

Degradation of hydroxypropyl guar gum at wide pH range by a heterogeneous Fenton-like process using bentonite-supported Cu(0)

Ling Zhou, Zhongying Xu, Jie Zhang, Zhifang Zhang and Ying Tang

ABSTRACT

To seek for efficient Fenton-like oxidation processing for treatment of waste fracturing fluid containing hydroxypropyl guar gum (HPGG), in heterogeneous reaction, five bentonite-supported zero-valent metal catalysts were prepared by liquid-phase reduction. The results showed that the bentonite-supported zero-valent copper exhibited best catalytic performance, attributed to the high dispersion of active sites of zero-valent copper. The effects of the most relevant operating factors (H_2O_2 concentration, catalyst dosage, temperature and pH) were evaluated in detail. Moreover, the chemical oxygen demand removal rate of HPGG can achieve 76% when the reaction time was selected at 45 min under optimal experimental conditions. The stability evaluation showed that the catalytic performance was almost unaffected after the catalyst was recycled and used once more showing the good stability of the bentonite-supported zero-valent copper in the application process.

Key words | heterogeneous oxidation, hydroxypropyl guar gum, zero-valent copper

HIGHLIGHTS

- An efficient supported catalyst was prepared for the Fenton reaction.
- The prepared catalyst has great catalytic performance for the degradation of polymers at high pH level.
- The prepared catalyst has great stability and can be reused many times.

INTRODUCTION

Hydraulic fracturing of wells during oil and gas exploration consumes a lot of fresh water and generates large volumes of polluted wastewater (Hickenbottom *et al.* 2013). The development of unconventional oil and gas resources usually results in the production of wastewater containing chemical additives and components from the depths of the formation (Mumford *et al.* 2018), such as oil, polyacrylamide, methanol, emulsions, cuttings and clay particles. Under high temperature working conditions, the oil extraction wastewater is characterized as corrosive due to high chemical oxygen

demand (COD), high salinity and strong acidity (Dai *et al.* 2019). If the wastewater is not disposed of in time, after a long period of storage, the release of a strong smell into the environment will become a threat to public health and cause environmental pollution. Hydroxypropyl guar gum (HPGG), polyacrylamide (PAM) and carboxymethyl cellulose (CMC) are widely used as thickeners during fracturing (Tang *et al.* 2019); they are the main cause of high COD and are hard to deal with effectively.

Currently, the policy agenda of many countries gives priority to wastewater treatment for environmental protection development (Kunjachan *et al.* 2017). Advanced oxidation processes, especially Fenton oxidation, have been shown to be effective and suitable processes for the abatement of persistent and recalcitrant water pollutants (Goi *et al.* 2008; Trapido *et al.* 2009; Dulova *et al.* 2011).

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However, traditional homogeneous Fenton catalysts work only in limited pH range to avoid the precipitation of iron, and the production of iron sludge needs a separation (Yang *et al.* 2015), which makes them uneconomical and limited in application. Heterogeneous Fenton-like processes have the advantage that they produce minimal sludge and coproducts (Zárate-Guzmán *et al.* 2020) and the working pH range is relatively wide (pH 3–7) (Lam *et al.* 2007); thus they are considered to be environmentally friendly. In the progress of the technology, the combinations of Fenton-like oxidation and zero-valent metals, such as iron, copper, nickel and zinc, have played a significant role in organic wastewater treatment (Chand *et al.* 2009). ElShafei *et al.* (2017) prepared the nano-zero valent metals of Fe, Cu, and Ni and examined them in degradation of nonylphenol (6 mg/L) by ultrasonic-assisted (20 kHz) Fenton-like process at the neutral pH under room temperature. Similarly, Babuponnusami & Muthukumar (2012) presented the removal of phenol using nano-zero valent iron in a heterogeneous photoelectro Fenton-like system, and they found that the removal efficiency was increased with an increase of nano-zero valent iron dosage, whereas it decreased with increase of initial phenol concentration and initial pH. However, it should be pointed out that zero-valent metals has some application limitations such as easy aggregation (Chen *et al.* 2011), difficult separation (Pliego *et al.* 2015) and low stability (Shi *et al.* 2011). Moreover, few research studies have explored the effective degradation of oilfield polymers containing HPGG through the heterogeneous Fenton-like processes using zero-valent metal catalyst at wide pH range. Therefore, it is meaningful to explore an appropriate heterogeneous catalyst to degrade wastewater of oil well drilling to an acceptable level.

Recently, it has been found that the dispersion of zero-valent metal particles can be enhanced by using porous materials as mechanical supports (Uezuem *et al.* 2009). Bentonite can be used as a good carrier due to its abundance, unique structural characteristics and good mechanical stability. In our research, five zero-valent metals are supported on the surface of bentonite as active phase to promote the heterogeneous Fenton-like reaction. The present study focuses on the following four objectives: (1) synthesis and screening of the bentonite-supported zero-valent metals; (2) characterization of the optical catalyst with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) technology; (3) evaluations of the relevant factors on HPGG degradation, such as H₂O₂ concentration, catalyst dosage, the temperature and pH; (4) free radical analysis and stability evaluation of the optimal catalyst.

MATERIALS AND METHODS

Materials

All chemicals used were of analytical grade without further purification. Hydrogen peroxide solution was 30% volume ratio to water. Bentonite was obtained from Fengyun Chemical Co., Ltd, Xi'an, China. HPGG with molecular weight of about 2 million was obtained from Changqing Oilfield. CMC and PAM (purity > 95%) were obtained from Xinhe Environmental Protection Co., Zhengzhou, China.

Synthesis of the bentonite-supported zero-valent metal nanoparticles

The bentonite-supported zero-valent metals were prepared by using conventional liquid-phase reduction where bentonite acted as a support material. Theoretically, the mass ratio of bentonite to metal in the supported catalyst was 1:1. Firstly, 4.53 g FeCl₂, 4.41 g CoCl₂, 4.28 g NiCl₂, 4.23 g CuCl₂ and 4.17 g ZnCl₂ were dissolved in a 100 mL beaker with distilled water, respectively. Then, about 2 g of bentonite was added in turn and the solution was stirred for 24 h so as to complete full exchange of metal ions in the chloride with cations on bentonite. Subsequently, a freshly prepared 0.13 M NaBH₄ solution (100 mL) was added into the mixture with constant stirring for 30 min under nitrogen atmosphere as described by Huang *et al.* (2012). Finally, the formed sample was centrifuged and washed three times with absolute alcohol and dried overnight at 80 °C for further using.

Characteristic analysis

SEM was performed with a JSM-6390A with 20.0 kV of an accelerating voltage. XPS measurements were carried out on an ESCALAB250Xi electron spectrometer using 300 W Al K_α radiations.

Fenton-like oxidation process

HPGG, CMC and PAM, weighing 1.2 g, were dissolved in 200 mL distilled water respectively, stirred at room temperature for 30 min and then settled for 12 h to make them completely swollen. The degradation experiments were conducted in a 10 mL Ubbelohde viscometer. Firstly, 5 mL HPGG glue (0.6%, w/w), a certain concentration of H₂O₂,

a certain amount of catalyst and distilled water were added in a small beaker and mixed uniformly by stirring. Then, the mixture was poured into the Ubbelohde viscometer at desired temperature and the absolute viscosity of glue solution was measured intermittently at different periods (0, 5, 10, 15, 20, 25, 30, 35 and 40 min) (Gu *et al.* 2013). In Fenton-like process, H_2O_2 concentration, pH value, catalyst amount and reaction temperature were studied thoroughly because of their significant effects on oxidation capacity. The initial pH was settled at 7 and then was adjusted to a designed value by adding sodium hydroxide solution (0.1 M). The COD values of polymers before and after degradation were determined by standard potassium dichromate method (Alves *et al.* 2010). Excessive H_2O_2 and appropriate amount of catalyst were required in order to remove most polymers under the optimal experimental conditions. The experimental data was obtained in triplicate to ensure the

relative errors could be minimized, and the results presented here represent the average values of independent measurements. Recovered experiments were performed to evaluate the stability of the supported catalyst by centrifuging after each cycle.

RESULTS AND DISCUSSION

Effect of the bentonite-supported zero-valent metals on HPGG degradation

Figure 1 shows the degradation of HPGG gum solution with the mass concentration of 0.6% by 6,000 mg/L H_2O_2 catalyzed by the bentonite-supported Fe(0), Co(0), Ni(0), Cu(0) and Zn(0) at 45 °C and pH 7.0. It can be found that the catalytic performance of all of the bentonite-supported catalysts kept improving during the initial 20 min and remained stable after 30 min if 6,000 mg/L H_2O_2 concentration and 6 g/L of catalyst were used. Among them, the viscosity reduction rate of HPGG catalyzed by the bentonite-supported zero-valence copper could be significantly enhanced. And the highest degradation performance reflected by the greatest absolute viscosity drop of HPGG from 18 mm²/s to 1.5 mm²/s was observed after 40 min, which might be due to the large specific surface area and large number of active sites (Elshafei *et al.* 2014). Therefore, the bentonite-supported zero-valent copper was used as catalyst for further experiments.

Characterization of the bentonite-supported zero-valent copper

The structure and morphology of the bentonite and the bentonite-supported zero-valent copper catalyst were analyzed by SEM at 20,000 times magnification and shown in Figure 2.

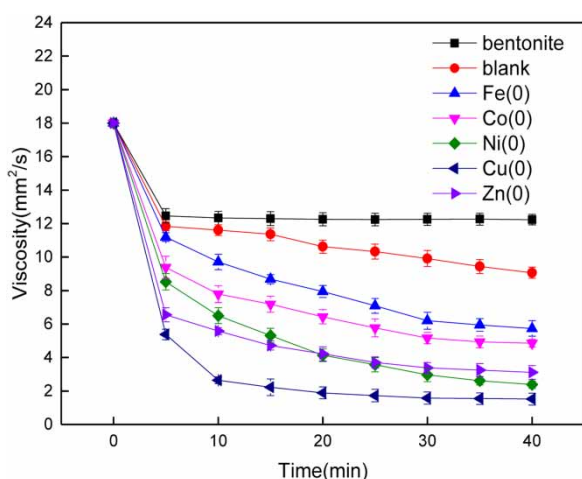


Figure 1 | Effect of the bentonite-supported zero-valent metals on HPGG degradation. Experimental conditions: 45 °C, pH = 7.0, $[\text{H}_2\text{O}_2] = 6,000$ mg/L, catalyst dosage = 6.0 g/L.

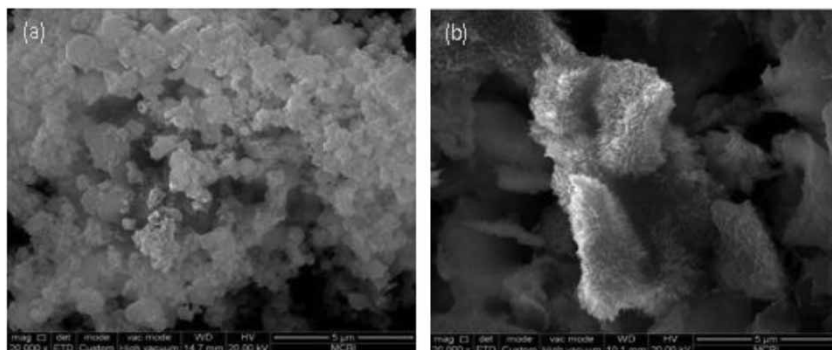


Figure 2 | SEM images of the bentonite (a) and the bentonite-supported zero-valence copper (b).

Figure 2(a) shows that the bentonite was composed of an aggregate of flake particles with smooth surface (Neetu et al. 2009), while Figure 2(b) clearly shows that the bentonite-supported zero-valent copper catalyst appeared as scattered clusters indicating the high dispersion of zero-valent copper. Consequently, it is suggested that the prepared supported zero-valent copper catalyst could effectively promote the catalytic effects of the fracturing wastewater containing HPGG.

XPS can be used to determine the chemical composition of samples as well as the oxidation state of the species (Su et al. 2011). Therefore, XPS technology was used to characterize the bentonite-supported zero-copper, shown in Figure 3. The photoelectron peak for C 1s at 284.8 eV is used for energy calibration. The binding energy peak at 933.67 eV can be assigned to Cu(0), indicating the presence of zero-valent copper supported on the bentonite (Zhu et al. 2016). In addition, it is worth mentioning that the small peak at 935.77 eV indicates a Cu(II) oxidation state, mainly caused by atmospheric oxygen.

Effect of H₂O₂ concentrations, catalyst dosage, the temperature and initial pH on HPGG degradation

In the Fenton-like processes, H₂O₂, as the dominant source of OH· under catalysis, plays a critical role in the treatment of organic wastewater. The effect of dosing of H₂O₂ on viscosity reduction rate was investigated under the operating conditions (T = 45 °C, pH = 7.0, catalyst dosage = 6.0 g/L). It can be found from Figure 4 that viscosity reduction rate increased observably with increasing the concentrations of H₂O₂ from 600 mg/L to 6,000 mg/L. During the initial

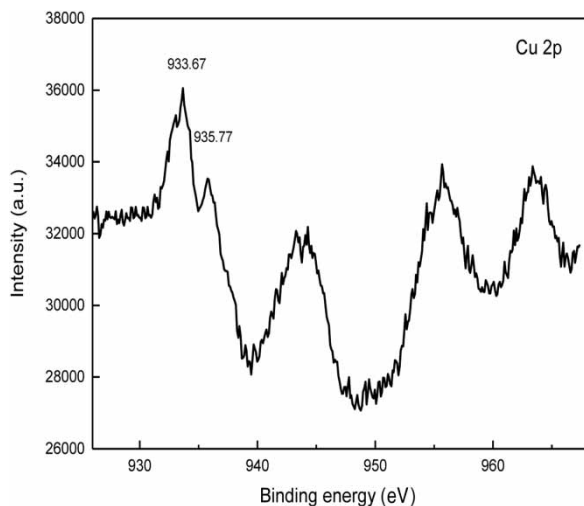


Figure 3 | The oxidation state of copper in the bentonite-supported zero-valent copper catalyst.

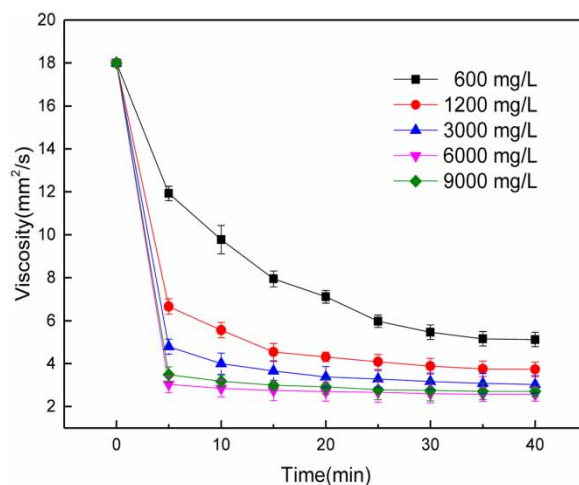
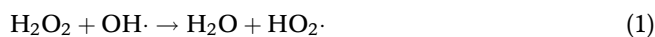


Figure 4 | Effects of H₂O₂ concentrations on HPGG degradation. Experimental conditions: 45 °C, pH = 7.0, the bentonite-supported zero-valent copper dosage = 6.0 g/L.

10 min, the highest viscosity reduction rate of HPGG was obtained, which was due to the production OH· by the accelerated decomposition of H₂O₂. The best degradation efficiency reflected by the great decrease of absolute viscosity of HPGG from 18 mm²/s to 2.55 mm²/s was found at 40 min when 6,000 mg/L H₂O₂ was used. However, the effect of reduction effect began to drop down when H₂O₂ dosage exceeded 6,000 mg/L due to the well-known hydroxyl radicals scavenging effect through Equations (1) and (2) (De Laat & Le 2006). In this case, although HO₂· radicals are produced with more H₂O₂ used, their oxidation potential is much weaker than that of OH· species (Ramirez et al. 2007). Hence, 6,000 mg/L was chosen as the optimum concentration of H₂O₂ in subsequent experiments.



An increase in the catalyst dosage is beneficial to improve the removal efficiency of the contaminant in the wastewater. However, excessive adding of catalyst may have a negative effect in the heterogeneous Fenton-like processes. Therefore, optimization of the solid catalyst should be conducted in wastewater treatment. Figure 5 shows the changes in HPGG absolute viscosity oxidized by 6,000 mg/L H₂O₂ over various amount of catalyst ranging from 0.6 g/L to 9 g/L at 45 °C and pH 7.0. Evidently, the viscosity reduction rate of HPGG could be significantly enhanced with increasing catalyst dosage in the range from 0.6 g/L to 3.0 g/L. However, lower viscosity reduction was obtained when using 3.0 g/L catalyst, so further adding of

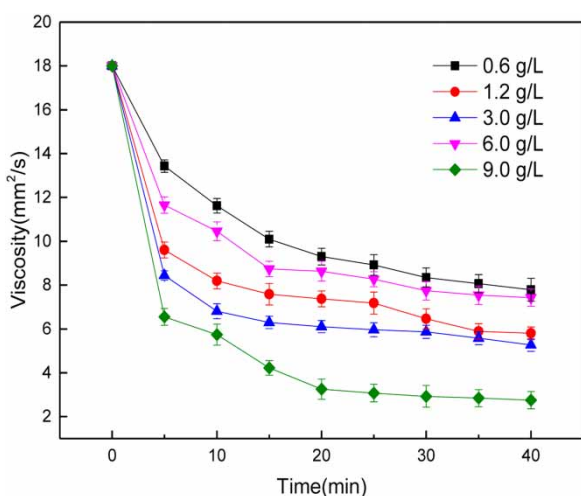


Figure 5 | Effects of the bentonite-supported zero-valent copper dosage on HPGG degradation. Experimental conditions: 45 °C, pH = 7.0, [H₂O₂] = 6,000 mg/L.

catalyst is not necessary. In fact, the generated OH· would be consumed by the excess catalyst in the aqueous solution as suggested by Wang *et al.* (2016). In addition, considering the preparation cost of the solid catalyst, 6.0 g/L was selected as the optimum dosage.

Temperature has a significant effect on the degradation efficiency of polymers, since the thermal degradation reaction will exhibit an Arrhenius-type behavior with increasing the activation energy (Wang *et al.* 2017). Considering the application temperature of HPGG in an oilfield, Figure 6 shows the variation of absolute viscosity of HPGG solution in presence of 6 g/L catalyst and 6,000 mg/L H₂O₂. The blank without H₂O₂ and catalyst showed that

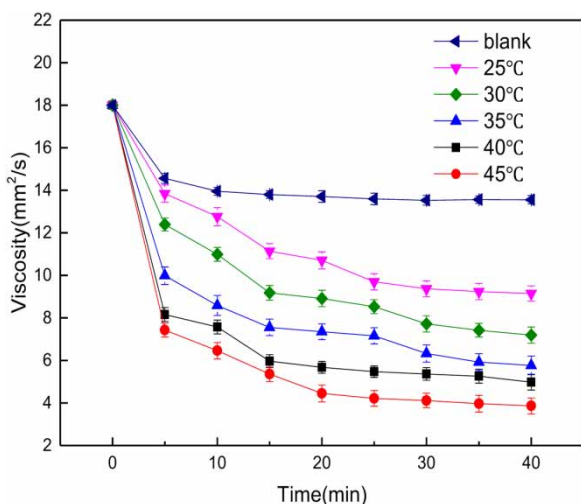


Figure 6 | Effects of the temperature on HPGG degradation. Experimental conditions: pH = 7.0, [H₂O₂] = 6,000 mg/L, the bentonite-supported zero-valent copper dosage = 6.0 g/L.

HPGG had limited biodegradability. However, the viscosity reduction rate of HPGG observably improved in the experiment group with the increase of temperature. Almost 79.1% of viscosity reduction rate was achieved after 40 min at a higher temperature of 45 °C. The possible reason is that higher temperature can provide enough energy to overcome the reaction activation energy and then accelerate the reaction rate by increasing the reaction rate constant according to the Arrhenius equation (Iebuegu & Ezenwa 2011). Taking energy consumption into account, 45 °C was selected as the optimum temperature in this work.

In previous studies, the researchers generally reached the conclusion that pH 3 was the best reaction condition (Yuan *et al.* 2013; Yang *et al.* 2014); however, Feng *et al.* (2012) revealed that neutral (pH 6) and slightly alkaline (pH 9) conditions could treat the organic waste water effectively. Since the heterogeneous reaction has revealed some satisfactory results in wastewater treatment under neutral/alkaline conditions, great effort has been made to broaden the pH range in view of the alkaline nature of the oilfield sewage. Figure 7 shows the change of absolute viscosity of HPGG solution with pH values at the same reaction condition of 6,000 mg/L H₂O₂ and 6 g/L catalyst at 45 °C. Obviously, the viscosity reduction rate increased when pH increased from 8 to 9 compared with the blank (pH = 7.0), and then decreased gradually when pH was raised from 10 to 11. The results showed that the bentonite-supported zero-valent copper catalyst has good alkali resistance, which could be attributed to the activities of zero-valent copper

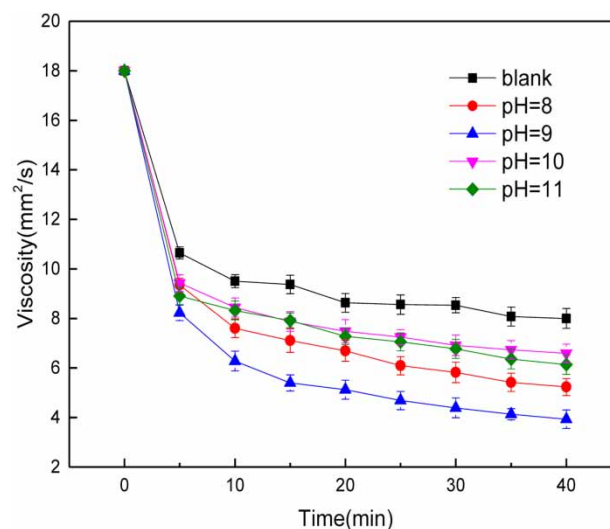


Figure 7 | Effects of the initial pH on HPGG degradation. Experimental conditions: 45 °C, [H₂O₂] = 6,000 mg/L, the bentonite-supported zero-valent copper dosage = 6.0 g/L.

rather than the solubility of metal ions on the catalyst surface (Wang *et al.* 2016). Therefore, the most suitable pH value is selected as 9 in following experiments.

Determination of COD

It has been widely accepted that HPGG, PAM and CMC can be used as thickeners during the oil fracturing process (Tang *et al.* 2019), so the three polymers were chosen to evaluate the COD removal of the bentonite-supported zero-valent copper/ H_2O_2 oxidation process. As can be seen from Figure 8, the COD removal rate of the three polymers increased as the reaction time increased. Almost 76, 70 and 68% of COD removal was achieved after about 45 min of reaction for COD₀ 8,747, 7,147, and 6,800 mg/L, respectively. The maximum COD removal rate of HPGG, PAM and CMC increased to 93, 91 and 92% at the reaction time of 240 min, respectively. In fact, as shown in Figure 9, guar gum is a kind of natural linear galactomannan gum consisting of a linear backbone of β -1,4 linked mannose units and randomly attached α -1,6 linked galactose units as side chains (Moreira 2008) indicating that it is more easily degraded than the other two polymers because of the easy decomposition characteristics of side chain galactose.

Free radical analysis and stability evaluation

In order to further understand the degradation mechanism of HPGG, radical quenching experiments were carried out. It is well known that 2-propanol can act as an effective

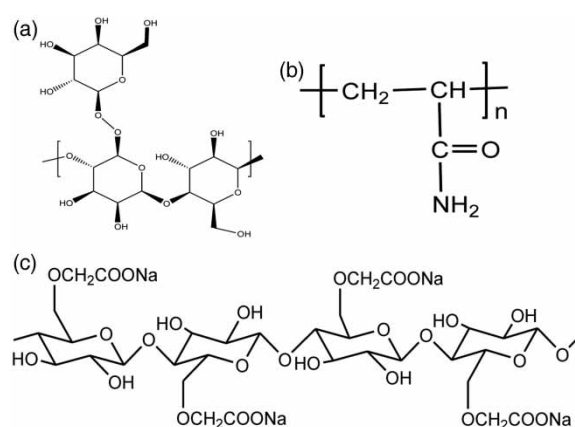


Figure 9 | The structure of guar gum (a), PAM (b) and CMC (c).

scavenging agent for $OH\cdot$ (Ji *et al.* 2013). In this study, methanol was used to explain the role of hydroxyl radical. As depicted in Figure 10, the viscosity reduction rate of HPGG decreased with relatively low concentration of methanol (50 mM) compared with the blank group at the same time, and the degradation effect was obviously inhibited while methanol was at higher concentration (100 mM), indicating that $OH\cdot$ was the dominant reactive oxygen species in presence of the bentonite-supported zero-valent copper.

In heterogeneous Fenton-like processes, the stability of recycled catalyst is of great importance from synthesis and economical points of view (Saeedi *et al.* 2013). Hence, the recycling of the bentonite-supported zero-valent copper catalyst was investigated. The absolute viscosity of the reused

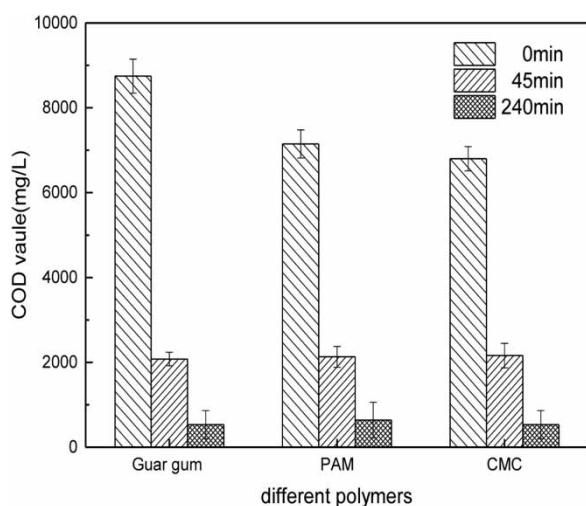


Figure 8 | COD values of three polymers before and after degradation. Experimental conditions: 45 °C, pH = 9.0, the bentonite-supported zero-valent copper dosage = 6.0 g/L, $[H_2O_2] = 9,000$ mg/L.

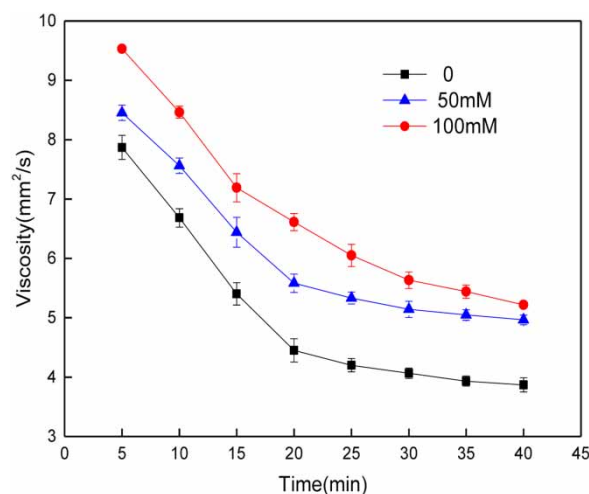


Figure 10 | Inhibitory effects of methanol on HPGG degradation. Experimental conditions: 45 °C, pH = 9.0, the bentonite-supported zero-valent copper dosage = 6.0 g/L, $[H_2O_2] = 6,000$ mg/L.

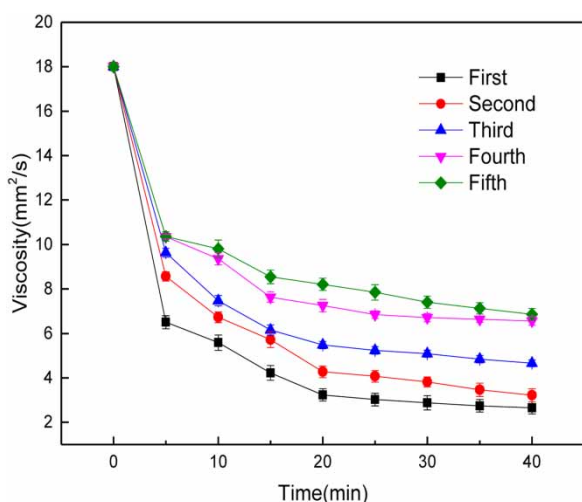


Figure 11 | The stability of the bentonite-supported zero-valent copper in repeated cycles of HPGG degradation. Experimental conditions: 45 °C, pH = 9.0, $[H_2O_2] = 6,000$ mg/L, the catalyst dosage = 6.0 g/L.

catalyst, recovered by centrifuging after each cycle, was measured at 45 °C and pH 9. As shown in Figure 11, the performance of viscosity reduction was almost unaffected after being reused twice at 45 min, changing from 85.2% to 82.1%, which showed the good stability of the supported catalyst in the application process. After five consecutive cycles, the viscosity reduction ratio decreased probably caused by the reduction of the specific surface area of the bentonite-supported zero-valent copper.

CONCLUSIONS

In this paper, five bentonite-supported zero-valent metal catalysts were prepared for catalytic degradation of HPGG solution so as to achieve the purpose of polymer wastewater treatment at wide pH range. The results showed that the bentonite-supported zero-valent copper exhibited high catalytic performance reflected by a large absolute viscosity drop of HPGG from 18 mm²/s to 1.5 mm²/s within 40 minutes. The high efficient degradation performance could be attributed to high dispersion morphology of the supported Cu(0) catalyst, and the XPS analysis demonstrated the presence of zero-valent copper on bentonite. Over 76% COD removal rate of the HPGG can be achieved when 9,000 mg/L H₂O₂ and 6 g/L bentonite-supported Cu(0) were used after 45 min at 45 °C and pH 9.0. The results will provide an attractive method for fracturing wastewater treatment containing HPGG in heterogeneous Fenton-like systems.

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DATA AVAILABILITY STATEMENT

All the data in this study are available on request to the corresponding author.

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