Fenton-like oxidation of Hydroxypropyl guar gum catalysed by Cu(II) complex at high pH

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Abstract. Large amounts of wastewater containing hydroxypropyl guar gum (HPGG), polyacrylamide (PAM) and carboxymethyl cellulose (CMC) are produced in the process of fracturing. In the work, a Fenton-like system in the presence of H2O2 was employed to degrade wastewater. The effects of oxidant concentration, catalyst dosage, the temperature and pH on the degradation efficiency of the polymer were studied in detail. Results showed that the prepared complex (Cu(II)L) exhibited a great catalytic effects in the range of pH 7-12. It was also found that under the conditions of 45°C and pH=10, when the amount of H2O2 was 5.0% (mass ratio to hydroxypropyl guar gum) and the amount of Cu (II)L complex was 10%, HPGG had a great reduction rate, and its viscosity value can be reduced from 18 to 6.47.

Keywords: Guar gum; wastewater treatment; Fenton-like oxidation.

1 Introduction

It is well known that a large amount of wastewater will be produced in the process of fracturing and oil recovery. Guar gum is often used as a fracturing agent in oil fields due to its high viscosity, and has now become the main source of oil field wastewater [1,2]. It is a galactomannan derived from the seed of a leguminous plant Cyamopsis tetragonolobus, which is an amazingly versatile and efficient high polymer hydrophilic hydrocolloid, economical in use and easy to handle [3,4]. Now, hydroxypropyl guar gum (HPGG), the derivative of guar gum, has been the main water-soluble additive in the oil extraction process [5,6]. What’s more, some soluble polymers, anionic carboxymethyl cellulos (CMC) and partially hydrolyzed polyacrylamide (HPAM) as thickeners are also widely in oil field fracturing. Adsorption [7,8], advanced oxidation, biological treatment and so on have been applied to treat the drilling wastewater. The Fenton chemistry, in which the decomposition of hydrogen peroxide is catalyzed by iron to form hydroxyl radicals, was the most effective way for the degradation of various persistent and refractory organic pollutants in wastewater [9-12]. Fenton oxidation has been used for a long time due to its high catalytic activity for organic pollutants in wastewater. However, the process works only in the range of pH equal to about 3, and the remaining trivalent iron needs a separation system, which make it uneconomical and limited in application. An advantage of a Fenton-like catalyst is its characteristics of a wide working pH range (pH 3-7) compared to the conventional Fenton catalyst [13]. In addition to the Fe^{2+}-catalyzed homogeneous Fenton-like processes, Cu^{2+} and Cu^{2+}-complex can also act as the catalyst. The basic mechanism of the Cu^{2+}-catalyzed Fenton-like processes has been reported by some researcher, as described in Eq.1 and Eq.2. Iboukhoulef et al. [14] applied a Fenton-like system H_2O_2/Cu(II) to treat phenolic compounds from olive mill wastewater and 62% removal rate was achieved at 65 min treatment at 50°C. Lee et al. [15] also applied the Cu^{2+}-H_2O_2 Fenton-like process to degrade diclofenac and carbamazepine with UV light. Under the optimum reaction conditions, the removal rates of the two pharmacetutical compounds can reach 47% and 66% within 4 h, respectively. Maekawa et al [16] studied the mineralization of phenol by Fenton oxidation with Cu^{2+} as the catalyst and found that 94% of phenol can be mineralized in dark conditions.

$$Cu^{2+}+H_2O_2 \rightarrow Cu^{+}+HO_2^{\bullet}+H^{+} \quad (1)$$

$$Cu^{+}+H_2O_2 \rightarrow Cu^{2+}+ HO^{\bullet}+OH^{-} \quad (2)$$

In this paper, using an convenient and eco-friendly one-pot two-step method [17], formaldehyde, piperazidine and p-methylphenol are refluxed for 2h in the formaldehyde solution, then the copper chloride solution is added under vigorous stirring to obtain homogeneous copper complex for treating polymer fracturing agent in the process of oil recovery under high pH conditions.

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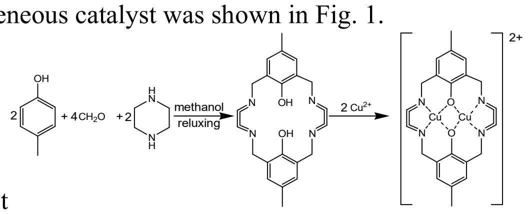
2 Experimental

2.1 Materials

All reagents used in the experiments are of analytical grade without further purification. HPGG is purchased by Changqing Oilfield, and CMC and PAM are purchased from Environmental Protection Co., Zhengzhou, Henan.

2.2 Catalyst preparation

According to our previous work [18], the "one pot two steps" method is also applied the preparation process of the catalysts. Firstly, p-methylphenol, formaldehyde and piperazine are added to absolute methanol solution and refluxed at 65℃ for 2 h to obtain the ligand solution (L). Subsequently, the L solution was added to the copper chloride under continuous stirring, which is named the complex Cu(II)L. The preparation process of homogeneous catalyst was shown in Fig. 1.



catalyst

Fig. 1 Synthesis of copper complex

2.3 Fenton-like oxidation process

Different polymers were dispersed in distilled water at room temperature and stirred 30 minutes on a magnetic stirrer with a stirring rate of 100 rpm to form 0.3% glue solution, then settled for 12 h to complete the swelling [19]. 5 mL hydroxypropyl guar gum glue, amount of H_2O_2 and catalyst dosage was added in an Ubbelohde viscometer and well-distributed by shaking at specific temperature. At a predetermined temperature, an Ubbelohde viscometer was used to measure the viscosity of the polymer under different degradation times [20]. The initial pH is selected under neutral condition and the pH of further experiment was adjusted by sodium hydroxide solution. In Fenton-like process, H_2O_2 concentration, pH value, catalyst amount, and degradation temperature were studied thoroughly because of their significant effect parameters in oxidation capacity.

3 Results and discussion

3.1 Effect of H_2O_2 dosage

H_2O_2, as the main of HO▪, plays a key role in the treatment of organic waste water in the Fenton-like processes [21]. As shown in Fig. 2, the viscosity of HPGG was investigated when H_2O_2 dosage was increased from 1% to 10% (mass ratio to HPGG) under 45℃ at pH 7.0. From the results, the viscosity of HPGG decreased significantly within 15 minutes and then remained stable. The enhancement of HPGG degradation was due to the increase of hydroxyl radicals produced from H_2O_2. Moreover, there was no significant improvement in viscosity reduction rate when H_2O_2 dosage exceeded 5%. This was because the scavenging of hydroxyl of hydroxyl radicals occurred at the high H_2O_2 concentration through Equations (1) and (2), which led to the increase in the number of hydroxyl radicals in the solution [22]. Hence, 5% was chosen as the optimum dosage of H_2O_2 in all subsequent experiments.

$$H_2O_2 + \blacksquare OH \rightarrow H_2O + \blacksquare HO_2 \quad (3)$$

$$\blacksquare HO_2 + \blacksquare OH \rightarrow H_2O + O_2 \quad (4)$$

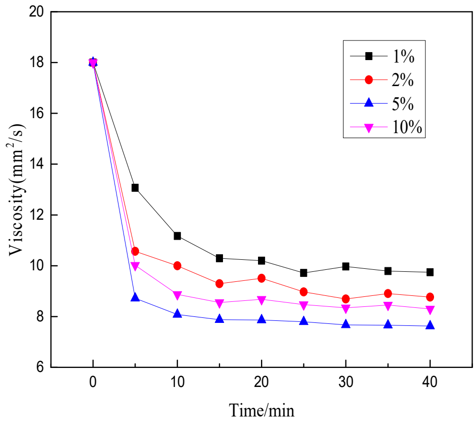


Fig. 2 Effect of concentration of $Na_2S_2O_8$

3.2 Effect of catalyst dosage

Generally, the amount of catalyst is directly proportional to the degradation rate of the polymer, but an excessive amount of catalyst is detrimental to the degradation results [23]. Fig. 3 showed consecutive experiments performed on the same wastewater sample. It can be seen from the figure that after adding the catalyst, the viscosity of HPGG decreases quickly and stabilizes after 20 minutes. Moreover, increasing the catalyst dosage by 1% to 10% can significantly increase the degradation rate of HPGG due to the produce of more hydroxyl radicals generated from H_2O_2. However, when the amount of catalyst reached 15%, the viscosity reduction rate of HPGG began to decrease, which is mainly due to the decomposition of specific free radical generated by H_2O_2. Therefore, 10% was selected as the optimum catalyst dosage for the degradation of hydroxylpropyl guar gum.

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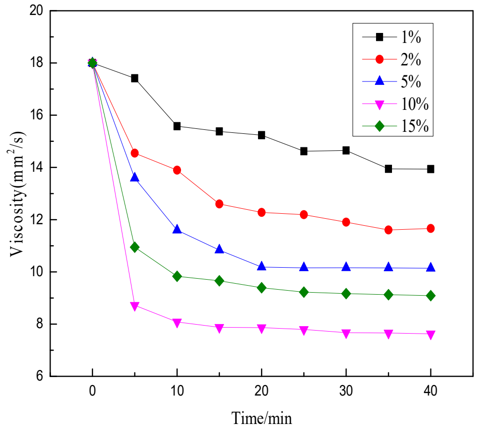

Fig. 3 Effect of dosage of catalyst

3.3 Effect of the temperature

Since the thermal degradation reaction is a non-spontaneous endothermic process, temperature affects the degradation rate of polymers [24]. Considering the application temperature of the catalyst in the oilfield, Figure 8 shows the change of viscosity of HPGG solution at different temperatures under the action of H_2O_2 and catalyst. It can be clearly seen from the figure, the higher the temperature, the faster the rate of oxidative degradation. According to Arrhenius equation, higher temperatures by increasing the reaction rate constant can provide more energy to overcome the reaction activation energy and then accelerate the reaction [25]. When the temperature increased to 45°C, the viscosity of HPGG decreases significantly, and the viscosity value can reach 7.88 after 15 minutes of degradation. Therefore, the following experiment was performed at 45℃.

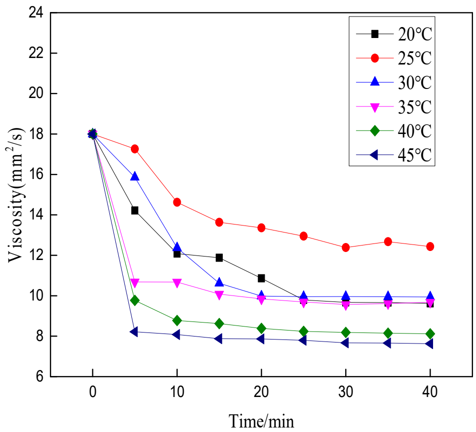

Fig. 4 Effect of reaction temperature

3.4 Effect of the pH

As we all know, conventional Fenton oxidation needs to adjust the pH to about 3 first to ensure the activity of the catalyst. The fracturing fluid is usually alkaline [26], so it requires a lot of cost to pre-treat the wastewater. This paper evaluated the removal effect of the prepared Cu(II) complex catalyzed by H_2O_2 to degrade HPGG under high pH conditions. The solution was adjusted with 0.1M NaOH solution to a pH in the range of 7-12, and the corresponding results are shown in Figure 5. Obviously, the removal efficiency under alkaline conditions is higher than that neutral condition. The highest removal performance reflecting by great viscosity drop of HPGG from 18 to 6.47 was observed at pH of 10. Different from the narrow pH required for conventional Fenton oxidation, using Cu(II)L complex as catalyst, the Fenton-like system had a wide applicable range of pH.

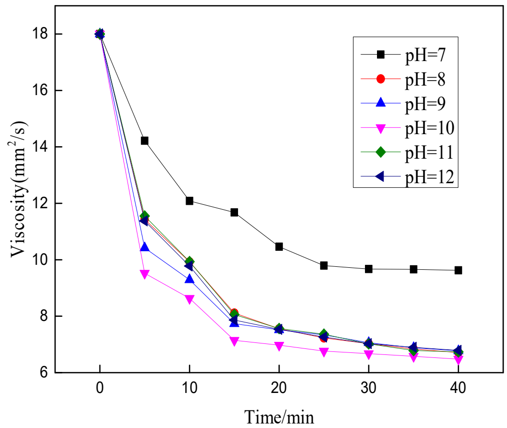

Fig. 5 Effect of pH value on the degradation

4 Conclusions

In this study, we used a Fenton-like system Cu(II) complex/H_2O_2 to degrade hydroxypropyl guar gum in oilfields. At 45℃ and pH in a wide pH rage of 7.0 to 12.0, Cu(II) complex, hydroxyl radical and temperature affect the catalytic degradation rate of HPGG. Therefore, the homogeneous Cu(II)L complex/H_2O_2 system has huge application prospects in the treatment of oilfield polymers.

Acknowledgements

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