High Efficient Degradation of Hydroxypropyl Guar Gum by Transition Metal-tetraethylenepentamine Complexes in a Wide pH Range

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Abstract

To seek for efficient Fenton oxidation processing for the treatment in waste fracturing fluid containing hydroxypropyl guargum under high pH value, a series of tetraethylenepentamine (L) complex was prepared for the Fenton oxidation catalysts. The results show that Co(II)L performs high catalytic activity 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_2O_2 (mass ratio to hydroxypropyl guar gum) and 10.0% Co(II)L (mass ratio to H_2O_2), and the relative molecular mass can be reduced dramatically. Most important of all, the COD value can be decreased to 185 mg/L from 8080 mg/L with enough H_2O_2, and Co(II)L also 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

Clean Oxidation; Transition Metal Complex; Fracturing Fluid; Waste Water.

1. Introduction

Guar gum 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[1,2]. The development of these guar gum derivatives was necessitated because of the concerns about solution clarity, alcohol solubility and thermal stability of natural guar gum[3,4]. The latter is chemically modified into various water soluble derivatives by using functional groups to substitute free hydroxyl groups along its macromolecular backbone. The derivatives find applications in numerous industries, such as, food, paints and pigments, oilfield mining, paper, water treatment, personal care, pharmaceutical and agriculture [5]. Hydroxypropyl guar gum (HPGG) is prepared from natural guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. The chemical and functional properties of HPGG are mainly dependent on the pattern of substitution, the distribution of the substituent and the average length of the hydroxypropyl substituents (DPn) [6,7]. HPGG is an important guar gum derivative commonly used as thickener for fracturing fluids in the field of petroleum industry [8]. HPGG, as well as polyacrylamide (PAM) and carboxymethyl cellulose (CMC), is widely used in oilfield as the thickener in fracturing fluid[9], and a mount of waste water containing polymers is produced after its operation. The waste water is treated to reduce pollution of rivers, lakes and fjords. This pollution might lead to the extreme growth of algae, sedimentation that uses all the oxygen in the waters and thereby kills bottom life. A method meeting these requirements and deserving attention is the Fenton oxidation process [10]. This method employs hydrogen peroxide (H2O2) and ferrous sulfate (FeSO4) to form a strong oxidizing agent (hydroxyl radicals) during the oxidation process. However, the oilfield sewage can not be used directly due to its nature (alkaline property) and should be pretreated because the Fenton oxidation process is effective at pH 2.0 to 3.0 [11]. As a result, much acid is usually consumed to reach the discharge standard [12-15], so great efforts have been made to improve the application of Fenton oxidation.

Our research aims at the clean processing of waste in oil field. To seek for a new efficient Fenton oxidation processing for the treatment in waste fracturing fluid containing polymers under high pH value, in this study, a series of transition metal complex was prepared for the Fenton oxidation catalysts. The catalysts were screened by the viscosity reduction of hydroxypropyl guar gum solution oxidized by H2O2. The experimental conditions of Fenton oxidation were optimized in detail and the structures of the prepared catalysts were characterized.

2. Materials and Methods

2.1 Materials

All reagents used were of analytical grade and were used as purchased without further purification. Hydroxypropyl guar was obtained from Renqiu City Tengda Chemical Co., Ltd. Relative molecular mass of 2 million. H2O2 (AR Grade, purity: P 30.0%) was purchased from Chengdu Cologne Chemical Co., Ltd.

2.2 Catalyst Preparation and Glue Preparation

Metal chloride solutions (FeCl2, CuCl2, CoCl2, NiCl2 and ZnCl2) with concentrations of 0.20 mol/L were added to 500 mL of 0.20 mol/L tetraethylenepentamine (L) solution under stirring at molar ratio of 1:2 respectively. Then the solution was diluted to a certain concentration for the catalysis.

2.3 Fenton Oxidation Process

A certain hydroxypropyl guar gum polymer was dispersed in water. After stirring continuously on a magnetic stirrer with a stirring rate of 100 rpm at room temperature for 12 h, a guar gum solution was formed. Batch experiments were carried out in a mixture of 20 ml glue solution, H2O2 and amount of catalyst solution using a heat-collection temperature magnetic stirrer to provide proper mixing and various temperatures. After the oxidation reaction, the samples was poured into an Ubbelohde viscometer at a certain temperature to measure the relative viscosity compared with water intermittently[16] and the relative molecular mass was measured using Ubbelohde viscometer at a certain temperature according to the previous report[17-19]. The chemical oxygen demand (COD) was determined by dichromate method according to the HJ808 of China and ISO6060[20]. Electronic spectra were recorded in the range of 200-400 nm, with spectral on as standard, on a UV-2600 spectrophotometer.

3. Results and Discussion

3.1 Chemistry

Chemically, guar gum is a straight chain galactomannan, which is 75-85% of the endosperm, has a chain of (1-4)-linked-D-mannopyranosyl units with single α-D galactopyranosyl units connected by (1-6) linkages to, on the average, every second main chain unit. The ratio of D-mannopyranosyl to D-galactopyranosyl units is about 2:1, and the molecular formula is about (C18H30O16)n. The average molecular weight of guaran is in the range of 1-2×106 dalton. So the oxidation of guar gum by H2O2 can be summarized as equation (1).

$$\mathrm{(C18H30O16)n + nH2O2} \longrightarrow \mathrm{CO2}\uparrow\mathrm{+H2O} \qquad (1)$$

3.2 Catalytic Performance of Different Metal Complexes

Informally, viscosity is the quantity that describes a fluid's resistance to flow especially for polymers which usually having relatively high viscosity. In our study the catalytic performance of catalysts have been investigated by relative viscosity of hydroxypropyl guar gum compared with water. The relative viscosity of 0.6% hydroxypropyl guar gum solution was measured after degradation by 10% H_2O_2 (mass ratio to hydroxypropyl guar gum) and 10% complex (mass ratio to H_2O_2) of Fe(II)L, Cu(II)L, Co(II)L, Ni(II)L and Zn(II)L at 45°C and pH 7.0. The results obtained are summarized in Table 1. It can be seen that all of the metal complexes show their catalytic performance to degrade hydroxypropyl guar gum in the presence of H_2O_2 under the condition, and the relative viscosity of hydroxypropyl guar gum solution showed a great decrease from 22 to 1.5 using Co(II)L as catalyst. Furthermore, the obviously decrease of viscosity in an initial reaction time of 10 min indicated that further extension of reaction time had no further effect on the degradation[21]. The high degradation effect of Co(II)L and Fe(II)L should be contributed their high rate of generation of oxidising species, however, in the case of Ni(II)L and Zn(II)L complexes, a marked decrease in the activity is an evident of an anti-oxidative effect suggested by Matijia et al[22-23].

3.3 Optimization of the Reaction Parameters

Considering that the metal to ligand ratio is an important structure directing factor to the process of crystallization of obtained complex, a set of tests was performed to chose the optimal ratio of Co^{2+}/Tetraethylenepentamine at the range from 1:1 to 1:3 in presence of 10% H_2O_2 (mass ratio to hydroxypropyl guar gum) and 10% complex (mass ratio to H_2O_2) of catalyst. It is observed from the Table1 that the relative viscosity of hydroxypropyl guar gum solution keep gradually low tendency when the molar ratio of Co^{2+}/tetraethylenepentamine increasing continuously up to about 1:2 and attained the optimal value at Co^{2+}/tetraethylenepentamine ratio of 1:2. The high degradation performance of Co(II)L complex at the molar ratio of metal to ligand should contribute to its more active to generate superoxide radical by substitution of coordinated water with H_2O_2, which is easier than the substitution of tetraethylenepentamine with H_2O_2.

To optimize the catalytic performance of Co(II)L, the concentration of catalyst in reaction was investigated in the following study. Table1 shows the results of the relative viscosity of hydroxylpropyl guar gum oxidized catalyzed by various concentrations of catalysts ranged from 1 to 15% (molar ratio to H_2O_2). The obtained results indicated that the viscosity of hydroxypropyl guar gum significantly influenced by catalyst concentration with an optimal value of 10%. The values of relative viscosity quickly increased when the amount of catalysts was raised from 1 % to 10 %, and then gradually drop off with increase of the catalyst amount was raised from in the range of 10-15 %. Above 10%, since the reactive sites were enough, no further increase of the hydroxypropyl guar gum degradation was obtained. Thus, 10% was chosen as the optimum concentration in following experiments. It should be demonstrated that the same effect tendency of the effect of Co^{2+}/ tetraethylenepentamine ratio and concentration of Co(II)L on the degradation indicated their great effect of generation rate of oxidising active species at the initial reaction time around 5 min and will be gradual in the following reaction time.

The temperature plays an important role in chemical oxidation, because it represents a determinant parameter in the kinetics of homogeneous reactions. The effect of reaction temperature was evaluated on degradation of hydroxypropyl guar gum at 20, 25, 30, 35, 40and 45°C using Co(II)L as catalyst. The results shown in Table1 indicate that the reaction rate was significantly influenced by the temperature and the lowest relative viscosity of hydroxypropyl guar gum solution was obtained 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 for the degradation process. Same result has been received by previous research about intensification of the Fenton Process by increasing the temperature. It has been demonstrated that working at a temperature well above the ambient provides a way of intensifying the Fenton process since it allows a significant improvement of the oxidation rate[24].

The typical Fenton oxidation with H2O2-Fe2+ only can be used below the pH 3.0, because of the hydration transformation of Fe2+ to Fe(OH)2 under higher pH value. As a result, a lot of acid should be consumed to reach the discharge standard. The effect of pH on the oxidation process has been studied in previous investigations and was found to be quite significant. The degradation of hydroxypropyl guar gum was examined in the pH range 7-13 with the mass concentration of 0.6% and summarized in Table1. From the results obtained, it can be seen that the reaction was conducted under high pH conditions, and the degradation efficacy decreased with increase in the solution pH up to 13. The generation of reactive oxygen species by Co-based catalyst is pH-dependent since it influences the dissolution and existential state of Co(II) from composites and the evolution of the superoxide radical. It was observed that the hydroxypropyl guar gum degradation was maximum at pH 10, at 10% H2O2 and at 10% catalyst[25].

Table 1. Effect of different conditions on the degradation

Condition	T/min	0	5	10	15	20	25	30	35	40
different metal complexes	Fe^{2+}	22.00	5.05	4.66	4.56	4.31	4.23	4.16	4.09	3.98
	Co^{2+}	22.00	3.07	2.20	1.89	1.72	1.58	1.58	1.49	1.47
	Ni^{2+}	22.00	10.77	9.90	9.58	9.36	9.24	9.11	9.00	8.98
	Cu^{2+}	22.00	7.81	7.14	6.79	6.62	6.41	6.23	6.11	6.00
	Zn^{2+}	22.00	7.09	6.77	5.93	5.44	5.14	4.97	4.88	4.79
Co2+/tetraethy-Lenepentamine ratio	1 : 1	22.00	3.46	2.40	2.05	1.93	1.86	1.79	1.76	1.73
	1 : 2	22.00	3.07	2.20	1.89	1.72	1.58	1.58	1.49	1.47
	1 : 3	22.00	3.96	2.80	2.34	2.11	2.04	1.95	1.93	1.89
concentration of Co(II)L	1%	22.00	4.66	3.13	2.53	2.20	2.01	1.85	1.74	1.70
	3%	22.00	3.07	2.20	1.89	1.72	1.58	1.58	1.53	1.50
	5%	22.00	2.96	2.31	2.03	1.93	1.91	1.67	1.62	1.58
	10%	22.00	2.33	1.85	1.73	1.62	1.54	1.51	1.50	1.47
	15%	22.00	2.40	2.10	2.00	1.95	1.86	1.87	1.84	1.84
reaction temperature	25°C	22.00	15.26	13.24	12.31	11.70	11.70	11.21	10.10	10.03
	30°C	22.00	12.34	11.29	10.01	9.88	9.01	8.26	7.93	7.23
	35°C	22.00	8.62	6.89	6.08	5.54	4.82	4.33	4.14	3.95
	40°C	22.00	8.45	6.13	5.24	4.17	3.41	2.82	2.99	2.86
	45°C	22.00	3.96	2.80	2.34	2.11	2.04	1.95	1.93	1.89
pH	7.00	22.00	10.77	7.79	5.91	4.51	3.97	3.76	3.60	3.52
	9.00	22.00	6.95	5.39	3.72	3.00	2.83	2.70	2.63	2.58
	10.00	22.00	4.07	2.20	1.89	1.72	1.58	1.58	1.49	1.47
	11.00	22.00	5.09	3.09	2.73	2.58	2.25	1.95	1.88	1.75
	13.00	22.00	4.85	3.01	2.47	2.38	2.18	1.57	1.31	1.29

3.4 Proposed Mechanism

The possible catalytic mechanism in the degradation process has been proposed based on the UV spectra results of ligand (L), corresponding complex (Co(II)L) and the complex after oxidation (Co(II)L+H2O2). From the results shown in Figure 1, it was found that the electronic spectrum of the ligand shows bands at 196, 223 and 314 nm. It was found that tetraethylenepentamine and the corresponding Co(II)L complex show similar UV spectra and obvious absorbance peaks at 190 and 260 nm, and the intensity of Co(II)L is much higher than that of tetraethylenepentamine, which indicates the coordination of Co2+ with tetraethylenepentamine as shown in Scheme 1. The UV spectra changed greatly when H2O2 was added in Co(II)L solution, and the absorption peak at 196 nm increase and move to higher wavelength, and the peak at 223 nm increase[26], which should be contributed to the coordination of H2O2 with Co(II)L. By this coordination with Co(II)L, H2O2 can be activated and generate ·OH radicals. As a result, the activity and stability of Co2+ can be greatly enhanced by coordination which made the complex become high stable even in the reaction condition with high pH[27].

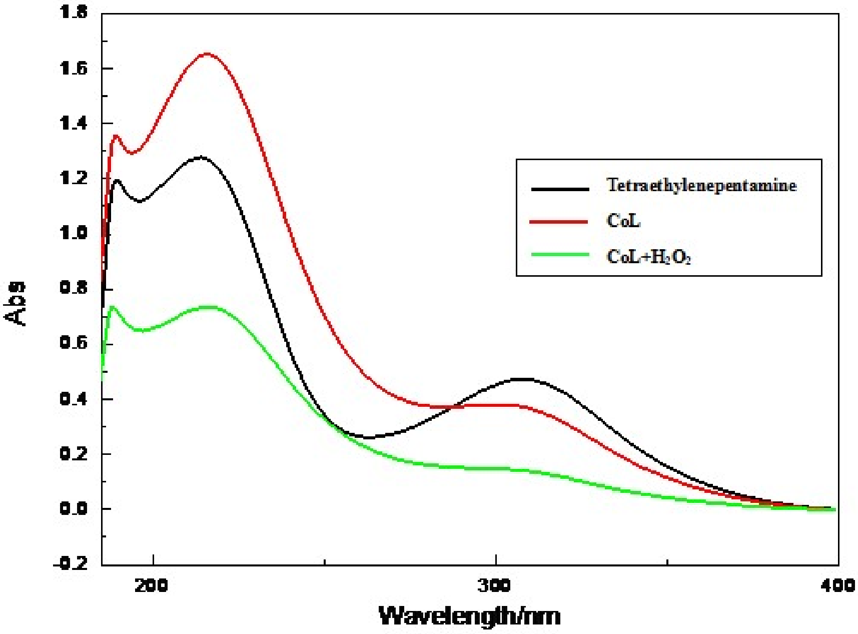

Figure 1. UV spectra of ligand and the corresponding Co(II) complex

3.5 Change of Molecular Weight

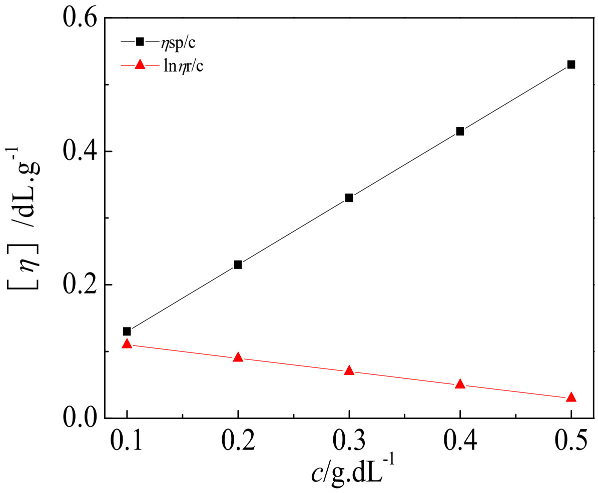

Figure 2. ηsP/c-c and lnηr/c-c

To determine the degree of degradation, relative molecular weight of the polymer catalyzed by Co(II)L was determined by the intrinsic viscosity ([η]) derived from specific viscosities (ηsp=ηr-1) and relative viscosity (ηr) over a range of polymer concentrations with 10% H2O2 at 45°C and pH 9. Reduced values of both ηsp and ηr were extrapolated to zero to obtain the intrinsic viscosity [28]. From the results shown in Figure 2, the viscosity average molecular weight of hydroxypropyl guar gum obviously decreased to 2797 after oxidation treatment. Furthermore, the specific viscosities measured at 45°C showed a complicated dependence on polymer concentration. It is possible that values of ηsp/c at low polymer concentrations are affected by adsorption of the capillary wall.

3.6 COD Removal

Hydroxypropyl guar gum, polyacrylamide (PAM) and carboxymethyl cellulose (CMC) are commonly used during fracturing process in oilfield, so the COD removal experiments of the proposed catalyst were carried out on the three polymers to evaluate its catalytic oxidation. The three polymers with the mass concentration of 0.6% were oxidized by 100% H2O2 (the demand of H2O2 to oxidize the polymer to CO2 and H2O) at 45°C and pH 10. According to Figure 3, it can be seen that the COD removal efficiency of guar gum, PAM and CMC was 68.4, 52.9 and 57.4% within 45 min, respectively, after 240 min at same conditions the removal efficiency was changed to 97.7, 93.5 and 93.7%. The results showed that Co(II)L had great catalytic degradation performance to various polymers. This degradation trend was in agreement with previous report which illustrated PAM is difficult to be oxidized due to its stable C-C [29].

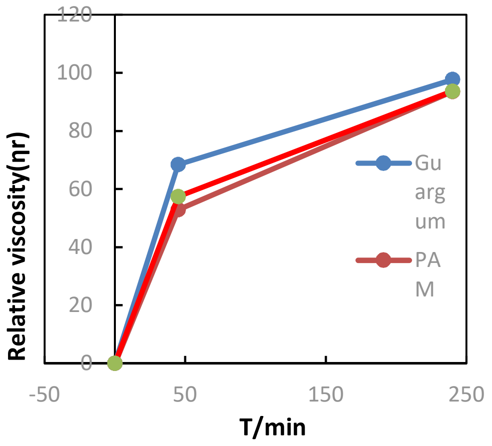

Figure 3. COD study of Co(II)L catalyzed oxidation of different polymers

4. Conclusion

A series of transition metal-tetraethylenepentamine complexes was prepared for Fenton oxidation catalysts under high pH value. The catalysts were screened by the viscosity reduction of hydroxypropyl guar gum solution oxidized by H2O2, among which Co(II)L exhibits high catalytic performance for degradation of hydroxypropyl guar gum in a wide pH range of 7.0-14.0, and the viscosity of hydroxypropyl guar gum can be reduced effectively with 10.0% H2O2 (mass ratio to hydroxypropyl guar gum) and 10.0% Co(II)L (mass ratio to H2O2). Obviously reduce of the relative molecular mass can be obtained from 2 million to 2797 and the COD removal efficiency was greatly enhanced from 185 mg/L to 8080 mg/L with enough H2O2 within 4 h in presence of the proposed catalyst[30,31]. Moreover, the degradation catalyzed by Co(II)L can be carried out for various polymers at high pH value up to 10, a high concentration of OH-, causing the formation of metal hydroxide if copper salt was used as catalyst directly. The results offer an attractive alternative in the disposing of the recalcitrant fracturing waste water.

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