

# Catalytic Oxidation of Hydroxypropyl Guar gum by a Fenton-like reaction

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**Abstract:** To seek for efficient Fenton-like oxidation processing for the treatment in waste fracturing fluid containing hydroxypropyl guar gum under high pH value, a series of *o*-phenylenediamine(L) metal complex was prepared for the oxidation catalysts. The catalyst was screened by the viscosity reduction of hydroxypropyl guar gum solution oxidized by H<sub>2</sub>O<sub>2</sub>. The results show that Fe (III)L exhibits high catalytic perform for degradation of hydroxypropyl guar gum in a wide pH range 7.0-13.0. The viscosity of hydroxypropyl guar gum can be reduced effectively with the 10.0% H<sub>2</sub>O<sub>2</sub> (mass ratio to hydroxypropyl guar gum) and 10.0% Fe (III)L (mass ratio to H<sub>2</sub>O<sub>2</sub>), and the COD value can be decreased to 630 mg/L from 7880 mg/L with enough H<sub>2</sub>O<sub>2</sub>, and Fe(III)L also shows great catalytic ability in the degradation of various polymers by H<sub>2</sub>O<sub>2</sub>. The proposed mechanism of the activation of H<sub>2</sub>O<sub>2</sub> by the complex was studied by UV spectrum.

**Keywords:** Catalytic; Fenton-like Oxidation; Hydroxypropyl Guar Gum; *o*-phenylenediamine Metal Complex.

## 1. Introduction

Guar gum is a galactomannan polysaccharide, that contains small amount of arabinose, glucose and uronic acid, besides galactose and mannose, which is a galactomannan derived from the seed of a leguminous plant *Cyamopsis tetragonolobus* with a molecular weight of 200,000-250,000. It is few of naturally available water-soluble gums, and it can form highly viscous colloidal dispersions at low concentrations, without heating, makes it one of the most interesting of the hydrocolloids. As one of the most powerful water binder and viscosity enhancer, superior to practically all known water-soluble gums (Zhang et al. 2022; Thombare et al. 2016; Thombare et al. 2018;), now its derivative, hydroxypropyl guar gum (HPG), has been widely used as oilfield fracturing additive because of its high viscosity of aqueous solutions even at low concentrations. Hence, there is a large quantity of hydroxypropyl guar gum in the produced water after fracturing needing to be treated (Deng and Zhao 2014). As most of the polymer remains in the produced water, the viscosity of the wastewater is rather high, so there is an urgent need for robust ways of decomposing hydroxypropyl guar gum effectively.

A method meeting these requirements and deserving attention is the Fenton oxidation process (Tony and Bedri 2014). The mechanism of Fenton oxidation is quite complex, and the different issues affecting to the efficiency of this process have been widely analyzed. It is generally accepted that Fenton oxidation is initiated by the formation of hydroxyl radical ( $\bullet\text{OH}$ ) in accordance with the classical Fenton's reaction (Abu-Shmeis et al. 2020 and Aitken et al. 2014). Then Fe<sup>2+</sup> is regenerated from the so-called Fenton-like reaction between Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub>. Lu and Wei (2011) applied the integration of Fenton-like oxidation and batch activated sludge process to treat polymer-containing oilfield wastewater, and a total COD removal efficiency of 92% was obtained (National Standard of the Peoples Republic of China.

2008) (Yazdanbakhsh et al. 2015). Zhang et al. reported Fenton-like oxidation of the industry wastewater in batch experiments using metal complexes as catalysts, the degradation can be proceeded in pH range from 5.0 to 9.0. Based on this study, the oxidative degradation of hydroxypropyl guar gum by H<sub>2</sub>O<sub>2</sub> in relative high pH range can be further explored by using complex metals (Yang et al. 2015).

Our research group have devoted to partially destroy hydroxypropyl guar gum contained in oilfield produced water, so as to improve degradability of the wastewater through the application of Fenton-like reactions (Hodaifa et al. 2018). Fenton chemistry encompasses reactions of hydrogen peroxide in the presence of iron to generate highly reactive species such as the hydroxyl radical and possibly others (Babuponnusami and Muthukumar et al. 2014; Wang et al. 2016). To seek for efficient Fenton-like oxidation processing for the treatment in waste fracturing fluid containing hydroxypropyl guar gum under high pH value, in this work, a series of *o*-phenylenediamine metal complex was prepared for the Fenton-like oxidation catalysts. The catalyst was screened by the viscosity reduction of hydroxypropyl guar gum solution oxidized by H<sub>2</sub>O<sub>2</sub>.

## 2. Materials and Methods

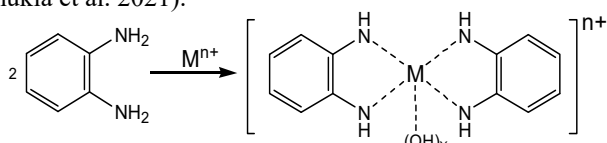
### 2.1. Materials

All of reagent were of analytical grade and were used as purchased without further purification. Hydroxypropyl guar gum has an average molecular weight of 2 million. Regent-grade hydrogen peroxide solution is 30% volume ratio to water.

### 2.2. Catalyst Preparation

Metal chloride solution (FeCl<sub>3</sub>, FeCl<sub>2</sub>, CuCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub> and ZnCl<sub>2</sub>) with concentration of 0.20 mol/L was added into 500mL of 0.20mol/L *o*-phenylenediamine solution under

stirring at molar ratio of 1:1 respective, and the mixture was stirred for 2h under refluxing. Then the solution was cooled to room temperature and diluted to a certain concentration for the catalysis. The synthesis of the *o*-phenylenediamine metal complexes was shown in Fig 1 (Shukla et al. 2021).



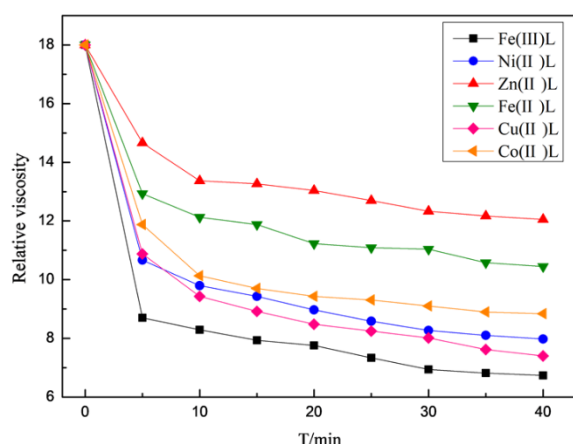
**Fig 1.** The pathway for synthesis of *o*-phenylenediamine metal-complex

### 2.3. Fenton Oxidation Process

The polymer was dispersed in water with a certain concentration and stirred continuously on a magnetic stirrer with a stirring rate of 100 rpm at room temperature for 12 h to form the glue solution. 20 ml glue solution, H<sub>2</sub>O<sub>2</sub> and amount of catalyst solution were added in a flask and stirred to homogenize the mixture. The mixture was poured in to an Ubbelohde viscometer at a certain temperature, and to measure the viscosity intermittently. The pH, degradation temperature and catalyst amount were varied systematically. After the desired duration of oxidation, solution was allowed to settle for 1h to complete the oxidation. The relative molecular mass was measured using Ubbelohde viscometer at a certain temperature (Abou Taha et al. 2021). The chemical oxygen demand (COD) was determined by dichromate method according the GB11914 of China and ISO6060. Electronic spectra were recorded in the range 200–400 nm, with spectral on as standard, on a UV-2600 spectrophotometer.

## 3. Results and Discussion

### 3.1. Catalytic Performance of Different Metal Complexes



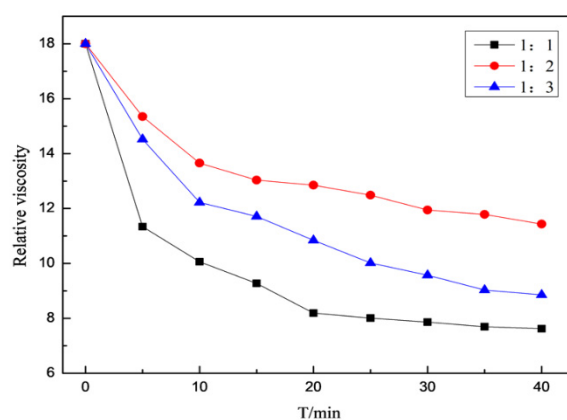
**Fig 2.** Effect of different metal complexes on the degradation

The hydroxypropyl guar gum solution with the mass concentration of 0.6% was degraded by 10% H<sub>2</sub>O<sub>2</sub> (mass ratio to hydroxypropyl guar gum) catalyzed by 10% complex (mass ratio to H<sub>2</sub>O<sub>2</sub>) of Fe(III)L, Fe(II)L, Cu(II)L, Co(II)L, Ni(II)L and Zn(II)L at 45°C, pH 10.0, and the results were summarized in Fig. 2. The experimental results indicate that the relative viscosity decreases greatly in initial reaction time of 10 minutes, and further extension of reaction time plays no more roles to the degradation. All of the metal complexes show their catalytic performance to degrade hydroxypropyl

guar gum in presence of H<sub>2</sub>O<sub>2</sub> under the condition (Ma et al. 2021), and the relative viscosity of hydroxypropyl guar gum solution showed a great decrease from 16 to 7.6 using Fe(III)L as catalyst.

### 3.2. Effect of Ratio of Fe to *o*-phenylenediamine

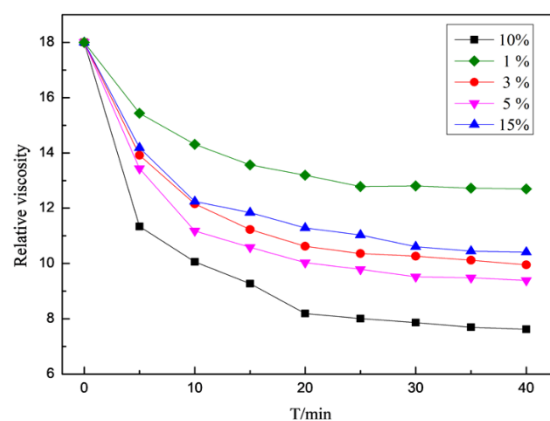
The effect of Fe:*o*-phenylenediamine ratio on the degradation of hydroxypropyl guar gum was investigated by varying the ratio from 1:1 to 1:3 under the same reaction conditions. It is observed from the Fig. 3 that the hydroxypropyl guar gum solution keeps gradually low tendency when molar ratio of Fe<sup>3+</sup> to *o*-phenylenediamine decreasing continuously to 1:3, so the optimal ratio of Fe to *o*-phenylenediamine was obtained as 1:1. The trend of viscosity decrease over Fe-based composition catalyst during degradation of hydroxypropyl guar gum could be due to the formation of generate superoxide radical.



**Fig 3.** Effect of ratio of Fe to *o*-phenylenediamine on the degradation

### 3.3. Effect of Amount of Catalyst

To optimize the catalytic performance of Fe(III)L, the amount of catalyst in reaction was investigated in the following work. Fig. 4 shown the results of the viscosity reduction of hydroxypropyl guar gum oxidized by H<sub>2</sub>O<sub>2</sub> catalyzed by various amount of catalyst ranged from 1% to 15% (molar ratio to H<sub>2</sub>O<sub>2</sub>). As shown in Fig. 4, the viscosity of hydroxypropyl guar gum decreased significantly with increasing catalyst dosage from 1% to 10%. Above 10%, since the reactive sites were enough, no further increase of the hydroxypropyl guar gum degradation can be obtained. Thus, 10% was chosen as the optimum dosage in following experiments.



**Fig 4.** Effect of different amount of catalyst on the degradation

### 3.4. Effect of Temperature

The effect of reaction temperature was evaluated on degradation of hydroxypropyl guar gum at 25 °C, 30 °C, 35 °C, 40 °C, 45 °C using Fe(III)L as catalyst. Fig. 5 demonstrates the variation of viscosity of hydroxypropyl guar gum solution at various reaction temperatures in presence of 10% H<sub>2</sub>O<sub>2</sub>. As shown, the viscosity of hydroxypropyl guar gum solution decreased significantly with the increase of reaction temperature up to 45°C. This is consistent with the results that the oxidation degradation is an endothermal reaction, and higher reaction temperature is good to the degradation process (Wu et al. 2020).

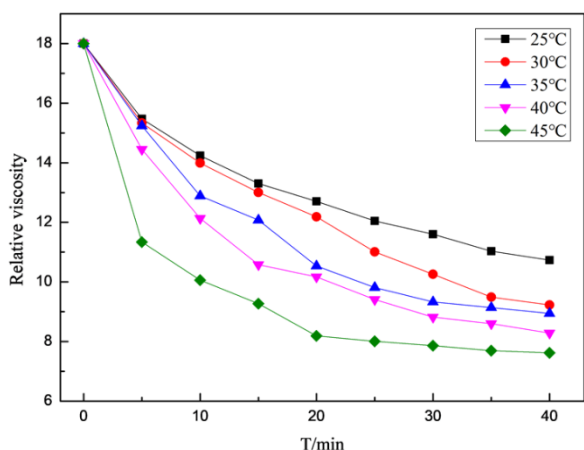


Fig 5. Effect of reaction temperature on the degradation

### 3.5. Effect of pH

The typical Fenton oxidation with H<sub>2</sub>O<sub>2</sub>-Fe<sup>2+</sup> only can be used below the pH 3.0, because of the hydration transformation of Fe<sup>2+</sup> to Fe(OH)<sub>2</sub> under higher pH value. As a result a lot of acid should be consumed to reach the discharge standard. The pH effect on the oxidation has been studied in the previous studies to be quite significant. The degradation of hydroxypropyl guar gum was examined in pH range 7-13 with the mass concentration of 0.6%, and the results were summarized in Fig. 6. From the result, it can be found that the reaction was conducted under high pH conditions, and the degradation efficacy decreases with increasing the solution pH up to 13. The generation of reactive oxygen species by Fe-based catalyst is pH-dependent since it influences the dissolution and existential state of Fe(III) from composites and the evolution of the superoxide radical. It was observed that the hydroxypropyl guar gum degradation was maximum at pH is 10.0, at 10% H<sub>2</sub>O<sub>2</sub> and at 10% catalyst (Feng et al. 2015).

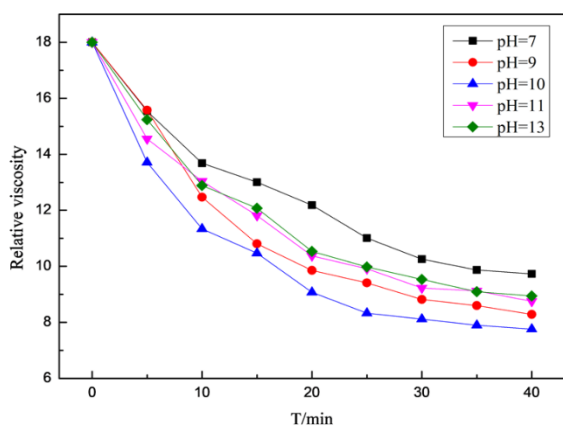


Fig 6. Effect of pH on the degradation

### 3.6. Proposed Mechanism

UV spectra have been widely used for characterization of complex substances and can provide valuable information on the structural and functional properties of complex. From the UV spectra results shown in Fig. 7, it was found that the *o*-phenylenediamine and the corresponding Fe(III)L complex show similar UV spectra and obvious absorbance peaks at 220 and 275 nm, and the intensity of Fe(III)L is much higher than that of *o*-phenylenediamine, which indicates the coordination of Fe<sup>3+</sup> with *o*-phenylenediamine as shown in Scheme 1. The UV spectra changed greatly when H<sub>2</sub>O<sub>2</sub> was added in Fe(III)L solution, and the absorption peak at 220 nm increases and moves to higher wavelength, and the peak at 275 nm increases, which should be contributed to the coordination of H<sub>2</sub>O<sub>2</sub> with Fe(III)L. By this coordination with Fe(III)L, H<sub>2</sub>O<sub>2</sub> can be activated and generate ·OH radicals. As a result, the activity and stability of Fe<sup>3+</sup> can be greatly enhanced by coordination which made the complex become high stable even in the reaction condition with high pH (Muruganandham et al 2014).

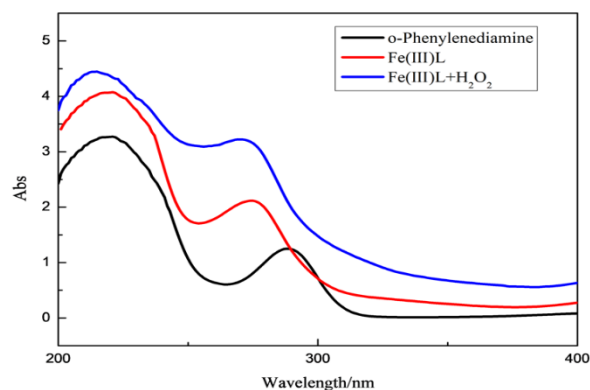


Fig 7. UV spectra of ligand corresponding Fe(III) complex

### 3.7. COD Removal

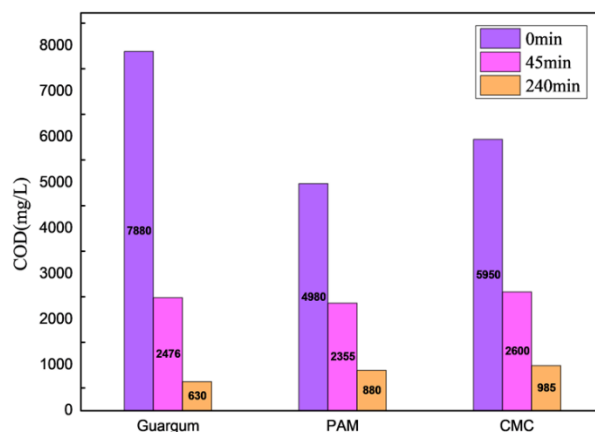


Fig 8. COD study of Fe(III)L for different polymers

Hydroxypropyl guar gum, polyacrylamide (PAM) and carboxymethyl cellulose (CMC) are commonly used in fracturing process, so the three polymers were used to evaluate the COD removal of this catalytic oxidation system. The three polymers with the mass concentration of 0.6% were oxidized by 100% H<sub>2</sub>O<sub>2</sub> (the demand of H<sub>2</sub>O<sub>2</sub> to oxidize the polymer to CO<sub>2</sub> and H<sub>2</sub>O) at 45°C and pH 10 respectively, and is shown in Fig. 8. The COD values of all polymers decreased rapidly within 45 min, the COD value was decreased by 68.6%, 52.7% and 56.3% respectively, and it was decreased by 92.0%, 82.3% and 83.4% respectively within 240 min. It also can be found that hydroxypropyl guar gum is easier to be

oxidized than that of others (Wang et al. 2017). The results showed that Fe(III)L has great catalytic degradation performance to various polymers.

## 4. Conclusion

A series of *o*-phenylenediamine-metal complex was prepared for the Fenton oxidation catalysts under high pH value. The catalyst was screened by the viscosity reduction of hydroxypropyl guar gum solution oxidized by H<sub>2</sub>O<sub>2</sub>, among which Fe (III)L exhibits high catalytic performance for degradation of hydroxypropyl guar gum in a wide pH range 7.0-13.0, and the viscosity of hydroxypropyl guar gum can be reduced effectively with the 10.0% H<sub>2</sub>O<sub>2</sub> (mass ratio to hydroxypropyl guar gum) and 10.0% Fe (III)L (mass ratio to H<sub>2</sub>O<sub>2</sub>). Furthermore, the COD value of various polymers can be greatly decreased with enough H<sub>2</sub>O<sub>2</sub> within 4h. Moreover, the degradation condition can be carried out for various polymers at high pH value up to 10. The results offer an attractive alternative in disposing of the recalcitrant fracturing waste water.

## Acknowledgments

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