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Catalytic oxidation of polymers used in oilfield by metal-1, 2-benzenediol complex

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ABSTRACT

To seek an efficient catalyst for Fen-ton oxidation processing to the treatment in waste fracturing fluid containing hydroxypropyl guar gum under high pH value, a series of metal-1,2-benzenediol(L) complex was prepared for catalyzing the Fen-ton oxidation. The results show that Ni(II)L complex exhibits high catalytic performance for degradation of polymer in a wide pH range from 7.0 to 13.0. The relative viscosity of hydroxypropyl guar gum can be reduced effectively to 2.3 after adding 10.0% H_2O_2 (mass ratio to hydroxypropyl guar gum) and using 10.0% Ni(II)L (mass ratio to H_2O_2) as catalysts. The COD value of the treated hydroxypropyl guar gum solution can be decreased to 195 mg/L from 7880 mg/L. It is worth noting that the high catalytic efficiency of Ni(II)L can be maintained even at high pH condition of 13. Moreover, Ni(II)L shows great catalytic ability in the degradation of various polymers by H_2O_2. The proposed mechanism of the activation of H_2O_2 by the complex was studied by UV spectrum.

Keywords: Fenton oxidation; Catalyst; H_2O_2; Metal-1,2-benzenediol complex; Hydroxypropyl guar gum

1. Introduction

Guar gum is a galactomannan polysaccharide that contains small amount of arabinose, glucose and uronic acid, besides galactose and mannose [1], which is derived from the seed of a leguminous plant Cyamopsistetragonolobus. It is a naturally available water-soluble gum possessing a molecular weight reported to be 200,000–250,000 [2–4]. A modification product, hydroxypropyl guar gum (HPG), is widely used in many industrial sectors such as oil recovery, fracturing fluid and drilling fluid additive, food systems, paints, mineral industry and personal care, etc due to its better solubility and thermal stability in solution [5].

In the oilfield production, many processes generate waste waters with a wide variety of contaminants, such as hydroxypropyl guar gum, polyacrylamide (PAM) and carboxymethyl cellulose (CMC) [6], which causes limitation for field application. A method meeting these requirements and deserving attention is the Fenton oxidation process [7]. Oxidation with Fenton reagent is based on ferrous ion and hydrogen peroxide, and exploits the reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H_2O_2 [8,9]. The typical Fenton oxidation with H_2O_2-Fe^{2+} only can be used below the pH 3.0, because of the reaction stops after the consumption of Fe^{2+} ions due to its hydration transformation to $Fe(OH)_2$ under higher pH value. As a result, a lot of acid should be consumed to reach the discharge standard. Some reported Fenton-like oxidation of the industry wastewater in batch experiments using metal complexes as catalysts [10,11]. As reported, the deg-

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radation can be proceeded in relatively wide pH range from 5.0 to 9.0 by catalyzed with metal complex catalysts, where in the removal efficiencies of pyridine and 3-cyanopyridine were 84% and >99%, respectively. Based on this study, the oxidative degradation of hydroxypropyl guar gum by H_2O_2 in relative high pH range can be further explored by using complex metals [12]. 1,2-benzenediolare well adapted model molecules and its interactions with metal have been extensively studied in detail in the literature because of their importance in catalytic processes during degradation of many naturally occurring aromatic substances [13]. In generally, metal-1,2-benzenediol complex was prepared in solution and UV–Vis spectrophotometry was used to evaluate its electro chemistry property [14].

To seek for efficient Fenton oxidation processing for the treatment in waste water containing hydroxypropyl guargum and other polymers under high pH value, in this work, a series of metal-1,2-benzenediol complex was prepared for the Fenton oxidation catalysts [15,16]. The catalyst was screened by the viscosity reduction of hydroxypropyl guargum solution oxidized by H_2O_2. The experimental conditions of Fenton oxidation were optimized in detail and the structure of prepared catalysts was characterized. Our work can be described as Fig. 1.

2. Materials and methods

2.1. Materials

All of reagent were of analytical grade and were purchased without further purification. Hydroxypropyl guar gum was obtained from Changing Oilfield with an average molecular weight of 2 million. Regent-grade hydrogen peroxide solution is 30% volume ratio to water.

2.2. Catalyst preparation and glue preparation

Metal chloride solution ($FeCl_2$, $CuCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$) with concentration of 0.20 mol/L was added into 500 L of 0.20 mol/L 1,2-benzenediol solution under stirring at molar ratio of 1:1/1:2/1:3 respective at room temperature. Then the solution was diluted to a certain concentration for catalysis. One of the categories of metal complex was shown in Fig. 2.

2.3. Fenton oxidation process

The polymer was dispersed in water with a certain concentration and stirred continuously at a stirring rate of 100 rpm under room temperature for 12 h to form the glue solution. Then 20 ml glue solution containing a certain concentration of H_2O_2 and catalyst were added in a flask and stirred to form a homogenize the mixture. The mixture was poured into an Ubbelohde viscometer at a certain temperature to measure the viscosity intermittently [17]. The pH, temperature and catalyst amount were varied systematically. After the desired duration of oxidation, solution was allowed to settle for 1 h to complete the oxidation. The relative molecular mass was measured using Ubbelohde viscometer at a certain temperature [18]. The chemical oxygen demand (COD) was determined by dichromate method according the GB11914 of China and ISO6060. Electronic

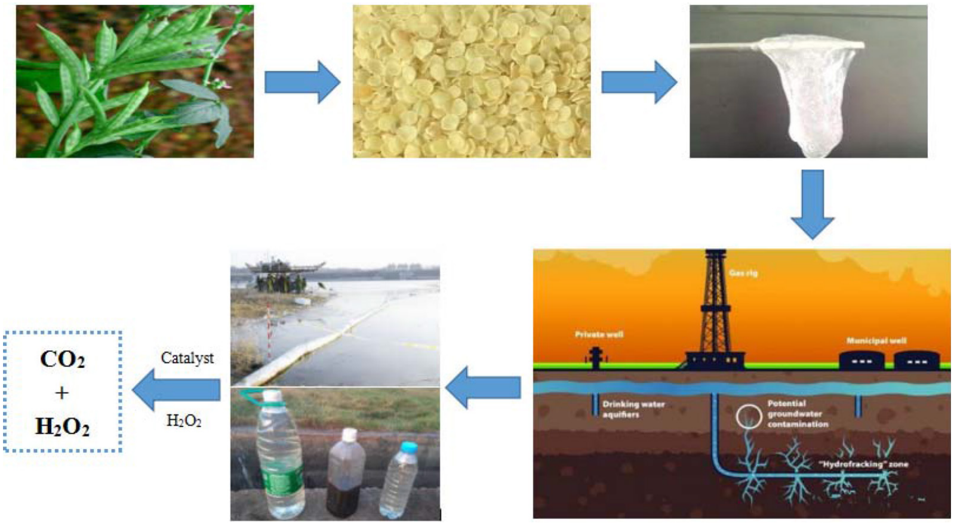

Fig. 1. The waste fracturing fluid and the clean processing.

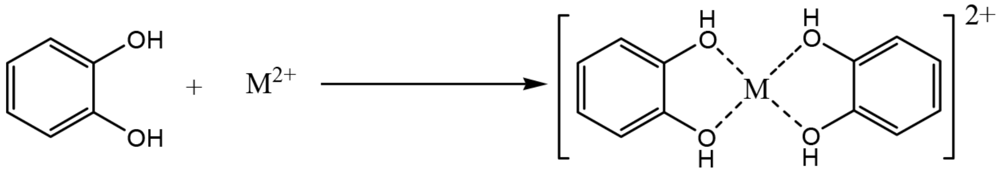

Fig. 2. Synthesis of metal-1,2-benzenediol complexes.

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

The degradation of 0.6% hydroxypropyl guar gum solution in presence of 10% H_2O_2 (mass ratio to hydroxypropyl guar gum) and 10% complex (mass ratio to H_2O_2), Fe(II)L, Cu(II)L, Co(II)L, Ni(II)L and Zn(II)L with metal to ligand ratio of 1:1 respectively, has been investigated under 45°C at pH 9.0. The results were summarized in Fig. 3. From the result, it can be found that all of complexes show their catalytic performance to degrade hydroxypropyl guar gum in presence of H_2O_2 under the condition, and the relative viscosity of hydroxypropyl guar gum solution shows a great decrease from 16 to 2.3 when Ni(II)L was used as catalyst, which is much more potent than the others, therefore it was selected for further investigation. The experimental results also indicate that the relative viscosity of hydroxypropyl guar gum solution decreases greatly in initial reaction time of 10 min, and further extension of reaction time plays no more roles to the degradation process.

3.2. Effect of different metal complexes on the degradation

The viscosity of 0.6% hydroxypropyl guar gum solution with time, during the oxidation using different 10% of metal chloride solution ($FeCl_2$, $CuCl_2$, $CoCl_2$, $NiCl_2$ and $ZnCl_2$)has been illustrated in Fig. 4. As can be seen, Fe^{2+} solution has a significant effect on the degradation of guar gum. The viscosity of guar gum solution decreased from 16 to 9.84 within 15 min reaction. As we now know that as a catalyst, ferrous ion initiates the decomposition of hydrogen peroxide to generate the very reactive HO. in Fenton's reactions and the optimum pH for the degradation of organics by the Fenton process is in low pH range and that the extent of degradation decreases with increasing pH for pH > 5 [19]. However, from our further experimental results, Fig. 11, it was illustrated that similar high degradation efficiency can be obtained even under the acidic condition reaches to high pH value (pH = 9) when $NiCl_2$ was coordinated.

3.3. Effect of ratio of benzenediol to Ni(II)

Considering that the metal to ligand ratio is an important structure directing factor to the process of crystallization of obtained complex, the effect of benzenediol to Ni(II) ratio on the degradation performance of hydroxypropyl guar gum was investigated by varying the ratio from 1:1 to 1:3 under the reaction conditions of 10% H_2O_2 (mass ratio to hydroxypropyl guar gum) and 10% complex (mass ratio to H_2O_2). It was observed from Fig. 5 that relatively viscosity of hydroxypropyl guar gum solution keeps gradually low tendency when benzenediol to Ni(II) ratio increasing continuously up to 1:3, and it is obvious that the optimal value with benzenediol to Ni(II) ratio is 1:1. As shown in Fig. 6, the high degradation performance of Ni(II)L complex with metal to ligand ratio of 1:1 should contribute to the moder-

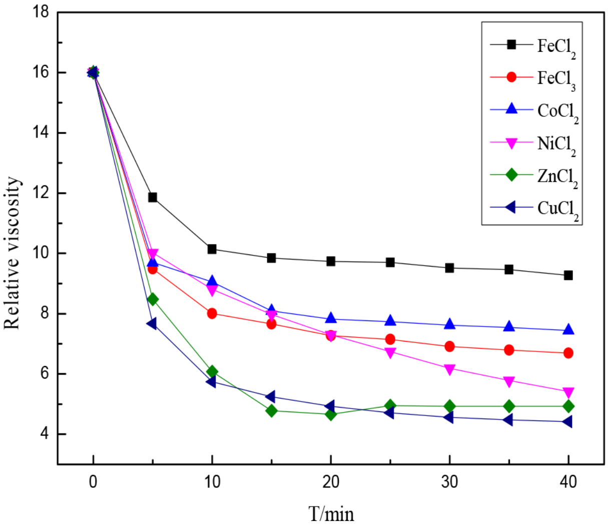

Fig. 4. Effect of different metal complexes on the degradation.

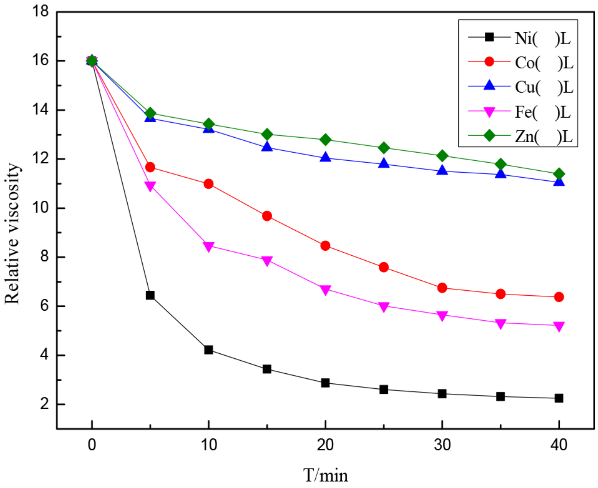

Fig. 3. Effect of different metal complexes on the degradation.

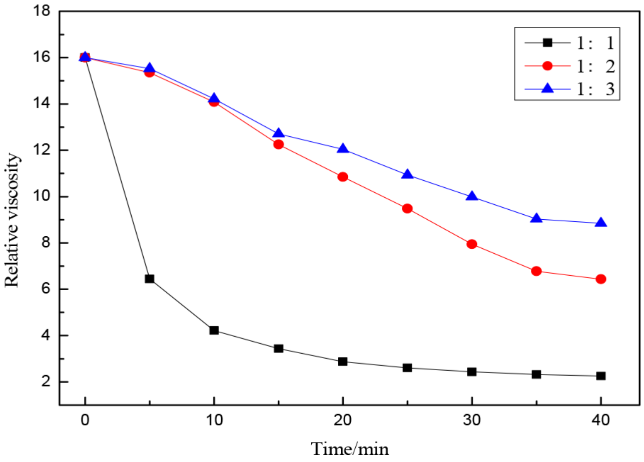

Fig. 5. Effect of metal-1,2-benzenediol complex ratio on the degradation.

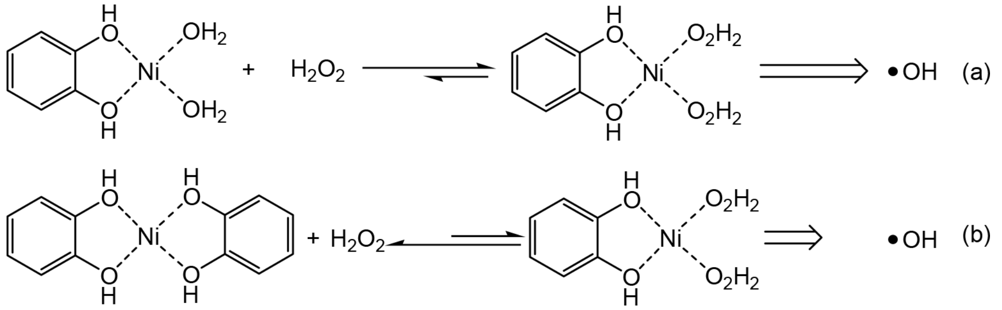

Fig. 6. The activation of H_2O_2 by different Ni(II) L complexes.

ate coordination of benzenediol with Ni(II) to form water coordinated Ni(II) which is easier to coordinate with H_2O_2. While the activation of Ni(II)L complex to H_2O_2 to generate super oxide radical decrease if metal to ligand ratio increase to 1:2.

3.4. Effect of concentration of catalyst

Fig. 7 illustrates the decrease of viscosity with time during the oxidation of guar gum using various amount of catalyst ranged from 3% to 15% (molar ratio to H_2O_2) [20]. As can be seen, the amount of catalyst has a significant effect on the degradation of hydroxypropyl guar gum solution. The viscosity of hydroxypropyl guar gum decreased significantly with increasing catalyst dosage from 3 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 for this Fenton process.

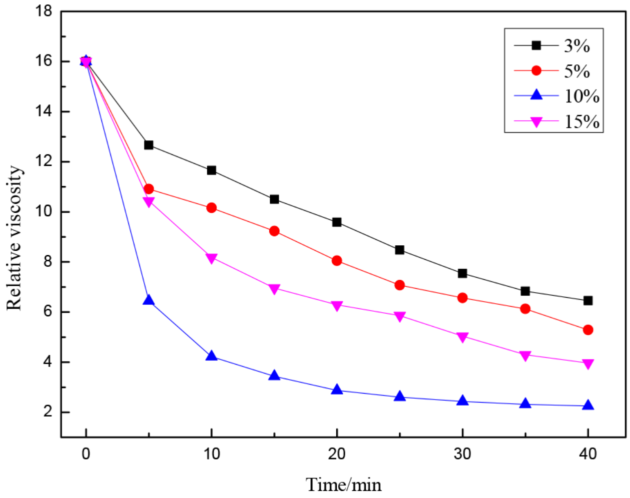

Fig. 7. Effect of different amount of catalyst on the degradation.

3.5. Effect of concentration of H_2O_2

In Fenton process the H_2O_2 dose is considered as one of the most important factors which should be considered. To optimize the catalytic performance of Ni(II)L, the concentration of H_2O_2 in reaction was investigated under the operating conditions . Fig. 8 shown the results of the relative viscosity reduction of hydroxylpropyl guar gum oxidized by various concentration of H_2O_2 ranged from 1% to 15%. From the results, it was found that the relative viscosity of hydroxypropyl guar gum decreased significantly from 16 to 3.75 with increasing H_2O_2 concentration. The higher reduce of relative viscosity was attained at 20 min when using 10% H_2O_2 concentration [21]. Further addition of H_2O_2 did not affect significantly the degradation of hydroxypropyl guar gum. Similar result was obtained by Wang et al. by confirming that the excessive H_2O_2 is not necessary due to the competing with polymers.

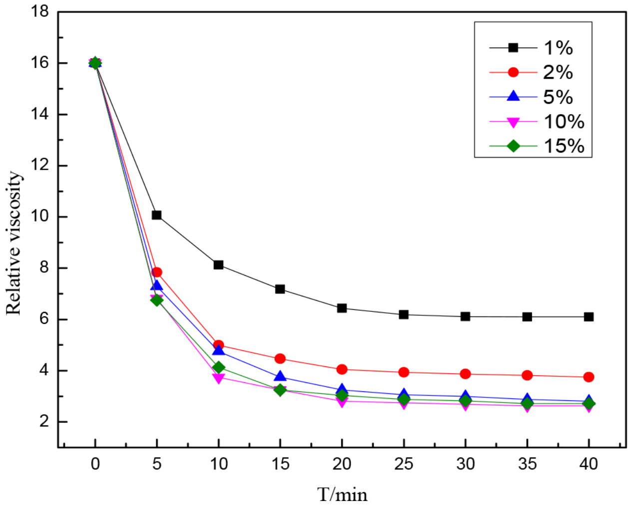

Fig. 8. Effect of molar ratio of hydroxypropyl guar gum/H_2O_2.

3.6. Effect of time on the concentration of H_2O_2

It is important to study the residual concentration of H_2O_2 for the better describing the influence of H_2O_2 as related to the plausible mechanism. Therefore, the concentration of H_2O_2 with time was investigated at the optimized reaction condition (a certain amount of DMP solution, copper sulfate solution, phosphate buffer and sample constant volume absorbance measurement) using DMP method at 45°C [22]. As presented in Fig. 9 we can see obvious decline of concentration of H_2O_2 with time, which confirms the high catalytic role of prepared Ni(II)L to increase of produced free hydroxyl radicals as suggested in Fig. 9.

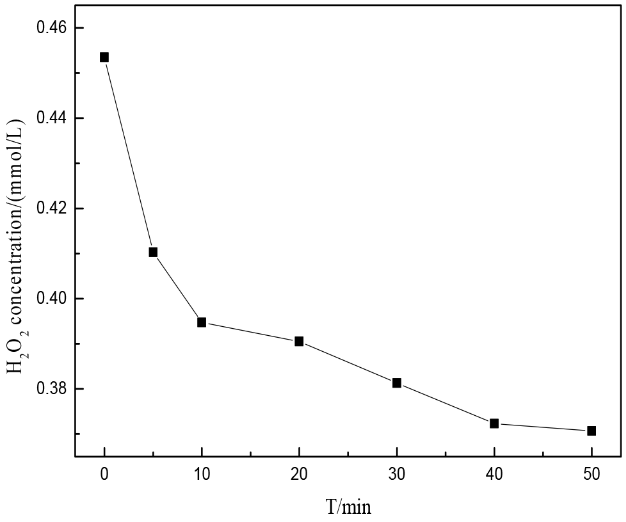

Fig. 9. Effect of time on the concentration of H_2O_2.

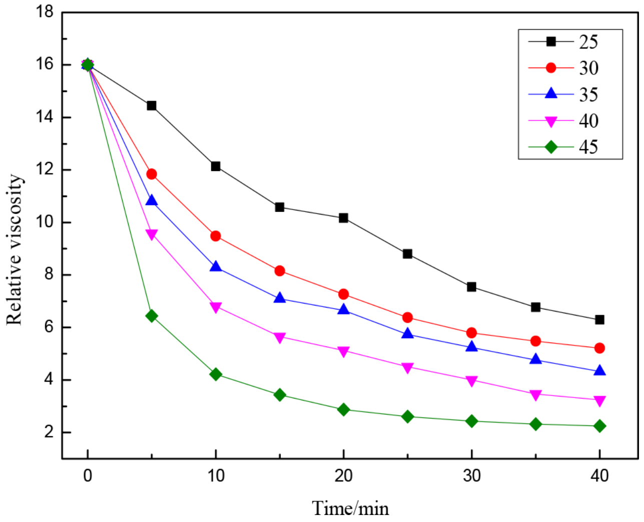

Fig. 10. Effect of reaction temperature on the degradation.

3.7. Effect of degradation temperature

The temperature plays an important role in chemical oxidation. The effect of reaction temperature was evaluated on degradation of hydroxypropyl guar gum solution using Ni(II)L as catalyst. Fig. 10 demonstrates the variation of viscosity of hydroxypropyl guar gum solution at various reaction temperatures in presence of 10% H_2O_2. As shown, the values of viscosity decreased when the temperature increased from 25°C to 45°C. The values quickly decreased in the beginning 10 min, and then gradually drop off with the increase of time. This is consistent with the results that the oxidation degradation is an endothermal reaction, and higher reaction temperature is good to the degradation process.

3.8. Effect of pH

The effects of pH on the degradation of guar gum organics by the Fenton reaction has been illustrated and acidic conditions are required to produce the maximum amount of HO· by the decomposition of H_2O_2 catalyzed by metal ions [23]. Several investigations have manifest that the optimum pH for the degradation of organics is in the range 8–11 [24]. The poor degradation performance at a high pH value was caused by the formation of ferrous and ferric hydroxide complexes with much lower catalytic capability than Fe^{2+} [25]. In our research work, the degradation performance of hydroxypropyl guar gum was examined in pH range 7–14 with the hydroxypropyl guar gum concentration of 0.6%, and the results are summarized in Fig. 11. From the result, it can be found that the reaction was conducted under high pH conditions, and the degradation efficiency decreases with increasing the solution pH up to 14. The generation of reactive oxygen species by Ni-based catalyst is pH-dependent since it influences the dissolution and existential state of Ni(II) from composites and the evolution of the superoxide radical. It was observed that in our research the maximum hydroxypropyl guar gum degradation was obtained at pH of 9.0 [26].

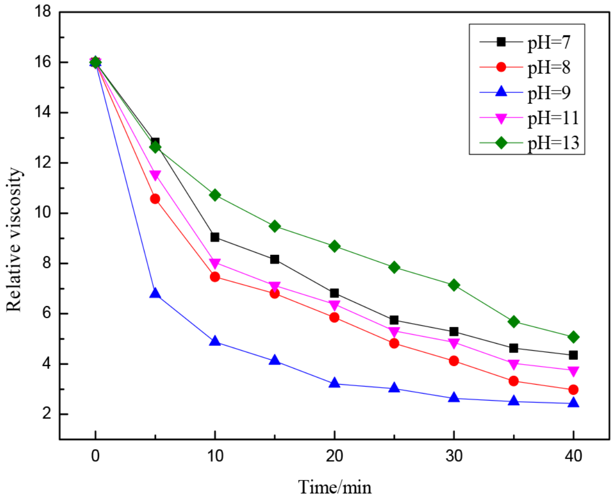

Fig. 11. Effect of pH value on the degradation.

3.9. 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. 9, it was found that the 1,2-benzenediol and the corresponding Ni(II)L complex show similar UV spectra with obvious absorbance peaks at 220 and 275 nm are known to be π-π* transformations in the aromatic ring and chromophore, which became less intense over Ni(II)L when 1,2-benzenediol is coordination with Ni(II) as shown in Fig. 2. Furthermore, the absorption intensity of peak at 220 nm and 275 nm increase obviously when H_2O_2 was added in Ni(II)L solution, which indicates the coordination of H_2O_2 with Ni(II)L, as a result, Ni(II)L can active $H_2O_2$to generate super oxide radical. It can be also confirmed by the decrease of H_2O_2 concentration with time as shown in Fig. 9, which demonstrate the activity and stability of Ni(II)L even in the reaction condition with high pH [27].

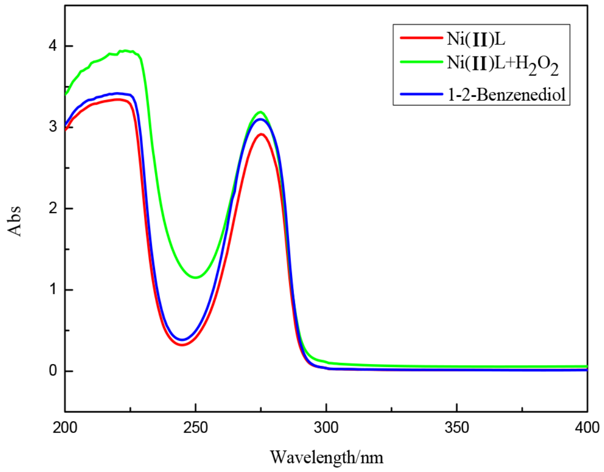

Fig. 12. UV spectra of ligand corresponding Ni(II) complex.

3.10. COD removal

Hydroxypropyl guar gum, polyacrylamide (PAM) and carboxymethyl cellulose (CMC) are commonly used in fracturing process, so the three polymers were choose 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_2O_2 (the demand of H_2O_2 to oxidize the polymer to CO_2 and H_2O) at 45°C and pH 9 respectively, and the results are presented in Fig. 13. As can be seen, the COD values of all polymers decreased rapidly within 45 min with high decreasing ratio of 75.1%, 55.8% and 65.5% respectively, and it was decreased by 97.5%, 95.5% and 96.5% respectively within 240 min. It also can be found that hydroxypropyl guar gum is easier to be oxidized than that of others [28]. The results showed that Ni(II)L has great catalytic degradation performance to various polymers.

4. Conclusions

A series of metal-1,2-benzenediol complex was prepared for catalyzing the Fenton oxidation of fracturing waste water containing much polymer under high pH value. The catalyst was screened through the viscosity reduction of hydroxypropyl guar gum solution oxidized by H_2O_2, among which Ni(II)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_2O_2 (mass ratio to hydroxypropyl guar gum) in presence of 5.0% Ni(II) L (mass ratio to H_2O_2). Furthermore, the COD value of various polymers can be greatly decreased from 7880 mg/L to 195 mg/L within 4 h and the degradation can be proceed efficiently for various polymers at high pH value up to 9. The results offer an attractive alternative in disposing of the recalcitrant fracturing waste water.

Acknowledgements

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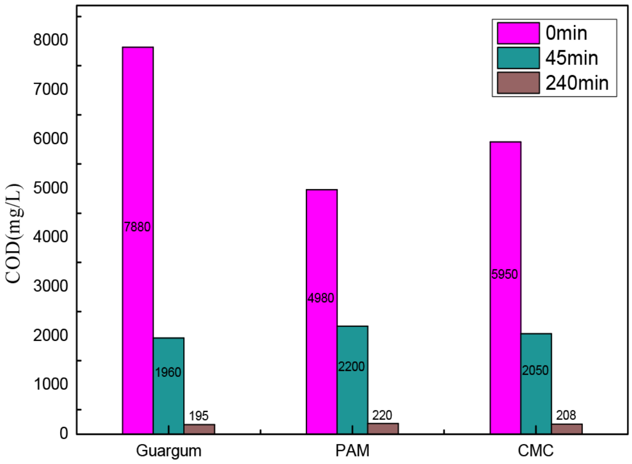

Fig. 13. COD removal of Ni(II)L catalyzed oxidation for different polymers.

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