ISSN 1001—0742
CN 11—2629/X
Journal of Environmental Sciences Vol. 18, No. 1, pp. 29—32, 2006

Article ID: 1001-0742(2006)01-0029-04 **CLC number**: X703 **Document code**: A

Advanced treatment of oil recovery wastewater from polymer flooding by UV/H_2O_2/O_3 and fine filtration

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Abstract: In order to purify oil recovery wastewater from polymer flooding (ORWPF) in tertiary oil recovery in oil fields, advanced treatment of UV/H_2O_2/O_3 and fine filtration were investigated. The experimental results showed that polyacrylamide and oil remaining in ORWPF after the conventional treatment process could be effectively removed by UV/H_2O_2/O_3 process. Fine filtration gave a high performance in eliminating suspended solids. The treated ORWPF can meet the quality requirement of the wastewater-bearing polymer injection in oilfield and be safely re-injected into oil reservoirs for oil recovery.

Keywords: oil recovery wastewater from polymer flooding; UV/H_2O_2/O_3 process; polyacrylamide

Introduction

In recent years, with the conducting of polymer flooding in tertiary oil recovery in China, a kind of new wastewater, oil recovery wastewater from polymer flooding (ORWPF) was produced. The biggest difference between ORWPF and oil recovery wastewater from water flooding is that the former contains a multitude of residual high molecular weight polymer, polyacrylamide (PAM). In ORWPF, the relative molecular weight of PAM is 2×10^6—5×10^6 (Taylor *et al.*, 1998) and sometimes its concentration may reach more than 500 mg/L (Wang *et al.*, 1999). Because of the presence of PAM, oil droplets in ORWPF become much smaller than that in wastewater from water flooding. Viscosity and emulsification extent of ORWPF are also much higher than that of wastewater from water flooding(Xia *et al.*, 2001).

The current physical treatment processes(settling-separation and filtration) in oilfield can not meet the requirement of quality changes in oil recovery wastewater. The treatment of ORWPF has become a key problem in concerning oilfield in China.

Oil, PAM and suspended solids are major substances that need to remove in ORWPF for its reuse in oilfield. Sulfate-reducing bacteria were investigated to degrade PAM in solution (Huang *et al.*, 1999; Cheng and Zhang, 2004). The research results showed the bacteria have an effect on viscosity reduction of PAM. PAM-degrading bacteria and hydrocarbon-oxidizing bacteria were used to treat ORWPF(Song *et al.*, 2003). Experimental results indicated the bacteria can degrade PAM. They also have some effects on removing oil and suspended solids in ORWPF. But the feasibility of these biological methods to treat ORWPF still needs to study further.

New flocculants were studied for treating ORWPF (Li *et al.*, 2000; Li and Zhang, 2000; Wen *et al.*, 2002). It was reported that the flocculants showed certain effects on removing PAM, oil and suspended solids in ORWPF.

It is well-known that chemical oxidation is very effective method to treat organics in aqueous solution. Some chemical methods were investigated to oxidize PAM in solution (Gao *et al.*, 1999; Nan *et al.*, 1997; Chen *et al.*, 2004; Wang *et al.*, 2004). Their researches showed that oxidants such as potassium persulfate, hydrogen peroxide, sodium thiosulfate and potassium ferrate may cause the viscosity reduction of PAM. Chen *et al.* (1995) demonstrated that photocatalytic oxidation was able to degrade PAM. But oxidation of PAM in solution by combination processes of UV, H_2O_2 and/or O_3 have not been reported.

In this paper, combination process of UV/H_2O_2/O_3 was investigated to oxidize PAM and oil in ORWPF. And fine filtration was carried out to filter suspended solids.

1 Materials and methods

A cylindrical reactor made of glass was used to treat ORWPF by UV/H_2O_2/O_3 process. It has a size of 6.9 cm in inner diameter and 70 cm in height. A low pressure mercury arc UV-lamp(wavelength 253.7 nm, 20 W, Jinzhou Optic Medical Instrument Factory, China) covered by a quartz tube was placed along the axial direction and positioned at the center of the

Foundation item: The National Basic Research and Development Program (973) of China (No. 2004CB418505) and the Key Project for Science and Technology of Heilongjiang Province(No. GB04C20102); *Corresponding author

reactor. 1000 ml of ORWPF and a predetermined amount of hydrogen peroxide (30% w/w) were added to the reactor. Ozone was produced from pure oxygen by an ozone generator (Harbin Jieke Science and Technology Development Co., Ltd). Then the flow of ozone-containing oxygen gas was introduced to the bottom of the reactor through a flow-meter and a bubble aeration device. Reaction in a batch mode was started when the UV lamp was turned on. Samples were withdrawn at time intervals and analyzed.

Samples of ORWPF were obtained from a wastewater treatment plant in Daqing oilfield, which has been pretreated by settling-separation and filtration.

Concentration of ozone in the gas phase was measured by starch-KI method. PAM concentration in liquid phase was determined by starch-CdI2 spectrophotometry (Hu *et al.*, 1997). The pH value was determined by a pHS-3C pH meter (Shanghai Leici Instrument Co., Ltd).

2 Results and discussion

PAM, oil and suspended solids are the main substances that need to be removed in ORWPF for its reuse in oilfield. UV/H_2O_2/O_3 and fine filtration were used to treat them in the following experiments.

2.1 PAM degradation by process of UV/H_2O_2/O_3

Dosages of H_2O_2 and O_3, UV radiation, and pH value are major possible factors to be considered in PAM degradation by UV/H_2O_2/O_3 process.

2.1.1 Effects of H_2O_2 dosages

Fig.1 shows the effects of H_2O_2 on the initial degradation rate of PAM. Upon increasing of H_2O_2 dosages, a rapid increase in the initial degradation rate of PAM can be observed at low H_2O_2 dosages, which is followed by a gradual saturation at high H_2O_2 dosages. Explanation of this scenery is that increasing photolysis of H_2O_2 by incrementing its dosages may be counterbalanced by ·OH scavenging by H_2O_2. The formulation was presented as follows:

$$\cdot OH + H_2O_2 \quad \cdot HO_2\cdot + H_2O \qquad (1)$$

That means excess H_2O_2 reacts with ·OH and competes with PAM in the solution while the photolysis is processing at the same time. So the initial PAM degradation rate does not increase continuously with the increase of H_2O_2. The saturation point in reaction rate is observed at 660 mg/L. From the results, 660 mg/L as a suitable dosage for H_2O_2 has been chosen.

2.1.2 Effects of O_3 dosages

Fig.2 shows the effect of O_3 on the initial PAM degradation rate. Upon increasing of O_3 dosages, a

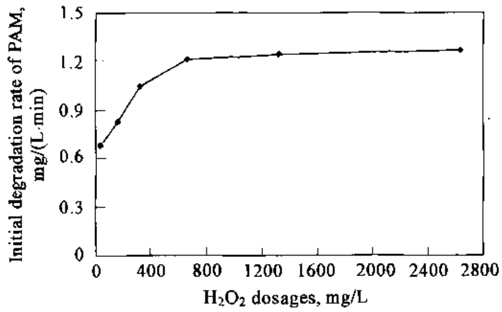

Fig.1 Effects of H_2O_2 dosages on initial degradation rate of PAM
ORWPF 1 L; pH 8.4; UV-lamp 20 W; O_3 230 mg/h

corresponding increase in initial PAM degradation rate can be observed. It indicates that with increasing of O_3 dosages, there is a corresponding increase in the amount of ·OH free radical generated by O_3 photolysis. The increase of ·OH free radical accelerates the PAM degradation reaction. 230 mg/h O_3 was chosen to do the following experiments in this paper.

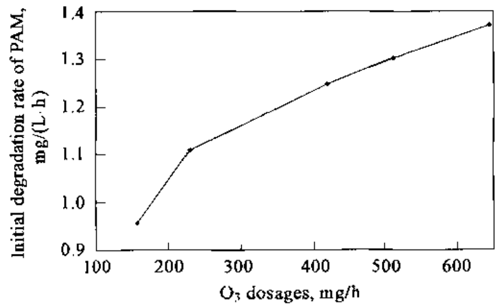

Fig.2 Effects of O_3 dosages on initial degradation rate of PAM
ORWPF 1 L; pH 8.4; UV-lamp 20 W; H_2O_2 660 mg/L

2.1.3 Effects of UV radiation

Fig.3 shows the effect of UV radiation on PAM degradation efficiency. PAM degradation efficiency with UV radiation is much higher than that without UV radiation, which indicates that UV radiation promotes the production of ·OH free radical and accelerates the degradation efficiency of PAM. With increasing of UV lamp power, there is a corresponding increase in PAM degradation efficiency within the tested ranges of UV lamp power. This can be

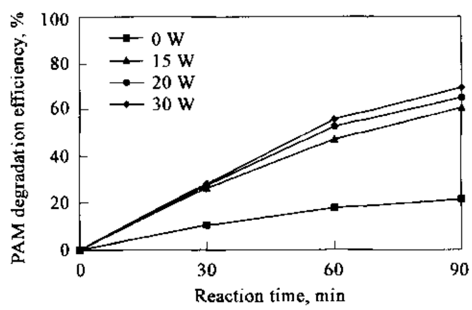

Fig.3 Effects of UV-intensity on PAM degradation efficiency
ORWPF 1 L; pH 8.4; O_3 230 mg/h; H_2O_2 660 mg/L

explained that the higher UV lamp power is, the more photons it produces. More photons may promote the photolysis of O_3 and H_2O_2 and more ·OH free radical is produced at a given time. Because of the limited experimental conditions, 20 W UV-lamp was chosen to do the experiments in this paper.

2.1.4 Effects of pH

The effect of pH on the degradation efficiency of PAM was studied. A solution of either sulfuric acid or sodium hydroxide was used to adjust the initial pH of ORWPF. Experimental results are shown in Fig.4. The degradation efficiency decreases gradually as pH increases. Especially an appreciable decrease can be seen when the solution turns into alkaline conditions. During the oxidation reaction, organic carbons were continuously oxidized to inorganic carbons. In acidic range, inorganic carbons can be emitted from solution in the form of CO_2. In basic range, however, accumulation of the inorganic carbons in the form of HCO_3^- or CO_3^{2-} may occur. These species are known to act as scavengers of ·OH free radical (Jiang *et al.*, 2001). And this surely slows down the degradation rate of PAM. Therefore, pH 4.0 was chosen as suitable pH.

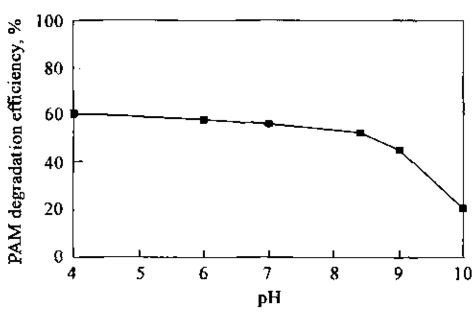

Fig.4 Effects of initial pH on PAM degradation efficiency
UV-lamp 20 W; O_3 230 mg/h; H_2O_2 660 mg/L; reaction for 1 h

The above experimental results confirm that process of UV/H_2O_2/O_3 has high performance in removing PAM in ORWPF.

2.2 Oil removal by process of UV/H_2O_2/O_3

Fig.5 shows the effect of initial oil concentrations on oil removal efficiency by process of UV/H_2O_2/O_3. The experimental results indicate that the oil removal efficiency is sensitive to the initial oil concentrations. It decreases rapidly with increasing of initial oil concentrations. A complete removal of oil can be achieved when the initial oil concentration is kept below 20 mg/L. The results suggest that it is necessary to adopt physical settling-separation or filtration steps as pretreatment method prior to the application of UV/H_2O_2/O_3 process.

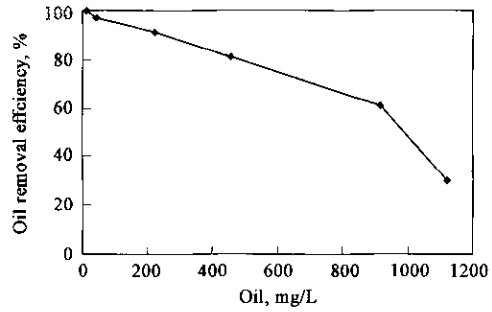

Fig.5 Effects of initial oil concentrations on oil removal
UV-lamp 20 W; O_3 230 mg/h; H_2O_2 660 mg/L; pH 8.4 reaction for 1 h

Through the above experiments, suitable reaction conditions were obtained, 230 mg/h of O_3, 660 mg/L of H_2O_2, 20 W UV lamp and 4.0 of pH. A 99.5% PAM degradation efficiency and 100% oil removal efficiency were achieved after reacting for 2 h.

2.3 Suspended solids removal by fine filtration

The process of UV/H_2O_2/O_3 can degrade PAM efficiently, but it is less effective for removing of suspended solids in ORWPF. So fine filtration was used to give a further treatment of ORWPF. A hollow fiber filter (Harbin Xinsheng Tap Water Equipment Company) was used to filter suspended solids in ORWPF. It is 270, 115 and 340 mm in length, width and height, respectively, and works at the pressure of 1.0—3.5 kg/cm^2. Results are shown in Table 1. It demonstrates that fine filtration can effectively remove suspended solids in ORWPF.

Table 1 Results of fine filtration

	Before filtration	After filtration	Reuse standard
Suspended solids, mg/L	12.25	2.50	10.0
Diameter median, μm	2.5	1.8	2.0

The ORWPF after treatment by UV/H_2O_2/O_3 and fine filtration has better quality and can come up to the standards for reuse in oilfield.

3 Conclusions

Process of UV/H_2O_2/O_3 can eliminate effectively PAM in ORWPF. Almost a complete removal(99.5%) of PAM can be achieved after reaction for 2 h while 660 mg/L of H_2O_2, 230 mg/h of O_3, 20 W UV lamp, and 4.0 of pH.

Fine filtration gave good results in removing suspended solids. The treated ORWPF can meet quality requirements for the wastewater-bearing polymer injection in oilfield and be safely re-injected into oil reservoirs for oil recovery.

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(Received for review March 4, 2005. Accepted July 25, 2005)