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Photocatalytic Degradation of Polyacrylamide in Oilfield Sewage by Nano-sized TiO_2 Doped with W Ion

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Abstract. The Nano-TiO_2 was modified by doping TiO_2 nanoparticles with W^{6+} as catalyst, improving the photocatalytic activity and photocatalytic properties of nanometer TiO_2. We have studied the tungsten doped TiO_2 nanoparticles' photocatalytic degradation performance and viscosity reduction properties to the polymer by the degradation of polyacrylamide in oilfield sewage (PAM). Different catalysts, different amount of catalyst and PAM aqueous solution's pH value effect the photocatalytic degradation rate. The results show that: tungsten doped nanometer TiO_2 has higher photocatalytic activity than the TiO_2 nanoparticles and its photocatalytic performance of viscosity reduction is very significant. The oil-field sewage degradation rate reached about 70% after 120min light reaction of 125 W high pressure mercury lamp as the light source with 3%tungsten doping amount and 1% photocatalyst dosage. TiO_2 nano-particles doped with tungsten had obvious viscosity reduction effect on the photolytic oxidation of oilfield wastewater containing PAM.

1 Introduction

With the further development of oil exploitation, tertiary oil recovery technology is widely applied. In order to improve the recovery efficiency as much as possible, polymer flooding is often used in tertiary oil recovery. Sewage containing poly-acrylamide (PAM) has the characteristics of high viscosity, difficult oil-water separation, poor B/C and the negative effect on the environment is becoming more and more obvious[1-2]. The treatment of wastewater containing PAM is a problem. Traditional processing method mainly relies on chemical method, biological method, curing method, sedimentation and filtration with the disadvantage of high cost, easy to cause secondary pollution, little removal effect, easy to jam, etc. Therefore, it is necessary to put forward a new processing technology[3].

Photocatalyst is inexpensive, non-toxic, able to be used repeatedly after high temperature activation, and effectively reduce the cost of wastewater treatment. Its performance is stable, reaction condition is mild. Photocatalytic oxidation tech-nology run at normal temperature and atmospheric pressure, whose operation is convenient and degradation speed is faster, can oxidize organic pollutants thor-oughly. The reaction product is CO_2 and H_2O who has no secondary pollution. Therefore, photocatalytic technology is a very promising wastewater treatment technology. In recent years, photocatalytic oxidation research's object is mainly to small molecule organic wastewater[4-6], the coverage of macromolecular polymer-PAM degradation is still very rare.

In this paper, we have used sol-gel method to prepare nano TiO_2 doped with tungsten and nano TiO_2 photocatalyst to degrade polymer in the oil field sewage. By studying several kinds of nano TiO_2 photocatalysts on their photocatalytic deg-radation properties and light catalytic viscosity reduction of polyacrylamide in the sewage, we put forward a processing method of oilfield sewage containing poly-acrylamide by nano photocatalyst.

2 Experiment

2.1 The preparation of nanometer TiO_2 photocatalyst doped with tungsten

Nanometer TiO_2 photocatalyst was prepared by using sol - gel method as follows. With butyl titanate as precursor and glacial acetic acid as chelating agent, homo-geneous solution was formed by dissolving titanium alkoxide into ethanol, Under magnetic stirring, the products gathered into about 10 nm particles and sol come into being after hydrolysis and polycondensation reaction. Then the sol turned into gel after retrogradation. To get dry gel, drying it in 80℃ oven to remove residual moisture, organic linkers and organic solvents was necessary. The dry gel was calcined for 5 h under 500 ℃ after grinding, to remove the alkyl groups and hydroxyl

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which are chemical adsorptive and organic solvents and water which are physical adsorptive. Nano TiO_2 powders had been synthesized.

After dissolving tungsten oxide into hydrochloric acid, the mixture was added to another mixed solution of titanium salt and ethanol. Stir it under magnetic stir-rer until gel was formed. Following other steps same as above, the nanometer TiO_2 photocatalyst doped with tungsten was prepared.

2.2 Photocatalytic reaction between catalyst and PAM

Simulated wastewater and oilfield wastewater containing PAM were used as ex-perimental aqueous solution containing PAM whose molecular weight is 25 mil-lion. The catalytic degradation experiment, which started at the same time the agi-tator began to stir, reacted at room temperature, under 125 W high pressure mercury lamp, Viscometer was used to determine the viscosity of interval sam-pling of the PAM system. Photocatalytic activity of the catalyst was expressed by actual photodegradation rate.

3 Results and discussion

3.1. The reaction conditions effect on the PAM photocatalytic degradation

3.1.1 The influence of photocatalyst added and light

The concentration of PAM aqueous solution was 0.05%, and the addiction of TiO_2 nanometer catalyst was 1.2%. The following 5 groups of compared experiment went on with the agitator stirring:

Table 1. PAM aqueous solution system of different conditions.

Number	Mercury lamp light	Nanometer photocataly（TiO_2）
1	×	×
2	×	√
3	√	×
4	√	√

Fig. 1 shows that degradation effect of these five systems differed from each other. Viscosity fell slightly under the condition of having neither UV light nor light catalyst as the effect of stirrer mechanical cutting which factor the other four all contain too. When under the condition of having catalyst but no mercury lamp light, polyacrylamide viscosity fell slightly which was caused by catalyst's adsorption of trace amounts of polyacrylamide; When under the mercury lamp light but without the presence of catalyst, slow photolysis reaction occured in polyacrylamide; When catalyst was added in PAM aqueous solution system, mercury lamp light not only speeded up the photolysis of PAM, but also made the reaction more completely. The degradation effect was the best and degradation effect of TiO_2 doped tungsten was better than TiO_2. This means that light and added catalyst are necessary conditions to make oxidation reaction of the PAM aqueous solution more thoroughly.

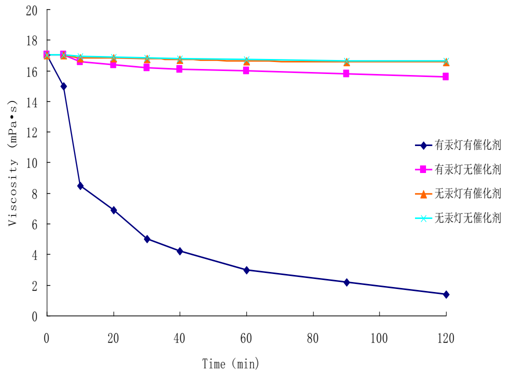

Figure 1. The effect of light and catalyst to the degradation of PAM.

3.1.2 The influence of different tungsten doping concentration

Fig. 2 shows different photocatalytic degradation performance of TiO_2 when it was prepared by doping with different tungsten doping concentration. The doping concentration was n(W) : n (Ti) = 0, 0.5%, 1%, 3%, 5%. The concentration of PAM aqueous solution was 0.05% and the adding amount of catalyst was 1.2%.

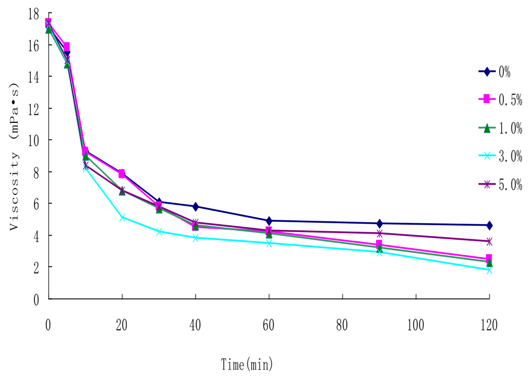

Figure 2. The effect of different W doping concentration.

From the diagram we know that the photocatalytic activity of all the W doping nanometer TiO_2 was better than pure TiO_2 and the activity increased with the increase of doping concentration. When the W doping concentration reached 3%, the catalyst degradation ability was the best. Then the catalytic activity turned worse instead with the increase of doping concentration. There is a optimal concentration of 3% when the 0.03 W-TiO_2 catalyst behaved the highest activity.

3.1.3 The influence of catalyst dosing quantity

Catalyst has distinct effect on the photocatalytic degradation rate of PAM. Fig.3 is the viscosity change curve of PAM along with the illumination time when the catalyst was 0.8% - 1.6% (PAM concentration was 0.05%, and TiO_2 doped with 3% tungsten was used as photocatalyst). As can be seen from the figure 3, the higher the dosage of photocatalyst, the faster the PAM photodegradation and the degradation rate was higher, too. But it was found that if the catalyst content in the water is too much, the light transmittance will drop and the efficiency will be lower. In our experiments we have used photocatalyst by the amount of 1.0% - 1.4%. Considering the economic factors, the best additive quantity is 1.0%.

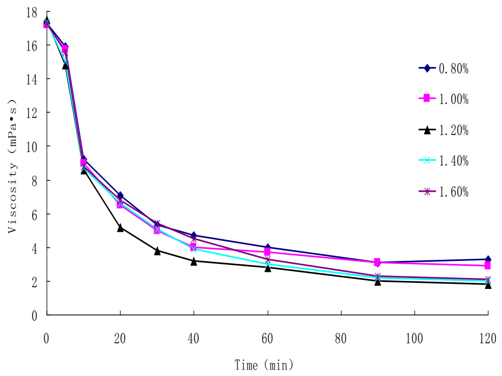

Figure 3. The influence of different dosing quantity.

3.1.4 The influence of pH on the degradation of PAM

Figure 4 illustrates that the photocatalytic effect in the acid condition was ideal than in alkaline condition to sol - gel method. When pH = 3, catalytic effect was the best.

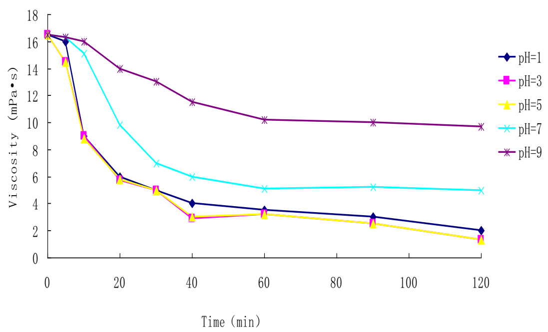

Figure 4. The influence of pH on the degradation of PAM.

4 Conclusion

Based on the understanding the current development of photocatalytic technology and photocatalysis principle, these paper used the sol gel method to prepare nanometer TiO_2 photocatalyst, and modified it by doping tungsten. At the same time, the performance of the prepared photocatalyst and the influence of different conditions to photocatalytic degradation rate were evaluated through the degradation experiment of polypropylene phthalein amine solution. Conclusions can be summed up as follows:

- The necessary conditions are light and catalyst added to make oxidation reaction of PAM aqueous solution more thoroughly;
- Nanometer TiO_2 particles doped tungsten have better photocatalytic activity than nanometer TiO_2, and 3% W - TiO_2 is the best;
- The best photocatalyst addition is 1.0%;
- pH = 3 is the best for the sol - gel method to prepare catalyst with best catalytic effect;

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