Study on photocatalytic degradation of pharmaceutical wastewater by heteropoly acid silver photocatalytic oxidation

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Abstract. The heteropoly acid silver was prepared by using sodium tungstate, two sodium hydrogen phosphate, sodium vanadate and silver nitrate. The silver polyoxometalate was characterized by IR. The results showed that the synthesized salt had Keggin type structure. A supported heteropoly acid silver catalyst was prepared by hydrolyzing titanium dioxide with titanate four butyl acetate gel as a carrier. In the self-made photocatalytic reactor, the effects of catalyst usage, initial pH of wastewater, concentration of experimental wastewater, catalyst dosage and catalyst repetition efficiency on the decolorization rate of pharmaceutical wastewater were investigated.

Key words: Ag₄PW₁₁VO₄₀·nH₂O; TiO₂; photocatalysis; pharmaceutical wastewater.

1. Introduction

Biological treatment is the best way to degrade organic wastewater. However, many compounds in pharmaceutical wastewater are toxic to microorganisms and inhibit them. As a result, the treatment effect of wastewater is not good enough to meet the discharge standards. If chemical oxidation is used at high cost, the enterprises cannot afford it. In order to effectively solve this problem, both at home and abroad are devoted to the research and development of new technologies, especially catalytic oxidation technology. By catalytic oxidation pretreatment, the residual bioactive substances in wastewater are destroyed and the B/C ratio is increased, which creates favorable conditions for the subsequent treatment of wastewater. Heteropoly acid compounds (POM) are excellent catalysts with redox function, and their applications have been extended to the field of environmental protection. However, most of the current studies are on the degradation of single substance, but few on the actual water samples. Heteropoly salts are insoluble in water, can maintain their unique cage structure, have a certain photocatalytic activity, can be used for a long time, low cost, environmentally friendly, and have broad market prospects. The study of photocatalytic degradation of pharmaceutical wastewater by Supported Heteropoly salts is not common. In this paper, the actual pharmaceutical wastewater from a pharmaceutical factory is taken as the research water sample, and the relationship between the use mode of catalyst, experimental conditions and decolorization efficiency is investigated, which provides a theoretical basis for the application of Heteropoly salts catalysts in the field of environmental protection.
2. Experiment

2.1. Chemicals and instruments
Sodium tungstate (dihydrate), analytical purity, South Wanbang Science and Technology Company; sodium dihydrogen phosphate (dihydrate), analytical purity, Chengdu Kelong Chemical Reagent Factory; sodium metavanadate, analytical purity, Beijing Fangshan Ceramic Painting Factory; concentrated sulfuric acid, ether, hydrogen peroxide, tetrabutyl titanate, etc. are analytical purity, chemical reagents of Guoyao Group. Limited company.

N\textsubscript{2} Visible Spectrophotometer, Shanghai Instrument and Electrical Analysis Instrument Co., Ltd; HJ-4 Multi-head Magnetic Heating Stirrer, Guohua Electrical Appliance Co., Ltd; FA2204N Electronic Balance, Changzhou Hengzheng Electronic Instrument Co., Ltd; PHS-2F Digital pH Meter, Shanghai Precision Scientific Instrument Co., Ltd; HH-4 Digital Display Constant Temperature Water Bath Pot Guohua Electrical Appliance Co., Ltd; DHG-9230A Vacuum Blower Dryer, Shanghai Jinghong Experimental Equipment Co., Ltd; MD-6Z Electromagnetic Pump, Iwaki Magnet Pump; TLD4 High Speed Centrifuge, Shanghai Titan Technology Co., Ltd; WQF-510A Fourier Transform Infrared Spectrometer, Beijing Rayleigh; High Pressure Mercury Lamp, Tianjin Lamp Factory, Light Degradation device (self-made); Pharmaceutical wastewater (provided by a chemical pharmaceutical company, brown, initial COD : 31000 mg/L).

2.2. Preparation of phosphotungstic vanadium heteropoly acid catalyst
The heteropoly acid was prepared by the method [1] and silver nitrate was added to form the catalyst. 3.580 g Na\textsubscript{2}HPO\textsubscript{4}·2H\textsubscript{2}O was weighed in beaker, dissolved in 20 mL deionized water, stirred to dissolve completely; 36.278 g Na\textsubscript{2}WO\textsubscript{4}.2H\textsubscript{2}O was dissolved in 40 mL deionized water, stirred to dissolve completely; acetic acid was used to mix the two to adjust the pH to 5.5, and magnetic stirring was heated to micro-boiling for 1 h, then 1.580 g was added to beaker. NaVO\textsubscript{3}, stirring and stirring, reacting for 1 hour under micro-boiling conditions, cooling the reactor to room temperature, slowly dripping silver nitrate saturated solution into beaker until no orange precipitation is produced, boiling and filtering while heat, Ag\textsubscript{4}PW\textsubscript{11}VO\textsubscript{40}.nH\textsubscript{2}O is obtained. Absorbing 10 ml tetrabutyl titanate from a dry syringe and dropping it into 20 ml anhydrous ethanol, stirring strongly in a pear-shaped bottle for 0.5 h, the anhydrous ethanol solution of tetrabutyl titanate was obtained. Continuous stirring and adding 1.5 g Ag\textsubscript{4}PW\textsubscript{11}VO\textsubscript{40}.nH\textsubscript{2}O, mixing evenly, dropping 1% dilute HNO\textsubscript{3} solution, stirring at low speed for 20 minutes, then standing, scaling and aging. Overnight, stirring at low speed for 20 minutes again, drying at 105 degrees Celsius in oven for 6 hours at constant temperature, and then grinding to obtain titanium dioxide supported silver Phosphotungsten vanadate catalyst.

2.3. Treatment of pharmaceutical wastewater by catalytic oxidation
A self-made thermostatic photocatalytic oxidation device was used as a reactor, 100 ml pharmaceutical wastewater was added, and a certain amount of titanium dioxide supported silver Phosphotungsten vanadate catalyst was added, stirring for 5 minutes to keep the absorbance constant. Adjust the pH value, turn on the circulating condensate, turn on the high-pressure mercury lamp, take samples every 10 minutes, analyze the change of its chroma, and inspect the pretreatment effect. The absorbance of waste water was measured at 510nm wavelength by N\textsubscript{2} visible spectrophotometer. Decolorization rate expressed by absorbance reduction.

2.4. Determination of polyacid structure
The structure of silver polynoxometalate was measured by Fourier transform infrared spectroscopy (FTIR). KBr was compressed and tested at room temperature.
3. Results and discussion

3.1. Characterization of Heteropoly salts

Fig. 1 shows that there are four distinct absorption phenomena at 794.5, 863.3, 962.3 and 1060.6 cm\(^{-1}\), respectively. It can be concluded that the prepared compounds are Heteropoly salts with Keggin structure.

![Infrared Spectra of Ag\(_4\)PW\(_{11}\)VO\(_{40}\)·nH\(_2\)O](image1)

**Fig. 1** Infrared Spectra of Ag\(_4\)PW\(_{11}\)VO\(_{40}\)·nH\(_2\)O

3.2. Comparison of catalytic oxidation of pharmaceutical wastewater

The degradation of 100 ml pharmaceutical wastewater (pH is about 8.6) under four conditions: supported silver heteropoly acid as catalyst, silver heteropoly acid as catalyst, titanium dioxide as catalyst and no catalyst. At room temperature, pharmaceutical wastewater was irradiated by 10 W irradiation. The absorbency of pharmaceutical wastewater was measured after centrifugation and separation every 10 minutes. Effect of dosing on photodegradation of pharmaceutical wastewater. The experimental results are shown in Figure 2. It is shown from the figure that the catalysts can promote the oxidation of air system greatly. In the absence of catalysts, the absorbance hardly changes after stirring for 10 minutes. After 30 minutes of reaction, the absorbance of pharmaceutical wastewater decreases by only 11%, but does not increase any more. When three kinds of catalysts equal to 1.5g/L are added, the reaction starts rapidly. The reaction rate of titanium dioxide and silver heteropoly acid...
began to slow down after 20 minutes, and the removal rate reached the peak of 25% and 45% at 30 minutes, respectively. The reaction rate of supported silver heteropoly acid as catalyst was always fast, and remained unchanged after the removal rate reached 56% at 30 minutes. The silver heteropoly acid has better catalytic activity and faster reaction speed.

3.3. Effect of catalyst dosage on degradation efficiency

100 mL pharmaceutical wastewater was irradiated by 10 W irradiation at room temperature with 0.5, 1, 1.5, 2.5, 3, 3.5 and 4 g/L titanium dioxide supported silver phosphotungstate vanadate catalysts. After 30 minutes of reaction, the absorbency of pharmaceutical wastewater was measured by centrifugal separation. The effect of water degradation. From Fig. 3, we can see that when the dosage is less than 3.0g/L, the optimal removal rate increases obviously. The more the catalyst dosage is, the faster the decolorization rate of pharmaceutical wastewater is. The higher the decolorization rate is after 30 minutes. When the dosage reaches 3g/L, the decolorization rate increases insignificantly. This is because in the catalytic reaction, the removal of pollutants is done at the surface of the catalyst active sites on the catalyst, the increase is conducive to the reaction, and the amount of catalyst and the adsorption time to pollutant degradation, the increase in catalyst has no meaning.

![Fig. 3 The influence of catalyst dosage on decolorization rate](image)

3.4. Effect of pH in reaction solution on degradation efficiency

Pharmaceutical wastewater pH affects the stability of pollutants and even the charge distribution and existing state of organic matter. It also affects the adsorption characteristics of polyacid skeleton. The pH value of common pharmaceutical wastewater is between 4 and 10, so the scope of our investigation is the same. Pharmaceutical wastewater was irradiated with 10 W light at room temperature by adjusting pH to 4, 5, 6, 7, 8, 9 and 10 respectively in a photodegradation reactor, adding 3 g/L titanium dioxide supported silver phosphotungstate vanadate catalyst. The absorbency of pharmaceutical wastewater was
measured by centrifugal separation after 30 minutes of reaction. The effect of photodegradation of wastewater. It can be seen from Fig. 4 that the removal rate can reach 79% with the increase of acidity. However, in the actual production of enterprises, too low acidity will affect the subsequent biological treatment effect and increase the corrosion of pipelines, so the pH value is between 6 and 7.

4. Conclusion
Ag₄PW₁₁VO₄₀·nH₂O synthesized according to the experimental method is in line with the characteristics of Keggin type heteropolyacid salt. Due to the limitation of experimental time and experimental conditions, the structure cannot be further characterized. In this experiment, the optimum conditions for the degradation of pharmaceutical wastewater were as follows: 100 mL pharmaceutical wastewater was used in the photodegradation reactor, the pH was adjusted to 6.5, and 3 g/L titanium dioxide supported silver Phosphotungsten vanadate catalyst was added to irradiate pharmaceutical wastewater under 10 W irradiation at room temperature. The highest degradation rate was 75% after 30 minutes of reaction.

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