, which shows that there is room for improvement in the performance of NH_4PW^1 and NH_4PW^2

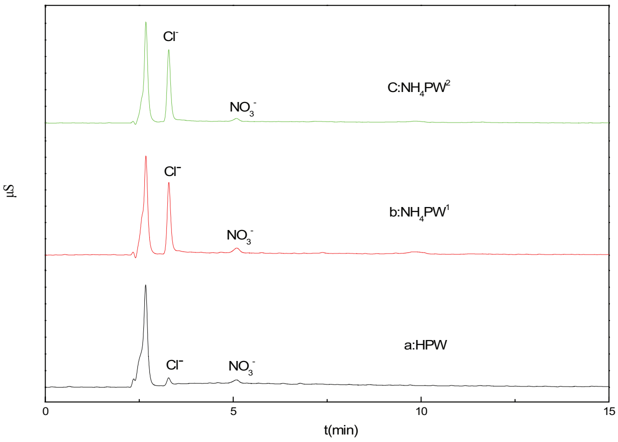

Fig. 7. IC patterns of modified (a) HPW, (b) NH_4PW^1, (c) NH_4PW^2.

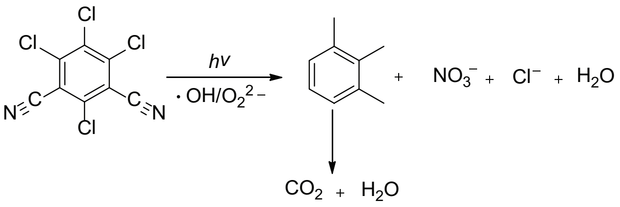

Fig. 8. The degradation pathway of chlorothalonil during photocatalysis using NH_4PW^1 and NH_4PW^2.

as catalysts. NH_4PW^1 and NH_4PW^2 have good recyclability and stability. The IC analysis indicates that chlorothalonil can be degraded to small organic materials which eventually will be converted to inorganic ions, CO_2 and H_2O. Therefore, NH_4PW^1 and NH_4PW^2 can be used to degrade chlorothalonil, since they can be recycled so as to reduce the production cost and become economically sound photocatalysts.

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