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Abstract. Attapulgite catalyst supported on titanium dioxide formed titanium dioxide supported silver Phosphotungsten vanadate composite catalyst, which can effectively degrade pharmaceutical wastewater solution by visible light. 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, pH was adjusted to 5, 0.5 g/L attapulgite catalyst was added, and at room temperature, pharmaceutical wastewater was irradiated by high-pressure mercury lamp illumination. The degradation rate reached 80% after 30 minutes of reaction.

Key words: Pharmaceutical wastewater; Attapulgite; Photocatalysis polyoxometalate.

1. Introduction

Recently, with the continuous improvement of people's living standards and the vigorous development of the medical and health products market, the pharmaceutical industry has developed rapidly, and its position in the national economy has been improved day by day. It has become an important component of the national industrial system. The problem of wastewater pollution caused by the industry has also attracted wide attention. Heteropoly acids have attracted much attention in the field of environmental photochemistry due to their special redox and photochemistry properties. Under the action of ultraviolet light, heteropoly acids exhibit characteristics similar to semiconductor photocatalysts, which can activate molecular oxygen to catalyze the degradation of toxic organic pollutants such as Chlorophenol and chlorobenzene. Attapulgite has the characteristics of large surface area, strong adsorption and decolorization, which meets the basic requirements of catalyst carrier, low cost and wide source. It has been widely used in chemical, metallurgical, environmental protection and other departments. In this study, the carriers of attapulgite were selected to prepare supported photocatalyst heteropoly acid titania attapulgite by sol-gel method, and the products were characterized by infrared radiation, and the pharmaceutical wastewater was used as substrate for degradation experiments.

2. Materials and methods

2.1. Materials and equipment

Heteropoly salts, Nanda Synthetic Chemistry Co., Ltd., concentrated sulfuric acid, nitric acid, hydrogen peroxide, tetrabutyl titanate, etc. are all analytical purity. China Pharmaceutical Group Chemical Reagents Co., Ltd., attapulgite, Hebei Jinghang Mineral Products Factory.N2 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. Degradation

2.2. Preparation of catalysts

Buty titanate and absolute ethanol were added to the three-neck bottle in a ratio of 1:3. A certain amount of heteropoly acid and attapulgite were weighed and placed in a mixed solution. The mixture was dispersed by ultrasound for 20 minutes and stirred at 30 C. The mixture of 10% nitric acid and absolute alcohol was slowly mixed with a mixture of 1:19 and a mixture of nitric acid and absolute alcohol. After dropping, the mixture was then stirred to gel, distilled for ethanol recovery, and then dried in a muffle furnace at 460℃. The heteropoly acid salt titania attapulgite catalyst was prepared.

2.3. Photocatalytic reaction

Photocatalytic experiments were carried out in a photochemistry reactor using high pressure mercury lamp as light source. The illumination distance was 10 cm, and the reactor was made of specially made glass products. Different concentrations of pharmaceutical wastewater were prepared in the reactor and the absorbance of the solution was determined. A certain amount of attapulgite catalyst was added, circulating cooling water was opened, magnetic stirrer was opened, light intensity, system temperature, air flow rate and other conditions were adjusted, reaction time was recorded, samples were taken regularly, supernatant was taken after centrifugal separation to determine absorbance, and decolorization rate was calculated. According to this method, the effects of pH value, catalyst dosage and initial concentration of pharmaceutical wastewater on decolorization rate were investigated.

3. Results and discussion

3.1. Decolorization of pharmaceutical wastewater by pH

The pharmaceutical wastewater from 100ml was used in the reactor, and the pH of the solution was adjusted to 4, 5, 6, 7, 8, and the absorbance was determined. According to the 0.5g/L attapulgite catalyst added to the reactor, adjust the operation parameters and start timing. After every 5min sampling, the supernatant solution was centrifuged to determine the absorbance. The photocatalytic activity of attapulgite catalysts at different values of pH was investigated. The result is shown in the figure. With the increase of pH, the decolorization rate of pharmaceutical wastewater decreases. Considering the subsequent biological treatment stage, pH should be controlled at about 5.

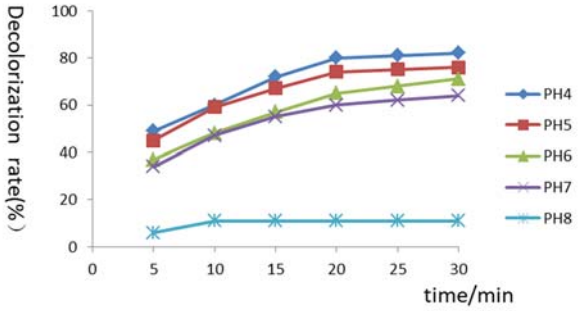

Fig.1 Effect of pH on decolorization of pharmaceutical wastewater

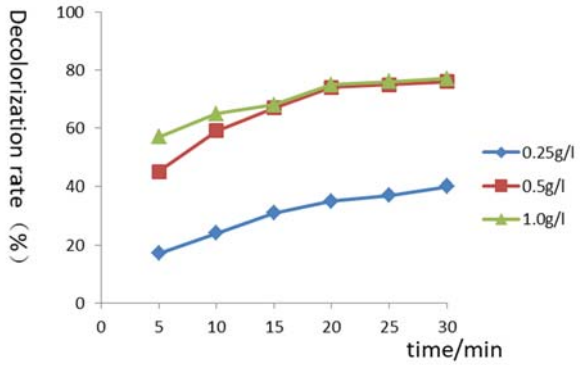

Fig.2 Effect of catalyst dosage on decolorization rate of pharmaceutical wastewater

3.2. Effect of catalyst dosage on decolorization rate of pharmaceutical wastewater

The pharmaceutical wastewater from 100ml was used in the reactor, and the initial absorbance was determined by adjusting the pH of the solution to 5. The attapulgite catalyst of 0.25, 0.5 and 1.0 g/L was added into the reactor to adjust the operation parameters and start timing. After every 5min sampling, the supernatant solution was centrifuged to determine the absorbance. Effects of different dosages on photocatalytic activity of attapulgite catalysts. The result is illustrated.

From Figure 2, it can be seen that the decolorization rate of pharmaceutical wastewater increases with the increase of catalyst dosage, but the results are close when the dosage of 0.5 and 1.0 is 25 minutes. This is because for a certain concentration of pharmaceutical wastewater solution, the dosage of catalyst has an appropriate value. When the dosage of catalyst is large, the turbidity of the solution increases, which will affect the transparency and the decolorization rate. No real impact. So the effect of initial concentration on the catalytic oxidation of pharmaceutical wastewater is investigated.

3.3. Effect of initial concentration of pharmaceutical wastewater on decolorization rate

The raw water was diluted 1, 2 and 3 times, and the diluted water sample of 100 ml was taken in the reactor to determine the absorbance of the solution. The attapulgite catalyst 0.5g/L was added into the reactor to adjust the operation parameters and start timing, and the photocatalytic activity of attapulgite was investigated. The result is shown in the figure. It can be seen from the diagram that the lower the initial concentration of pharmaceutical wastewater is, the higher the decolorization rate is. The concentration of substrate should be selected in practical application. It can be seen from Fig. 5 that the decolorization rate decreases with the increase of its initial concentration for pharmaceutical wastewater. Considering the complex composition of pharmaceutical wastewater, when the concentration and illumination intensity of catalyst remain unchanged, the active site of catalyst tends to be saturated with the increase of initial concentration of wastewater, and the intermediates and intermediates produced during degradation process occupy the active site, which prevents the reaction from occurring. The

hydroxyl radicals produced by photocatalysis are not selective, and the intermediates are not selective. Competition with non-ferrous groups and reaction with free radicals will reduce the probability of reaction between non-ferrous groups and free radicals, thus resulting in the reduction of decolorization rate.

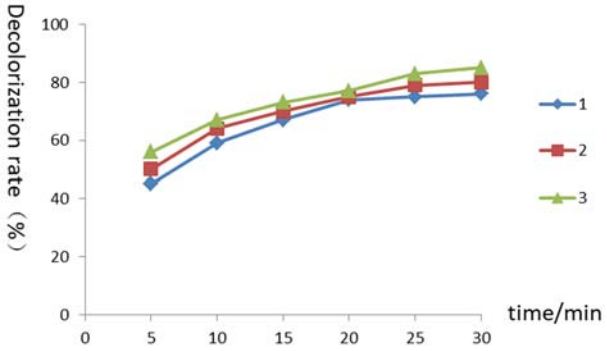

Fig. 3 Effect of initial concentration of phar-maceutical wastewater on decolorization rate

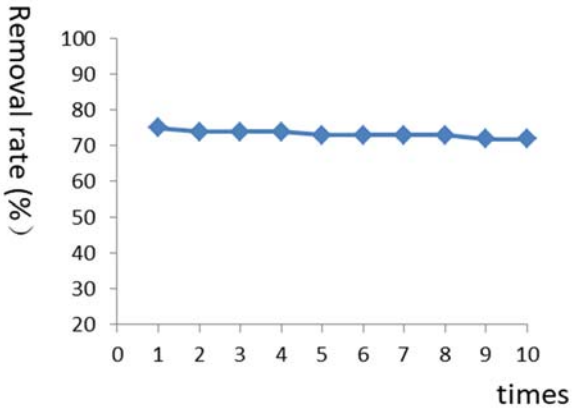

Fig.4 Effect of multiple use of catalyst on degradation efficiency

3.4. Effect of multiple use of catalyst on degradation efficiency

Because heteropoly acid is very soluble in water, it is difficult to recycle in homogeneous system. In this experiment, the heteropoly acid was made into water-insoluble salt and formed a composite catalyst with titanium dioxide. Catalyst separation and recovery is relatively simple, insoluble in water itself, recovery can be achieved by sedimentation or centrifugation. That is, after the photocatalytic reaction, the reaction liquid is filtered, and the catalyst is washed and dried, which can be used for recycling. In order to investigate its stability, a cycle experiment of catalyst in the process of pharmaceutical wastewater degradation was made. The 100 mL pharmaceutical wastewater was irradiated with attapulgite catalyst of 0.5 g/L at room temperature. The absorbency of pharmaceutical wastewater was measured by centrifugal separation after 30 minutes of reaction. The effect of catalyst reuse on the photocatalytic degradation of pharmaceutical wastewater was investigated. Fig. 6 shows that the decolorization rate of pharmaceutical wastewater has been stable at 72-75% in 10 cycles, and there is no obvious change in the decolorization rate. It shows that the catalytic capacity of silver Phosphotungsten vanadate catalyst supported on titanium dioxide has not obviously decreased during the recycling process, and the load is firm and the loss is small, indicating that the heterogeneous catalyst can be used many times. And give full play to its functions.

4. Conclusion

Attapulgite catalyst supported on titanium dioxide formed titanium dioxide supported silver Phosphotungsten vanadate composite catalyst, which can effectively degrade pharmaceutical wastewater solution by visible light. 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, pH was adjusted to 5, 0.5 g/L attapulgite catalyst was added, and at room temperature, pharmaceutical wastewater was irradiated by high-pressure mercury lamp illumination. The degradation rate reached 80% after 30 minutes of reaction.

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