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**Study on Defluorination of aqueous perfluorooctane  
photocatalyzed by  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$**

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**Abstract**

A Photocatalytic system combined of low-pressure mercury lamp and heteropoly acid  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  was used for defluorination of aqueous Perfluorooctane sulfonate (PFOS). The effects and mechanism of reaction time,  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  concentration and pH on defluorination were investigated. In addition, the effects and mechanism of improved methods of potential, such as  $\text{H}_2\text{O}_2$  and low-frequency ultrasound, were also studied. The results show that photocatalytic system had weak effect on the defluorination of PFOS, while the PFOS could be oxidatively defluorinated with long reaction time. Introduction of  $\text{H}_2\text{O}_2$  could significantly enhance defluorination of PFOS and low-frequency ultrasound had no obvious effect on defluorination of PFOS in photocatalytic system.

**Keywords:** heteropoly salts ; PFOS ; defluorination.

**Introduction**

Perfluorinated compounds have a good surface activity, chemical stability and hydrophobic oleophobic characteristics, which widely used in printing and dyeing, textiles, electricity Sub-as well as light industrial manufacturing field. PFCs are widely used, however also bring a lot negative environmental problems, the PFC content can be measured in paper-making wastewater, electroplating wastewater, printing and dyeing wastewater [1]. Once PFCs are released into the environment, it is difficult to degrade by the natural side method, therefore, the development of efficient and practical processing technology has become a hot issue. In view of the chemical inertness and thermal stability of PFCs, conventional biochemical and physicochemical methods are difficult to effectively degrade them. Photocatalytic degradation is easy to achieve, whereas the reaction cycle is longer; electrochemical, sonochemical degradation of PFCs are mainly in the experimental stage due to energy consumption, the operation of large-scale energy-saving, high cost, even if

has good effect. Heteropolysalts catalyst is a new kind of catalyst which is composed of heteroatoms (such as P, Si, Fe, Co, etc.) and polyatomic atoms (such as Mo, W, V, Nb and Ta). As a multi-functional new photocatalyst, has good stability, low toxicity and high catalytic activity [5,6]. In this paper, PFOS (potassium perfluorooctylsulfonate) was prepared by phosphotungstic acid  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  and low pressure mercury lamp (11W, 254nm). The effects of reaction time,  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  concentration and pH on the defluorination of PFOS were investigated. The effects of  $\text{H}_2\text{O}_2$  and low frequency ultrasound on the photocatalytic system were also investigated.

**1. Experimental part**

**1.1 Reagents and instruments**

$[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  made by ourself; Potassium perfluorooctane sulfonate (C8F17KO3S), British Alfa

Aesar Company; 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), Sinopharm Group Chemical Reagent Co., Sodium hydroxide (NaOH) Beijing Chemical Reagent Factory, the above reagents are of analytical grade.

Low-pressure mercury lamp (Guangzhou Philips Lamps Co., Ltd., 254 nm), electronic balance (BS223S), ion chromatography (ICS-1000), Kunshan desktop dual-frequency digital ultrasonic cleaning device (20 & 40 kHz), The United States Diane company), pH meter (PHS-25, Shanghai-magnetic instrument factory).

## 1.2 Experimental device

A low-pressure UV lamp (11W, 254nm) was used as the light source. A cylindrical PTFE bottle with a volume of 1 L was used as the reactor. The whole reaction apparatus was placed on a thermostatic magnetic stirrer. When low-frequency ultrasound is introduced, the entire reaction device is placed in an ultrasonic water bath, and the bottom surface of the reactor directly contacts the vibration surface of the ultrasonic generator.

## 1.3 Experimental and analytical methods

The 10 mg / L PFOS solution was prepared in a 1 L volumetric flask and placed in a bottle made of ethylene-propylene-propylene copolymer (EFA). Each

experiment with a plastic cylinder from the amount of 200 mL, packed in PTFE reactor, weighing a certain amount of [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, adding the reaction solution prepared into different concentrations of heteropoly salts solution, with NaOH, HCl adjusted to the set pH, the reaction device placed in a magnetic stirrer, 11 W UV lamp placed across the surface of 2 cm, respectively, in the set time sampling. The mobile phase consisted of 3.5 mmol / L NaCO<sub>3</sub>, 1.0 mmol / L NaHCO<sub>3</sub>, and scanning was performed on the column. The mobile phase consisted of the following components: AS4A-SC 4X250 mm; column: AS4A-SC 4X 50 mm; The F-concentration in the reaction solution in the sample was calculated by quantifying the peak area of F-. The flow rate was 1.20 mL/min; the standard curve of fluoride ion was:  $y = 2.4517x + 0.0529$  (R<sup>2</sup> = 0.9997).

## 2. Results and Discussion

### 2.1 Effect of [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> Concentration

0.10 g, 0.30 g, 0.40 g of heteropoly acid were respectively weighed into the reaction solution to prepare [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> solution with the concentration of 0.50 g / L, 1.00 g / L, 1.50 g / L and 2.00 g / L in the photocatalytic system, the results are shown in Fig1.

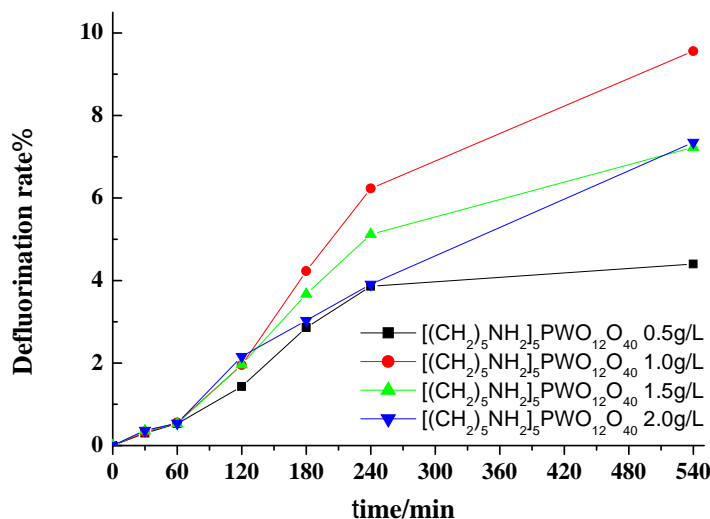


Fig.1 Effects of [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> concentration on PFOS defluorination in photocatalytic system

It can be seen from Figure 1 that UV / [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> system has a poor effect on defluorination of PFOS, and the defluorination rate increases first and then decreases with the increase of [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> concentration. When the concentration of [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is 1.0 g / L, reaching a maximum of 9.7%. [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> has a band structure similar to that of TiO<sub>2</sub>. Due to the

poor energy of LUMO and HOMO, the [(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> can produce photon-electron-space-pair separation under the excitation of ultraviolet light [7]. There are two main pollutants Path: (1) empty cave own very strong oxidation, which can oxidative degradation of pollutant itself; (2) react with H<sub>2</sub>O to generate ·OH. However, according to Moriwaki [8] and other studies have shown that ·OH on PFOS

reaction rate is very low, it can be inferred that the direct oxidation of the hole is the main mechanism of PFOS defluorination. PFOS and heteropoly salts can be mixed with each other before the concentration of heteropoly salts reaches 1 g / L. The PFOS molecules can be effectively contacted with the photogenerated holes and then oxidized. However, when the concentration of heteropoly salts is more than 1g / L, the interaction between molecules is strong, which hinders the contact between photogenerated hole and

PFOS. At the same time, the efficiency of absorption of photon is decreased, and the degradation effect is decreased.

## 2.2 Effect of pH

The pH value of the mixed solution of 1g/L heteropoly salts and 10mg /L FOS was adjusted to 2, 3, 4, 5, 6 and 7 with 1mol /L NaOH and 1mol/L HCl, respectively. The results are shown in Fig.2.

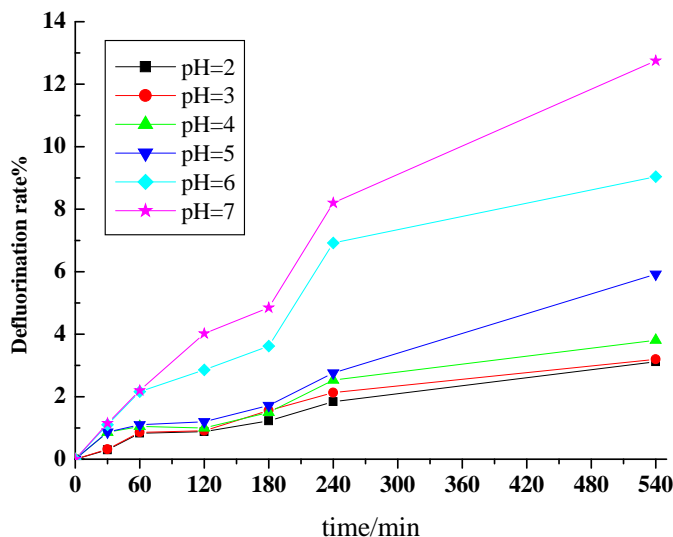


Fig.2 Effects of pH on PFOS defluorination in photocatalytic system

It can be seen from Fig.2 that the strong acidic environment favors the defluorination of PFOS in UV /  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  system, and the best effect is at pH = 3. After 480 min reaction, the defluorination rate of PFOS reaches 12.83% , The fluoride removal rate decreased by half, only 6.84%, while in the weak acid to neutral range, PFOS is difficult to effectively degrade. Wang Li and other studies have shown that [9], heteropoly salts itself is weak acid substances, it is in strong acidic environment, its activity is better, but the degradation of heteropoly salts is  $\text{PW}_{12}\text{O}_{40}^{3-}$  ion form, so too acidic Which is not conducive to the decomposition of heteropoly salts molecules; when pH is greater than 3.5, the heteropoly acid itself will be degraded, which will also affect the catalytic activity. In addition, PFOS itself is a weak organic acid, in aqueous solution in the molecular state and ionic state in two forms, the smaller the solution pH, PFOS in aqueous solution in the molecular form of the amount of the more; the other hand, the solution The higher the pH, the more the amount of PFOS is present in the ionic state, whereas the molecular state of PFOS is more favorable for photodegradation [10].

## 2.3 Effects of $\text{H}_2\text{O}_2$

It can be seen from Fig. 3 that the strong acidic environment favors the defluorination of PFOS in UV /  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  system, and the best effect is at pH = 3. After 480 min reaction, the defluorination rate of PFOS reaches 12.75% , The fluoride removal rate decreased by half, only 5.92%, while in the weak acid to neutral range, PFOS is difficult to effectively degrade. Wang Li and other studies have shown that [9], heteropoly salts itself is weak acid substances, it is in strong acidic environment, its activity is better, but the degradation of heteropoly salt a is  $\text{PW}_{12}\text{O}_{40}^{3-}$  ion form, so too acidic Which is not conducive to the decomposition of heteropoly salts molecules; when pH is greater than 3.5, the heteropoly salts itself will be degraded, which will also affect the catalytic activity. In addition, PFOS itself is a weak organic acid, in aqueous solution in the molecular state and ionic state in two forms, the smaller the solution pH, PFOS in aqueous solution in the molecular form of the amount of the more; the other hand, the solution The higher the pH, the more the amount of PFOS is present in the ionic state, whereas the molecular state of PFOS is more favorable for photodegradation [10]. Effects of  $\text{H}_2\text{O}_2$  on UV /  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  system.

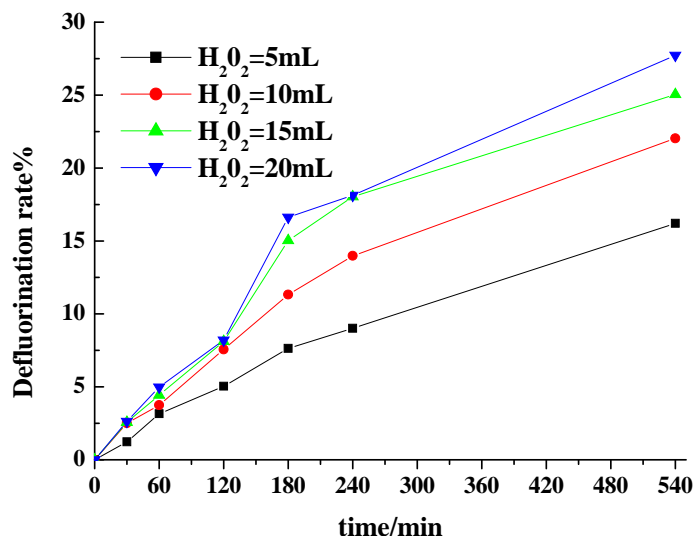


Fig.3 Effects of H<sub>2</sub>O<sub>2</sub> amounts on PFOS defluorination in photocatalytic system

#### 2.4 Effect of Low - frequency Ultrasound on System

In the solution of 10mg/L PFOS and 1g /L heteropoly salts, 20 mL volume of 30% H<sub>2</sub>O<sub>2</sub> was added into the

photocatalytic system, and 20 and 40 kHz low-frequency ultrasound assisted degradation were setted. The results are shown in Fig. 4.

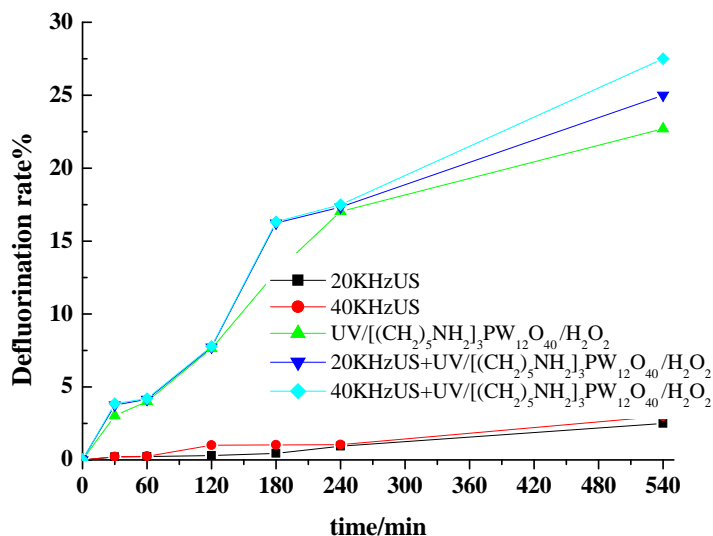


Fig.4 Effects of low-frequency ultrasound on PFOS defluorination in photocatalytic system

It can be seen from Fig. 4 that the degradation effect of 10 mg / L PFOS solution is not obvious under low frequency ultrasound of 20 kHz and 40 kHz, and the defluorination rate is very low. High-frequency ultrasound (> 200kHz) has been shown to be effective in the degradation of PFOS [12], but high-frequency ultrasound life is short, difficult to use in practice. From the experimental results, low-frequency ultrasound is difficult to effective defluorination of PFOS, according to Vecitis [13] and other studies have found that low-

frequency ultrasonic degradation mechanism is to promote the production of hydroxyl radicals to the degradation of organic matter, but studies have shown that hydroxyl radical PFOS did not have any degradation, and low-frequency ultrasound can produce pyrolysis is very small, resulting in the PFOS and no significant degradation. The reaction process of US-UV/[(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> was similar to that of UV/[(CH<sub>2</sub>)<sub>5</sub>NH<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and its degradation effect was mainly caused by photocatalysis.

From the view of the defluorination rate of the reaction process, Low-frequency ultrasound on the photocatalytic reaction does not have any role in promoting, but there are some obstacles, there may be two reasons: (1) low-frequency ultrasound have less effect on PFOS and not a good degradation result, so the reaction process is promoted by the oscillation effect, which is not as good as that of the magnetic stirrer, so that the catalyst is not in contact with the PFOS. Therefore, the defluorination rate of the coupling system is lower than that of the UV /  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  alone. (2) low-frequency ultrasound environment will accelerate the decomposition of  $\text{H}_2\text{O}_2$ , but also to promote the dissolution of dissolved oxygen in the reaction solution, reducing the concentration of catalyst regeneration agent, the reaction rate slows down. Although low-frequency ultrasound has a weak degradation of PFOS, but it is difficult to compensate for its negative effects, so the overall performance of the antagonistic effect.

### 3. Conclusion

PFOS in the UV /  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  system defluorination efficiency is low, and the defluorination rate increases with  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$  concentration was first increased and then decreased, strong acidic environment is conducive to defluorination of PFOS;  $\text{H}_2\text{O}_2$  can significantly increase the introduction of PFOS fluoride. The results showed that low-frequency ultrasound had no obvious degradation effect on PFOS and had no effect on UV /  $[(\text{CH}_2)_5\text{NH}_2]_3\text{PW}_{12}\text{O}_{40}$ , but promoted the decomposition of hydrogen peroxide and hindered the regeneration of the catalyst. So that the reaction rate of the whole photocatalytic system decreases and the defluorination rate decreases.

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