Photo-Fenton degradation of ethyl xanthate catalyzed by bentonite-supported Fe(II)/phosphotungstic acid under visible light irradiation

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ABSTRACT

In this study, using bentonite-supported Fe(II)/phosphotungstic acid composite (HPW-Fe-Organicbent) prepared by mechanochemical synthesis as heterogeneous catalyst, the photo-Fenton degradation of ethyl xanthate under visible light irradiation was studied in detail. The results showed that the degradation of ethyl xanthate was mainly impacted by H2O2 dosage, catalyst dosage and reaction time. HPW-Fe-Organicbent catalyst had a wide applicable range of pH and kept a high catalytic activity even at high pH in the photo-Fenton degradation of ethyl xanthate. It was found that the degradation of ethyl xanthate in the photo-Fenton process catalyzed by HPW-Fe-Organicbent mainly resulted from the hydroxyl radicals. HPW-Fe-Organicbent had an excellent stability in use, and retained almost all of its catalytic activity for four recycling times. Moreover, the kinetics study showed the degradation of ethyl xanthate, with the initial concentration below 50 mg/L, was well fitted by the pseudo-first-order rate model.

INTRODUCTION

Alkyl xanthates as efficient and common sulfide collectors are widely used in froth flotation of sulfide minerals. However, in mineral flotation processes, alkyl xanthates can remain in tailings and flotation effluents, and a large amount of flotation wastewater containing alkyl xanthates is produced. Due to the toxicity of alkyl xanthates, the flotation wastewater can cause severe environmental pollution, and has become an ecological issue in some areas of mineral processing. It has been reported that alkyl xanthates can be removed from flotation wastewater by some methods, including flocculation coagulation, physical adsorption and bioremediation (Cheng et al. 2012). However, compared with these methods, the method of advanced oxidation process has been proposed as an alternative approach to degrade the residual xanthates in the flotation effluent due to no secondary pollution, high efficiency of xanthate removal, relatively low treatment costs, and short treatment time (Molina et al. 2013). Photo-Fenton as an advanced oxidation process has been proven to be a promising technology for wastewater treatment (Trabelsi-Souissi et al. 2011). However, the homogeneous photo-Fenton process has some significant drawbacks, including narrow applicable range of pH, difficult separation of catalyst, and no reuse of catalyst (Zhang et al. 2013). Therefore, many efforts have been made to develop heterogeneous photo-Fenton catalysts for the immobilization of active iron species on various supports (Gumy et al. 2005; Guo et al. 2013; Lan et al. 2015). Heteropolyacid (HPA) is a multi-function catalyst among the most promising catalysts because of its special catalytic action and wonderful application foreground (Okuhara et al. 1996), and photo-catalysis catalyzed by HPA under visible light irradiation is a new branch in the field of photo-catalytic chemistry (Hu & Xu 2004; Wei et al. 2012; Zhang et al. 2013; Mokbel et al. 2015; Huang et al. 2017). Recently, some attractive progress in the HPA-catalyzed photo-Fenton process has been made (Hu & Xu 2004; Kamiya et al. 2008; Zhang et al. 2013). Due to the low specific surface area of HPA, incorporation/impregnation of HPA on inorganic mesoporous materials, such as mesoporous molecular sieves (MCM-41),
mesoporous silicas (SBA-15), carbon gels, and c-alumina (Kim et al. 2007), has been applied. Unfortunately, the high solubility of HPA in polar solvents makes it relatively difficult to be immobilized on the above mesoporous materials (Nowińska & Kaleta 2000). At present, chemical immobilization has become a very popular approach for the immobilization of HPA. Through this method, the surfaces of mesoporous materials are modified by grafting appropriate organic reagents to provide anchoring sites for the successful immobilization of phosphotungstic acid (H₃PW₁₂O₄₀, HPW) (Kim et al. 2007; Zhang et al. 2010), which is a common HPA compound with Keggin structure. Even so, porous materials with good properties, such as big specific surface area, relatively high chemical activity and accessibility of organic reagents, are needed for immobilization of HPW.

Bentonite has a large surface area and pore volume with uniform micropore size distribution. Moreover, bentonite is made up of a primary mineral called montmorillonite. Montmorillonite is a layered and dual-dimensional mineral which consists of hydrated aluminum silicate. The crystal unit of montmorillonite is a tetrahedral-octahedral-tetrahedral (TOT-type) layer structure, which is assembled by two silicon-oxygen tetrahedral sheets fused to one edge-shared aluminum-oxygen octahedral sheet. The interlayer cations in the crystal of montmorillonite can be exchanged, i.e. the cation exchange property of bentonite (Gumy et al. 2005; Zhang et al. 2015). Due to the relatively low costs, quite abundant sources, high stability in acidic or alkaline environments and cation exchange property, bentonite clay has become a good candidate as catalyst support (Ramírez et al. 2010; Zhang et al. 2013). Mechanochemical synthesis (MCS), as a technique of solid-phase synthesis, has been regarded as an effective, simple and environmentally friendly way to prepare some solid composites (Deris et al. 2014; Terzić et al. 2015). Using bentonite as support, a photo-Fenton catalyst of bentonite-supported Fe(II)/HPW composite (HPW-Fe-Organicbent), which has excellent catalytic activity under visible-light, has been prepared through the method of MCS using a high energy ball milling in our recent work (Wei et al. 2018).

In this work, to gain information of treatment of a xanthate-type sulfide collector with the prepared HPW-Fe-Organicbent by photo-Fenton process, the degradation of ethyl xanthate, a typical xanthate-type sulfide collector and widely used in froth flotation, under visible light irradiation has been studied in detail. The ethyl xanthate was effectively removed through the treatment system of photo-Fenton catalyzed by HPW-Fe-Organicbent. The results also showed HPW-Fe-Organicbent had a wide applicable range of pH for ethyl xanthate treatment and had a long-term stability in use.

EXPERIMENT

Materials

Bentonite (chemical grade) was obtained from Xilong Chemical Company Limited. The specific surface area of bentonite was about 80.5 m²/g, and the mean pore diameter of bentonite was about 7.2 nm. FeSO₄·7H₂O and H₂O₂ (40%) were of analytical grade and supplied by Shanghai Guanghua Chemical Company Limited. Cetyltrimethylammonium bromide (CTMAB) and HPW were of analytical grade and supplied by Shanghai Chemical Reagent Company. Ethyl xanthate (C₂H₅OCS₂Na) was of chemical grade and purchased from Shanghai Haisheng Chemical and Mechanical Company Limited.

MCS of bentonite-supported Fe(II)/HPW composite

As has been reported in our previous work (Wei et al. 2018), the MCS of bentonite-supported Fe(II)/HPW composite was carried out in a 100 mL milling chamber, in which 20 mL of Φ20 balls plus 10 mL of Φ6 balls provided a grinding medium, using an ND8 planetary ball mill (Nanjing University Tianzun Electronic Co., Ltd, China). One gram of bentonite and 0.14 g of FeSO₄·7H₂O were added into the milling chamber, and the powder mixtures in the chamber were subjected to milling for 15 min at motor frequency of planet carrier (MFPc) 10 Hz. Then, 0.11 g of CTMAB was added quickly, and the mixtures were milled for another 15 min at MFPc 40 Hz. After that, 0.5 g of HPW was added, and the new mixtures were milled for 25 min at MFPc 20 Hz. After the mechanical milling, the milled materials were taken out and thoroughly washed with deionized water. Subsequently, the solid product was dried overnight at 105 °C in an oven. The obtained composite was bentonite-supported Fe(II)/HPW composite, named as HPW-Fe-Organicbent, which was ground to less than 0.15 mm.

Characterization of catalyst

UV–visible (UV–Vis) diffuse reflectance spectra (DRS) of the composite were measured by using a PE Lambda 650s UV–Vis spectrophotometer. Pore structure of the composite, degassed under vacuum at 473 K for 5 hours, was measured
by N₂ adsorption-desorption isotherm at 77 K using a surface area and porosimetry analyzer (Tristar 3032, Micromeritics, USA).

Heterogeneous photo-Fenton degradation of ethyl xanthate

Photo-Fenton degradation of ethyl xanthate catalyzed by HPW-Fe-Organicbent under visible light irradiation was carried out in a self-constructed photo-Fenton reactor equipped with a fluorescent high-pressure mercury lamp (380–780 nm). The schematic diagram of the reactor is shown in Figure 1. The vertical distance between the lamp and the liquid level is about 30 cm, and the irradiation luminance of visible light at the surface of ethyl xanthate solution was about 7,000 lux. After the HPW-Fe-Organicbent was dispersed into the ethyl xanthate solution, the degradation reaction started with adding a certain amount of H₂O₂ to the suspension. During reaction, an electromagnetic stirrer was applied to ensure good dispersion. The solution samples were taken at desired time intervals, and then centrifuged to separate catalyst from the suspension. The remaining ethyl xanthate in sample solution was determined by using a UV–Vis spectrophotometer (UV-1201, BFRL, China) at 301 nm, which is the maximum absorbance wavelength of ethyl xanthate. The catalytic activity of catalyst was evaluated by the removal ratio of ethyl xanthate (η) which was calculated with the following formula:

\[ \eta = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% \]  

where \( C_0 \) and \( C_t \) represent the initial concentration (mg/L) and the time-dependent concentration (mg/L) of ethyl xanthate, respectively.

RESULTS AND DISCUSSION

Characterization of HPW-Fe-Organicbent

In order to investigate the visible-light response of different catalysts, namely bentonite, HPW-Organicbent (without FeSO₄·7H₂O addition), HPW-Fe-Bent (without CTMAB addition), Fe-Organicbent (without HPW addition) and HPW-Fe-Organicbent, UV–Vis DRS measurements of them were analyzed. The results are shown in Figure 2(a). In the visible light region (400–800 nm), the absorbance of bentonite was the weakest, followed by that of HPW-Fe-Bent, the result of which fitted well with the Fourier transform infrared spectroscopy (FT-IR) analysis in the previous work (Wei et al. 2018). From the previous characterization of FT-IR, HPW could be successfully immobilized with the existence of...
CTMAB, because HPW-Fe-Bent contained only $\equiv$Fe$^+$ (Fe$^+$ active component on the catalyst) and almost little HPW actually. Furthermore, the visible light region can be divided into two regions, namely 400–600 nm and 600–800 nm. From the absorbance of five samples in 600–800 nm, it could be noted that the absorbance could improve greatly by adding HPW with the existence of CTMAB. Moreover, in 400–600 nm, the absorbance of HPW-Organicbent showed a smooth trend while that of Fe-Organicbent and HPW-Fe-Organicbent both showed an upward trend, indicating the absorbance could be improved greatly by adding FeSO$_4$$\cdot$7H$_2$O. In conclusion, the strong absorbance in 400–600 nm might be caused by the iron active component on the catalyst, while the strong absorbance in 600–800 nm was closely related to the HPW which was immobilized by CTMAB. Hence, as shown in Figure 2(a), the prepared HPW-Fe-Organicbent which contained three functional components (Fe$^+$, CTMAB and HPW) showed great absorbance in the visible light region, indicating HPW-Fe-Organicbent was a good photo-Fenton catalyst under visible light irradiation.

The N$_2$ adsorption–desorption isotherm and pore size distribution of HPW-Fe-Organicbent are shown in Figure 2(b). The isotherm of HPW-Fe-Organicbent exhibited a type-IV shape with the type-H3 hysteresis loops. According to the IUPAC nomenclature, it could be inferred from the type-H3 hysteresis loops that the pore structure of HPW-Fe-Organicbent was characterized as parallel plate slit or ‘house-of-cards-like’ wedge-shaped pore. Furthermore, some pore properties of HPW-Fe-Organicbent for N$_2$ adsorption–desorption experiments are gained through BJH (Barrett–Joyner–Halenda) adsorption as follows: mean pore diameter was about 19.2 nm; mesopore volume was about 45.83%; macropore volume was about 53.16%. It was clear that HPW-Fe-Organicbent was a catalytic composite with excellent macro-meso pore structure. Regarding the excellent pore structure of HPW-Fe-Organicbent, the macromolecular substances of alkyl xanthates could easily reach the surface of catalytic composite and react with the active component on the catalytic composite (Xia et al. 2014).

Photo-Fenton degradation of ethyl xanthate catalyzed by HPW-Fe-Organicbent

Effect of pH on the degradation of ethyl xanthate

In order to investigate the effect of pH on the degradation of ethyl xanthate catalyzed by HPW-Fe-Organicbent, the degradation of ethyl xanthate was carried out at different pH. As shown in Figure 3, the degradation ratios of ethyl xanthate all reached around 100% in the pH change from 2 to 12. Our finding was significantly different from previous reports (Hu & Xu 2004; Tokumura et al. 2006), in which the effective degradation of organic pollution in the photo-Fenton system occurred at low pH values. It was interesting to note that the removal ratios of ethyl xanthate all kept relatively high percentages even at high pH values in our work. As shown in Figure 3, compared with the removal ratio of 93.3% at pH 6, the degradation ratios at pH 2, 4, 9, and 12 all increased slightly, and the removal ratio was 99.0%, 99.0%, 98.3% and 98.2% at pH 2, 4, 9, and 12, respectively. It is well known that the pH of a homogeneous photo-Fenton system should be adjusted into a strongly acidic range, which favors the Fenton reaction to gain the high degradation efficiency for organic pollution in the wastewater. Furthermore, another reason for the demand of low pH value in the homogeneous photo-Fenton process is that the catalyst of metal ions in the system would produce hydroxide sludge in the high pH range, which usually makes the metal ions lose their catalytic activity. Different from the demand of low pH in the conventional Fenton system, using HPW-Fe-Organicbent as catalyst, the photo-Fenton system had a wide applicable range of pH, and kept a high catalytic activity even at high pH. When pH $<$ 7, the final products were SO$_2$ and S, which made the final removal ratio high after centrifugation, when pH $>$ 7; the final product was SO$_4^{2-}$, which also made the final removal ratio high (Chen et al. 2015). For the broad adaptability of the photo-Fenton system catalyzed by HPW-Fe-Organicbent to the acidic and the alkaline environment, the ethyl xanthate...
solution without adjustment of its pH (ca. 6.64) was used in all subsequent experiments.

**Effect of H₂O₂ dosage and reaction time on the degradation of ethyl xanthate**

As shown in Figure 4, the increase of H₂O₂ dosage from 1.36 mmol/L to 4.08 mmol/L increased the removal ratio of ethyl xanthate. The enhancement of removal ratio by addition of H₂O₂ was due to the increase of hydroxyl radicals produced from H₂O₂. However, there was no significant improvement in removal ratio of ethyl xanthate when the H₂O₂ dosage exceeded 4.08 mmol/L. This was because the scavenging of hydroxyl radicals occurred at the high H₂O₂ concentration through Equations (2) and (3) (Wei et al. 2012), which led to the decrease in the number of hydroxyl radicals in the solution. Hence, 4.08 mmol/L was chosen as the optimum dosage of H₂O₂ in all subsequent experiments.

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{HO}_2 \tag{2}
\]

\[
\cdot\text{HO}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \tag{3}
\]

Moreover, as shown in Figure 4, the removal ratio at different H₂O₂ dosages increased with the reaction time, which was due to the sustainable generation of hydroxyl radical with the reaction time. As for the degradation of ethyl xanthate catalyzed with H₂O₂ dosage of 4.08 mmol/L, the removal ratio increased to 99.0% even at reaction time of 50 min, indicating that the degradation reaction of ethyl xanthate almost reached a balance at 50 min.

**Effect of catalyst dosage on the degradation of ethyl xanthate**

As shown in Figure 5, with the increase of catalyst dosage from 0 to 0.8 g/L, the removal ratio of ethyl xanthate at reaction time of 50 min gradually increased from 57% to 99.8%. With the increase of catalyst dosage, more hydroxyl radicals could be easily generated from H₂O₂, which accelerated the degradation of ethyl xanthate. Moreover, the removal ratio at 50 min catalyzed by 0.8 g/L HPW-Fe-Organicbent was almost the same as the removal ratio catalyzed by 1 g/L HPW-Fe-Organicbent. Therefore, 0.8 g/L was selected as the catalyst dosage for the degradation of ethyl xanthate in all subsequent experiments.

**Comparative experiment and reusability of HPW-Fe-Organicbent**

In order to investigate the reaction function of photo-Fenton catalyzed by HPW-Fe-Organicbent, the catalytic performances were investigated in the degradation experiments under different reaction conditions. As shown in Table 1, the removal ratio of ethyl xanthate by the adsorption of HPW-Fe-Organicbent was only 4%, whereas it reached 99.8% in the photo-Fenton process using HPW-Fe-Organicbent as catalyst. Isopropanol, as one kind of scavenger for hydroxyl radicals, is often used to verify the hydroxyl radicals existing in solution. Compared with the removal ratio of 99.8% in the photo-Fenton process catalyzed by HPW-Fe-Organicbent, when isopropanol was added into the solution, the removal ratio dropped significantly to 77.0%.
reaction solution, the removal ratio in the photo-Fenton process was only about 5%. The results indicated that the removal of ethyl xanthate in the photo-Fenton process catalyzed by HPW-Fe-Organicbent mainly resulted from the hydroxyl radicals.

Furthermore, in order to compare the effects of different reaction conditions on the degradation of ethyl xanthate, different reaction systems were carried out. The results are shown in Figure 6. Under the adsorption of catalyst, the removal ratio of ethyl xanthate by adsorption was less than 5%. As for the reaction system of ‘H2O2’, the removal ratio was relatively low as well and reached about 57% at the reaction time of 50 min. However, when adding H2O2 and catalyst to the reaction system, namely in the reaction system of ‘catalyst + H2O2’, the removal ratio improved greatly, indicating that both catalyst and H2O2 played significant roles in the photo-Fenton system. Also, compared to system ‘H2O2’ or ‘catalyst + H2O2’, the removal ratios of both ‘H2O2 + light’ and ‘catalyst + H2O2 + light’ improved obviously, suggesting the effect of visible light was significant. Therefore, visible light, catalyst and H2O2 all played significant roles in the photo-Fenton reaction catalyzed by HPW-Fe-Organicbent, which could achieve the complete degradation of ethyl xanthate within 50 min.

Moreover, the stability and reusability of HPW-Fe-Organicbent were tested by contacting fresh ethyl xanthate solution with prepared catalyst recycled from previous runs under the conditions: [HPW-Fe-Organicbent] = 0.8 g/L, [H2O2] = 4.08 mmol/L, C0 = 30 mg/L, initial pH of solution and reaction time 50 min. It was found that HPW-Fe-Organicbent had an excellent reusability and a long-term stability in the photo-Fenton process (Wei et al. 2018).

### Kinetics study

The effect of initial concentration on removal ratio of ethyl xanthate is shown in Figure 7. As shown in Figure 7, the removal ratios of ethyl xanthate with initial concentration of 10–50 mg/L increased quickly with the reaction time, and all the removal ratios exceeded 98% at reaction time 50 min. The heterogeneous catalytic kinetics of Fenton’s oxidation of pollution are often analyzed via the pseudo-first-order rate model (Equation (4)).

\[
\ln \left( \frac{C_0}{C_t} \right) = kt
\]

where \( k \) denotes the rate constant, and \( t \) denotes the reaction time.

Figure 8 shows the linear relationships between \( \ln (C_0/C_t) \) and reaction time under different initial

### Table 1 | Result of comparative experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>Treatment process</th>
<th>( \eta/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>HPW-Fe-Organicbent</td>
<td>4.0</td>
</tr>
<tr>
<td>II</td>
<td>HPW-Fe-Organicbent + H2O2 + light</td>
<td>99.8</td>
</tr>
<tr>
<td>III</td>
<td>HPW-Fe-Organicbent + H2O2 + light, isopropanol(^b)</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\)Experimental conditions: C0 = 30 mg/L, t = 50 min, [H2O2] = 4.08 mmol/L and [HPW-Fe-Organicbent] = 0.8 g/L.

\(^b\)10 mL of isopropanol was added.
concentration of ethyl xanthate (corresponding to Figure 7). The corresponding apparent rate constants were calculated from the slopes of the ‘best-fit’ straight lines. The kinetic equation and the fitting parameter are presented in Table 2. As shown in Figure 8 and Table 2, the experimental data of photo-Fenton degradation of ethyl xanthate were well fitted with the pseudo-first-order rate model, and the coefficient of determination also indicated a good fit for all the obtained parameters ($R^2 > 0.95$). Moreover, it was found that the kinetic rate constant increased with the increase of initial concentration of ethyl xanthate. It has been reported that at low concentration of contaminant, ·OH in the Fenton-like reaction system could be consumed more by active iron species and H$_2$O$_2$ (Duesterberg & Waite 2006). Hence, for the photo-Fenton degradation of ethyl xanthate catalyzed by HPW-Fe-Organicbent, when the initial concentration of ethyl xanthate was low, degradation of ethyl xanthate by ·OH could compete with the quenching reaction of ·OH by $\equiv$Fe$^{II}$ and H$_2$O$_2$ through Equations (5) and (6). However, at high initial concentration of ethyl xanthate, ·OH formed during the photo-Fenton reaction could be used for the degradation of ethyl xanthate mostly, even though it could be consumed to some degree by the quenching reaction in the photo-Fenton reaction system (Duesterberg & Waite 2006; Che et al. 2011). Therefore, the kinetic rate constant increased with the increase of initial concentration of ethyl xanthate, and the initial concentration of ethyl xanthate affected the removal rate of ethyl xanthate significantly. By using the proposed model, it was useful to understand the photo-Fenton degradation of ethyl xanthate in solution and obtain the optimal operating conditions to accelerate the degradation process (Liu et al. 2015).

\[ \equiv \text{Fe}^{II} + \cdot \text{OH} \rightarrow \equiv \text{Fe}^{III} + \cdot \text{OH}^{-} \] (5)

\[ \text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^{-}/\text{O}_2^{*} + \text{H}_2\text{O} \] (6)

### CONCLUSIONS

HPW-Fe-Organicbent catalyst was prepared by MCS in a ball mill. Catalyst characterization indicated that the catalyst was a good photo-Fenton catalyst under visible light irradiation. The photo-Fenton degradation of ethyl xanthate catalyzed by HPW-Fe-Organicbent under visible light irradiation was studied. The degradation of ethyl xanthate was mainly impacted by H$_2$O$_2$ dosage, catalyst dosage and reaction time. HPW-Fe-Organicbent used as heterogeneous catalyst had a wide applicable range of pH and kept a high catalytic activity even at high pH in the photo-Fenton degradation of ethyl xanthate. The degradation of ethyl xanthate in the photo-Fenton process catalyzed by HPW-Fe-Organicbent mainly resulted from the hydroxyl radicals. HPW-Fe-Organicbent had an excellent stability in use, and retained almost all of its catalytic activity for four recycling times. Moreover, the kinetics study showed the degradation of ethyl xanthate, with the initial concentration below 50 mg/L, was well fitted with the pseudo-first-order rate model.

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