

Kinetics study on photochemical oxidation of polyacrylamide by ozone combined with hydrogen peroxide and ultraviolet radiation

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Abstract: An investigation on the process of ozone combined with hydrogen peroxide and ultraviolet radiation has been carried out in order to establish the kinetics for photochemical oxidation of polyacrylamide (PAM) in aqueous solution. Effects of operating parameters, including initial PAM concentration, dosages of ozone and hydrogen peroxide, UV radiation and pH value on the photochemical oxidation of PAM, have been studied. There was an increase in photochemical oxidation rate of PAM with increasing of dosages of O₃, H₂O₂ and ultraviolet radiation. Upon increasing of the initial PAM concentration, the photochemical oxidation rate of PAM decreased. Slight effect of pH value on the photochemical oxidation rate of PAM was observed in the experiments. The kinetics equation for the photochemical oxidation of PAM by the system has been established.

Keywords: photochemical oxidation; polyacrylamide; kinetics; ozone/hydrogen peroxide/ultraviolet radiation

Introduction

Polyacrylamide (PAM) is a water soluble synthetic linear polymer made of acrylamide or the combination of acrylamide and acrylic acid. Based on its linear form and corresponding solubility properties, PAM is a highly versatile material used in a multitude of applications (Caulfield *et al.*, 2002), including clarification of drinking water, flocculants for wastewater treatment, oil recovery, soil conditioning, agriculture, and biomedical applications.

Although PAM is a safe material, its monomer acrylamide is neurotoxic. Researches on PAM abroad mainly investigate the pathway of PAM degradation and whether acrylamide monomer was produced. The pyrolysis, photochemical, biological, thermal and mechanical degradation of PAM have been studied by a number of researchers and have been reviewed (Caulfield *et al.*, 2002). Linear PAM (Caulfield *et al.*, 2003a) and PAM gel (Caulfield *et al.*, 2003b) in aqueous solution were stable and no released acrylamide was found under fluorescent light and in aqueous solution at 95°C. Very small levels of released acrylamide were observed for both of PAM gel and linear PAM under UV irradiation, which indicated that PAM may undergo random chain scission under UV irradiation conditions. Under conditions of ultrasonic and pulsed laser radiation, PAM in aqueous solution may degraded. Researches demonstrated that the number average molecular weight of PAM decreased with prolonging time. Degradation rate of PAM by ultrasonic declined with increasing temperature (Vijayalakshmi and Madras, 2004). The amount of PAM degradation by laser pulsed decreased with increase in initial PAM concentration and increased with laser light intensity initially and

gradually attained a saturation value (Vijayalakshmi *et al.*, 2005).

The application of PAM in enhancing oil recovery develops rapidly in recent years in China. With its application, oil recovery wastewater containing large amount of PAM was produced. At present, how to treat PAM in oil recovery wastewater has become a key problem in environmental field. More and more researchers begin to study the treatment of PAM in the oil recovery wastewater. The relative molecular weight of PAM in the oil recovery wastewater is 2×10^6 – 5×10^6 and its concentration sometimes may reach more than 500 mg/L (Wang *et al.*, 1999; Taylor *et al.*, 1998). Gao and Yu (1999), Nan *et al.* (1997), Chen *et al.* (2004) and Wang *et al.* (2004) studied the chemical oxidation of PAM. Their researches showed that oxidants such as potassium persulfate, hydrogen peroxide, sodium thiosulfate and potassium ferrate may cause the reduction of PAM molecular weight. It is well-known that advanced oxidation processes are very effective methods to treat organics in aqueous solution. Chen *et al.* (1995) also demonstrated that TiO₂ photocatalytic oxidation was able to degrade PAM. But literature about oxidation of PAM in solution by combination processes of UV, H₂O₂ and O₃ and its reaction kinetics study have not been seen.

The aim of this work was to investigate the kinetics of photochemical oxidation of PAM in aqueous solution by ozone combined with hydrogen peroxide and ultraviolet radiation. The effects of factors such as initial PAM concentration, dosages of ozone and hydrogen peroxide, UV radiation and pH value on the PAM degradation were studied in order to offer scientific data for the treatment of PAM in oil recovery wastewater.

1 Experimental

1.1 Materials

All the reagents used in the experiments were of analytical grade. Polyacrylamide (molecular weight ≥ 5000000) was obtained from Tianjin No.3 Chemical Reagent Factory. Hydrogen peroxide (30% w/w) was purchased from Tianjin Bodi Chemical Co.

1.2 Experimental procedure

The experimental study on photochemical oxidation of PAM by ozone combined with hydrogen peroxide and ultraviolet radiation was accomplished in a bubble column reactor made of stainless steel, which has a size of 1.5 L in available volume and 35 cm in height. The reactor was equipped with a low pressure mercury vapor lamp (wavelength 253.7 nm, Jinzhou Optic Medical Instrument Factory, China) placed in axial position in a quartz sleeve allowing an annular pathlength of 3.3 cm.

Ozone was produced from pure oxygen by a laboratory scale ozone generator (Harbin Jieke Sci. & Tech. Development Co., Ltd, China). The formed ozone/oxygen mixture was fed into the reactor through a flow-meter and a porous plate situated at the bottom. Gas flows were 16 to 120 L/h and inlet ozone dosages were 135.6 to 315.1 mg/h. Aqueous solutions of different concentrations of hydrogen peroxide were continuously added by a peristaltic pump (Baoding Longer Precision Pump Co., Ltd., China) and inlet hydrogen peroxide dosages were 165 to 2460 mg/h. Different radiation intensities (1.45 to 3.05 mW/cm²) of UV lamps were used in the experiments. The reactor was charged with 1 L of PAM solution, with an initial concentration in the range of 40.59 to 284.39 mg/L. The experiments were carried out in a batch mode. Samples were withdrawn at time intervals and analyzed.

1.3 Analysis

PAM concentration in aqueous solution was determined by starch-CdI₂ spectrophotometry method (Hu *et al.*, 1997). Ozone concentration in the gas phase was measured iodometrically. The pH value was determined by a PHS-3C pH meter (Shanghai Leici Instrument Co., Ltd, China).

2 Results and discussion

Different variables (initial concentration of PAM, dosages of ozone and hydrogen peroxide, UV radiation intensity and pH value) were studied in order to estimate their effects on reaction rate of PAM photochemical oxidation.

2.1 Effects of initial concentration of PAM

Under different initial concentrations of PAM, the logarithmic changes in normalized PAM concentration (C/C_0) with time were plotted in Fig.1.

Fig.1 shows that the photochemical oxidation of

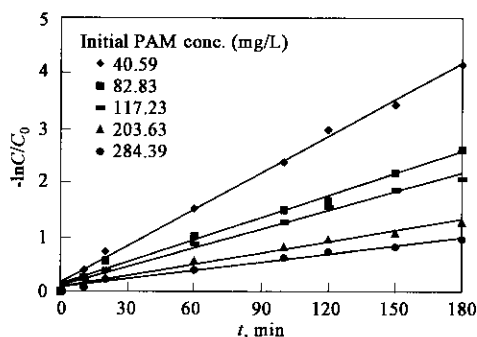


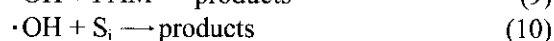
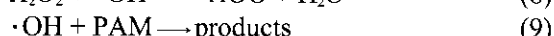
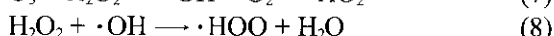
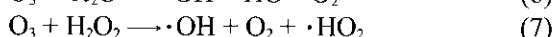
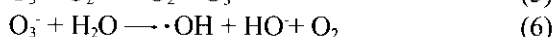
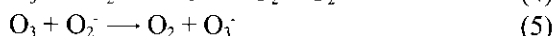
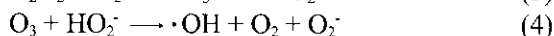
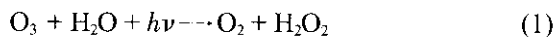
Fig.1 Effects of initial PAM concentration on PAM photochemical oxidation

UV radiation intensity: 2.02 mW/cm²; pH 6.9; O₃ dosage: 223.2 mg/h; H₂O₂ dosage: 660 mg/h

PAM follows the pseudo-first order kinetic model. The photochemical oxidation rate of PAM declined significantly by raising initial PAM concentration. But at a given time interval, the absolute amount of oxidized PAM increased. When initial concentrations of PAM were 40.59 and 284.39 mg/L, the absolute amounts of PAM oxidized within 2.5 h were 39.25 mg and 159.39 mg, respectively. This phenomenon was likely due to the production of more intermediate species which acted as scavengers for hydroxyl radicals at higher initial PAM concentration, thereby reducing the photochemical oxidation rate of PAM. Similar observations have been made in the literature for different pollutants such as methyl-tert-butyl ether (MTBE)(Safarzadeh, 2001; Stefan *et al.*, 2000) where high MTBE concentrations required proportionally higher oxidant concentration to compensate for significant generation of a number of intermediate products such as alcohols, esters, organic acids and so on.

2.2 Effects of ozone

The effect of ozone on the PAM photochemical oxidation rate is shown in Fig.2. It can be seen from Fig.2 that the photochemical oxidation rate of PAM increased rapidly with increasing ozone dosage. According to the theory of photochemical oxidation, the oxidation of PAM by O₃/H₂O₂/UV process can be described by the following simplified reactions (Staelin and Hoigne, 1982; Glaze and Kang, 1989; Lei and Wang, 2001):



where S_i represents intermediate oxidation products,

that compete with PAM for reaction with hydroxyl radicals.

As the reactions show, the oxidation of PAM by ozone with the presence of hydrogen peroxide and UV radiation is $\cdot\text{OH}$ free radical reaction process. O_3 reacts with H_2O to form H_2O_2 under UV radiation. Then H_2O_2 absorbs UV light to generate $\cdot\text{OH}$ free radical. O_3 also can react with H_2O_2 or $\text{HO}_2\cdot$ to produce $\cdot\text{OH}$ free radical. And then PAM is oxidized by the formed $\cdot\text{OH}$ to intermediates or final products. When ozone dosage increases, more $\cdot\text{OH}$ free radicals are formed. And in turn more PAMs are oxidized. Therefore, the photochemical oxidation rate of PAM increases with increasing of ozone dosage.

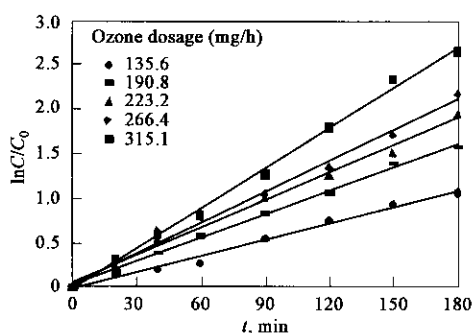


Fig.2 Effects of ozone dosage on PAM photochemical oxidation
Initial PAM concentration: 103.18 mg/L; H_2O_2 dosage: 660 mg/h;
UV radiation intensity: 2.02 mW/cm²; pH 6.9

2.3 Effects of hydrogen peroxide

Under different dosage of H_2O_2 , the logarithmic changes in normalized PAM concentration (C/C_0) with time were plotted in Fig.3. From the reactions listed above, we can see that hydrogen peroxide is essential for the generation of $\cdot\text{OH}$ and hence is a necessary promoter for the reaction. But it also functions as scavenger for $\cdot\text{OH}$ and could act as inhibitor when used at high concentration. Therefore, there should exist an optimum H_2O_2 dosage which is dependent on the concentration of organic compound being treated, as well as on the rate of ozone being delivered to the system and the presence of other inhibitors and/or initiators (Jung and Madjid, 2004). But as shown in Fig.3, the PAM photochemical oxidation rate increases with increasing the dosage of H_2O_2 . The inhibition of H_2O_2 on the PAM oxidation was not observed under the experimental conditions. The rather complex role of hydrogen peroxide has been well studied in literature. Kamenev *et al.* (1995) investigated the effect of H_2O_2 dosage on the removal of phenol in $\text{O}_3/\text{H}_2\text{O}_2$ process and did not observe any significant impact on the oxidation efficiency for H_2O_2 dosage ranging between 10–30 mg/L. But Gulyas *et al.* (1995) reported on the significant influence of H_2O_2 concentration on the removal of triethylene glycol dimethylether during $\text{O}_3/\text{H}_2\text{O}_2$ oxidation process. Further study will be carried out to investigate PAM

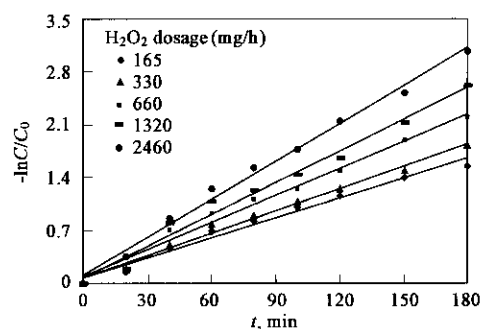


Fig.3 Effects of hydrogen peroxide dosage on PAM photochemical oxidation
Initial PAM concentration: 103.18 mg/L; O_3 dosage: 223.2 mg/h;
UV radiation intensity: 2.02 mW/cm²; pH 6.9

oxidation by $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ process to establish the optimal H_2O_2 dosage.

2.4 Effects of UV radiation

Experiments have been carried out to investigate the effects of various UV radiation intensities on the PAM photochemical oxidation. The results are represented in Fig.4.

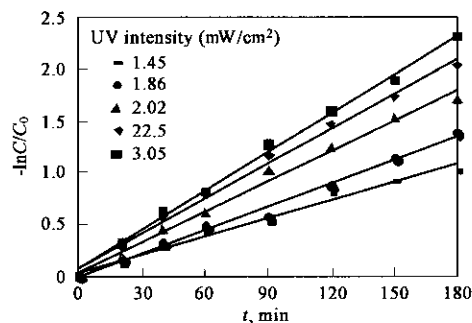


Fig.4 Effects of UV lamp power on the PAM photochemical oxidation
Initial PAM concentration: 103.18 mg/L; O_3 dosage: 223.2 mg/h;
 H_2O_2 dosage: 660 mg/h; pH 6.9

As shown in Fig.4, the PAM photochemical oxidation rate increases with increasing UV radiation intensity, while keeping other factors constant. From Reaction (1) and (2), we can see that ozone and hydrogen peroxide can absorb UV light to form $\cdot\text{OH}$ and UV light is a necessary promoter for $\cdot\text{OH}$ generation in the process of $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$. Hence, the higher UV radiation intensity is, the more photons it emits. More $\cdot\text{OH}$ free radicals in turn are produced after ozone and hydrogen peroxide absorb photons. Therefore, a faster photochemical oxidation rate of PAM was obtained with increasing of UV radiation intensity.

2.5 Effects of pH value

The photochemical oxidation of PAM at different pH has been studied. Results show that (Fig.5) the photochemical oxidation rate of PAM decreases slightly with an increase in pH value. This may be due to the accumulation of intermediate species or final

products such as carbonates and bicarbonates at higher pH, which acted as scavengers for ·OH free radicals. The impact of pH was also noticed by other investigator (Santiago *et al.*, 2002) working on phenol degradation, where the optimal pH was also in acidic range.

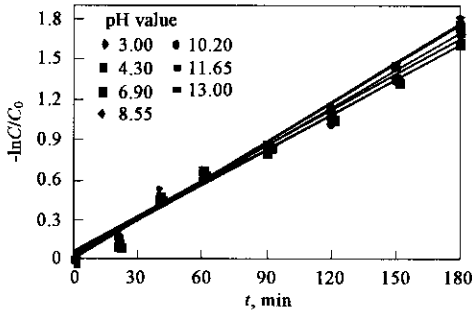


Fig.5 Effects of pH value on PAM photochemical oxidation
Initial PAM concentration: 103.18 mg/L; O₃ dosage: 223.2 mg/h;
H₂O₂ dosage: 660 mg/h; UV radiation intensity: 2.02 mW/cm²

2.6 Kinetics analysis

From the data in Figs.1—5, we can see the photochemical oxidation of PAM follows the pseudo-first order kinetic model. The photochemical oxidation rate expression of PAM can be expressed as follows:

$$-dC/dt = k_{obs} C \tag{11}$$

where *C* represents PAM concentration and *k_{obs}* expresses the pseudo-first order kinetic constant. By integrating the both sides, the equation can be written as:

$$-\ln(C/C_0) = k_{obs} t \tag{12}$$

$$\text{or } C = C_0 \exp(-k_{obs} t) \tag{13}$$

where *C₀* and *t* represent initial concentration of PAM and reaction time, respectively. The observed pseudo-first order rate constant (*k_{obs}*) can be calculated from slopes of straight line in Figs.1—5. Initial PAM concentration (*C₀*), dosages of ozone (*C_{O₃}*) and hydrogen peroxide (*C_{H₂O₂}*), UV radiation intensity (*U*) and pH value (*P*) are major factors affecting photochemical oxidation rate of PAM. The relation expression may be written as:

$$k_{obs} = f(C_0, C_{O_3}, C_{H_2O_2}, U, P) = \varepsilon C_0^a C_{O_3}^b C_{H_2O_2}^c U^d P^e \tag{14}$$

and

$$\ln k_{obs} = \ln \varepsilon + a \ln C_0 + b \ln C_{O_3} + c \ln C_{H_2O_2} + d \ln U + e \ln P \tag{15}$$

where ε, a, b, c, d and e are constants. Base on the above equation constants of a, b, c, d and e can be obtained by log-log plots of the experimental data. The results are shown in Table 1.

The value of ε is 1.65×10^{-4} , which was obtained

Table 1 Constants values in the Equation (14)

Linear regression	Square of relative coefficients	Constants
$\ln k_{obs} = -0.7456 \ln C_0 - 1.0071$	0.9923	-0.7456 (a)
$\ln k_{obs} = 1.0084 \ln C_{O_3} - 10.034$	0.9606	1.0084 (b)
$\ln k_{obs} = 0.2359 \ln C_{H_2O_2} - 5.9564$	0.9959	0.2359 (c)
$\ln k_{obs} = 0.9685 \ln U - 5.4485$	0.9191	0.9685 (d)
$\ln k_{obs} = -0.0929 \ln P - 4.5151$	0.9525	-0.0929 (e)

from Equations (12) and (15) while 90.02 mg/L of PAM, 223.2 mg/h of O₃, 660 mg/h H₂O₂, 2.02 mW/cm² UV radiation intensity and 6.9 of pH value. Thus the Equation (14) can be written as:

$$k_{obs} = 1.65 \times 10^{-4} C_0^{-0.7456} C_{O_3}^{1.0084} C_{H_2O_2}^{0.2359} U^{0.9685} P^{-0.0929} \tag{16}$$

And the kinetics equation of photochemical oxidation of PAM can be expressed as follows:

$$C = C_0 \exp \left(-1.65 \times 10^{-4} C_0^{-0.7456} C_{O_3}^{1.0084} C_{H_2O_2}^{0.2359} U^{0.9685} P^{-0.0929} t \right) \tag{17}$$

The above kinetics equation was verified(Fig.6). It is observed that the calculated data are close to the experimental data. The average relative error is 5.49%, which indicates the kinetics equation has a better ability to predict the photochemical oxidation process of PAM.

From Equation (17), we can see that the ozone dosage and UV radiation intensity have very big effects on the PAM photochemical oxidation rate constant. There are almost linear increases in the rate constant with increasing ozone dosage and UV radiation intensity, which indicates increase in ozone dosage or UV radiation intensity is a good way to promote the oxidation rate of PAM. Effect of H₂O₂ dosage on the PAM photochemical oxidation rate constant is limited. Explanation of this phenomenon is that increasing photolysis of H₂O₂ by increasing its concentration may be counterbalanced by ·OH free radical scavenging by H₂O₂. That means excess H₂O₂ react with ·OH and competes with PAM in the solution while the photolysis is processing at the same

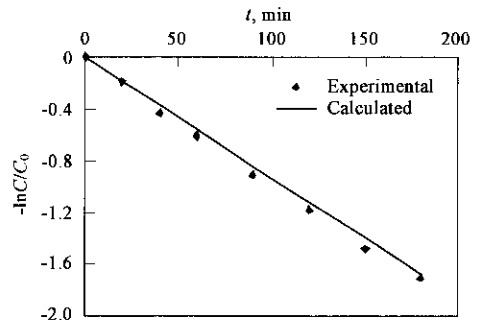


Fig.6 Comparison between experimental and calculated data
Initial PAM concentration: 90.02 mg/L; O₃ dosage: 223.2 mg/h; H₂O₂ dosage: 660 mg/h; UV radiation intensity: 2.02 mW/cm²; pH 6.9

time (Shu *et al.*, 2004). There should be an optimal H_2O_2 dosage in the reaction system, which needs further study to establish. Initial PAM concentration and pH have negative effects on PAM photochemical oxidation rate constant. This means lower concentration of PAM and acidic conditions are preferred in the photochemical oxidation of PAM by $O_3/H_2O_2/UV$.

3 Conclusions

Process of ozone combined hydrogen peroxide and UV ultraviolet was used to oxidize PAM in aqueous solution. Dosages of ozone and hydrogen peroxide, initial PAM concentration, UV radiation have significant effects on photochemical oxidation rate of PAM. A slight effect of pH value on the photochemical oxidation rate of PAM was observed. The photochemical oxidation of PAM follows the pseudo-first order reaction rate equation. The relationship between the observed rate constant and operating parameters was established.

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