Degradation of amyl xanthate by manganese dioxide
Shaohua Chen, Yan Sun, Jia Li and Ling Xiong

ABSTRACT
Amyl xanthate (AX), a widely used reagent in sulfide mineral flotation, has caused serious environmental problems. Manganese dioxides (MnO2), ubiquitous in natural soils and sediments, are one kind of important oxidant or catalyst in facilitating organic pollutant decomposition. In this study, the oxidative degradation of AX by MnO2 was investigated in batch experiments. It was found that up to 90% AX was decomposed by MnO2 in 30 min and the removal efficiency of AX depended strongly on the loading of MnO2 and pH value in the solution where the reactions closely followed a pseudo-first-order model. The reaction orders with respect to the initial AX concentration, MnO2 concentration and pH value were 0.4573, 0.2034, and –0.1701, respectively. Coexisting metal ions, such as Mn2+, Fe3+, Ca2+ and Mg2+, displayed suppressive effects and the inhibitive capacity of the metal ions followed the order Mn2+ > Fe3+ > Ca2+ > Mg2+. However, the effect of humic acid (HA) on reaction rates was significant only at higher concentrations. This study provided meaningful information to elucidate the oxidative degradation of AX by MnO2.

Key words | amyl xanthate, kinetic, MnO2, oxidative degradation

INTRODUCTION
Xanthates are widely used as collectors in sulfide mineral flotation (Bulatovic 2007). Although most of the xanthates enter into the floated product, residual xanthate in the wastewater obtained from flotation processing has serious environmental consequences (Molina et al. 2013; Yan et al. 2016). The toxicity of xanthates and their oxidation byproducts is high. Xanthates harm nervous systems and livers of human and other animals, and also may have a teratogenic effect on fish embryos (Fu et al. 2015). And soil and groundwater pollution due to xanthate from tailings dams is a worldwide concern (Chen et al. 2011a, 2011b). Therefore, it is necessary to remove residual xanthates from flotation wastewaters.

In recent years, bioremediation techniques have become popular for the treatment of flotation wastewater. Nevertheless, biodegradation takes several days or even weeks, therefore cannot be used in sites when rapid action is required. Consequently, the need for a rapid and efficient treatment of flotation wastewater is imperative.

Chemical oxidation technologies have attracted more attention in recent years owing to their proven effectiveness on a wide variety of biorefractory organic compounds (Hammouda et al. 2016). Manganese oxides are among the most important natural oxidants (with reduction potentials of 1.50 and 1.23 V for MnOOH and MnO2, respectively) that are capable of oxidizing various organic contaminants (Zhang et al. 2008), including bisphenol A (Lin et al. 2009a), methyl parathion (Liao et al. 2016), tetracycline (Mahamallik et al. 2015), chlorophene (Zhang & Huan 2005), pyrene (Chang Chien et al. 2011), benzene (Yodsa-nga et al. 2013) pentachlorophenol (Petrie et al. 2002), and glyphosate (Barrett & McBride 2005). Moreover, MnO2 is a nontoxic material as well as being cheap, and the particles are easily separable and reusable. And manganese dioxides are ubiquitous in natural soils and sediments. However, to the best of our knowledge, the oxidative degradation of amyl xanthate (AX) by MnO2 has not yet been explored. The objective of this study was to systematically explore the oxidative removal of AX with MnO2 by investigating removal efficiency and influencing factors such as MnO2 concentrations, pH, coexisting metal ions (e.g., Mn2+, Fe3+, Cu2+ and Mg2+) and humic acid (HA). Furthermore, the reaction kinetic model was established.

MATERIALS AND METHODS
Materials
AX was obtained from Zhuzhou Mineral Processing Reagent Plant (Zhuzhou, P.R. China). All other chemicals
used in this investigation were of analytical grade from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Manganese oxide ($\delta$-MnO$_2$) was synthesized according to Murray's method (Murray 1974). The chemicals were used without further purification, and all the solutions were prepared with deionized water obtained from a Milli-Q system to the required concentrations.

**Experimental setup**

All glassware was soaked with 5N HNO$_3$, thoroughly rinsed with deionized water, and baked at 105°C for 2 hours prior to use. All experiments were conducted in 250 mL beakers kept in a thermostated water bath at 150 rpm and 28°C under ambient O$_2$ conditions in the absence of light. For the oxidation reaction experiments, the initial AX concentration was 30 mg/L. Sodium chloride (NaCl) was added to adjust the ionic strength. Reaction pH was adjusted using 2 mM glacial acetic acid (HAc)-sodium acetate (NaAc) buffer system. All the experiments were conducted in triplicate.

The effect of initial MnO$_2$ concentration on AX removal was investigated at five different MnO$_2$ concentrations (0, 50, 100, 200, and 500 mg/L) under the fixed conditions of pH 5.0 and 0.01 M ionic strength. pH effect was evaluated in solutions with various pH values (4.5, 5.0, 5.6, and 6.22) under the fixed conditions of 200 mg/L MnO$_2$, and 0.01 M ionic strength. The coexisting metal ions effect was investigated by two different concentrations (e.g., 0.01 and 0.05 M) background solutions containing 0.01 or 0.05 M of chloride salts of Mn$^{2+}$, Fe$^{3+}$, Mg$^{2+}$ or Ca$^{2+}$ in addition to 0.01 M of NaCl under the fixed conditions of 200 mg/L MnO$_2$, and pH 5.0. To evaluate the HA effect, the reaction solutions were supplemented with HA to a concentration of 0.1, 1 or 10 mg/L under the fixed conditions of 200 mg/L MnO$_2$, pH 5.0, and 0.01 M ionic strength.

**Analytical methods**

A pH meter (HACH, USA) was used for pH measurement. The experimental mixtures were separated by filtration through a 0.22 μm Millipore membrane filter prior to being centrifuged at 10,000 rpm for 15 min (HC-3518, China). The supernatants were measured at 300 nm using a UV-vis spectrophotometer (Shimadzu, Japan). The Mn$^{2+}$ concentration generated was determined by inductively coupled plasma mass spectrometry (ICP-MS) (NexION 300 ICP-MS). X-ray diffraction (XRD) analysis of the prepared MnO$_2$ was done by Bruker Advanced D8 X instrument. JSM-5510LV instrument was used for scanning electron microscopic (SEM) images. MnO$_2$ solids before and after reaction with AX were analyzed by Fourier transform infrared (FTIR) spectrometer (NEXUS6700, USA). The degradation was carried out with 30 mg/L AX, 200 mg/L MnO$_2$ at pH 5.0 and 28°C for 90 min. After the reaction, the MnO$_2$ was collected by centrifugation, and washed with deionized water. Then the MnO$_2$ was dried under vacuum 60°C for 4 hours and used for laboratory analyses.

**RESULTS AND DISCUSSION**

**Characterization of $\delta$-MnO$_2$**

As shown in Figure 1, the X-ray diffractogram of synthesized $\delta$-MnO$_2$ displayed poor crystalline characteristics. Diffraction peaks of $2\theta$ = 12.2°, 18.3°, 37.1°, and 66.1° are observed, which are in line with characteristic peaks of $\delta$-MnO$_2$ (Sun et al. 2015).

**Effect of initial MnO$_2$ concentration on AX removal**

Effect of initial MnO$_2$ concentration on AX degradation by MnO$_2$ and generation of Mn$^{2+}$ are shown in Figure 2. Control experiments showed that the loss of AX was less than 5% without MnO$_2$ after 90 min. However, AX was rapidly removed in the presence of MnO$_2$. For example, 68.56% of AX was removed in less than 30 min under experimental conditions of pH 5.0, 30 mg/L AX and 50 mg/L MnO$_2$. Up to 79.01% of AX disappeared as the reaction was prolonged to 90 min. An increase in initial MnO$_2$ concentration would
supply more active surface sites, which could, in turn, increase the reaction rate. And the removal efficiency was further enhanced with higher concentrations of MnO₂: for example, the removal of AX in 30 min was increased from 79.67% for a system amended with 100 mg/L MnO₂ to 97.98% with 200 mg/L MnO₂. But when the initial MnO₂ concentration exceeded 200 mg/L, the removal efficiency of AX increased slowly. The reason for this was that excessive active sites on the surface of MnO₂ were only slightly beneficial to AX degradation. Meanwhile, Mn²⁺ was generated and its concentration increased along with the concentration of MnO₂ and reaction time. No Mn²⁺ was detected in the control experiment. The generation of Mn²⁺ shows that MnO₂ was an oxidant and AX could be readily oxidized by MnO₂.

**Effect of pH on AX removal**

Numerous studies indicate that pollutant removal from aqueous solutions by MnO₂ is facilitated in acidic solutions, whereas neutral and alkaline conditions hinder the reaction. The effect of pH on AX degradation by MnO₂ is shown in Figure 3. It can be seen that the removal of AX was significantly influenced by solution pH. AX removal declined with increasing pH. The degradation process remains efficient and feasible up to pH 6.22 with the degradation rate of AX being 64.03% within 30 min compared to 91.98% at pH 5.60, 97.98% at pH 5.0 and 98.56% at pH 4.5.

The pH dependence could be attributed to two facts. First, pH influences sorption of AX to oxide surfaces and the electron transfer processes. Second, pH influences the redox potential of MnO₂. For example, when the pH was decreased from 8.0 to 4.0, the reduction potential of MnO₂ increased from 0.76 to 0.99 V (Lin et al. 2009a, 2009b). It is likely that for this reason, AX removal decreased as the pH was increased from 4.5 to 6.22.

**Effect of coexisting metal ions on AX removal**

Because flotation wastewater contains metal ions, their effect on how the oxidation of AX with MnO₂ varies with species and concentrations was studied and the results are shown in Figure 4.

Organic oxidation by MnO₂ is also considered to be a surface reaction, which depends on surface charge...
It can be seen that higher concentrations of metal ions resulted in a higher inhibitory effect. For example, the AX removal rates were 96.21%, and 88.76% in 90 min, in the presence of 0.01 and 0.05 mmol/L of Fe$^{3+}$, respectively. The concentration dependence may be attributed to two facts. First, metal ions can occupy the reactive surface sites of MnO$_2$. Second, the reactive sites on the MnO$_2$ surface are limited and can be saturated by relatively low concentrations of reactants (Xiao et al. 2013). The results show that Mn$^{2+}$ had the strongest inhibitory effect, followed by Fe$^{3+}$, Ca$^{2+}$, and then Mg$^{2+}$. The more obvious inhibitive effect of Mn$^{2+}$ on oxidation of AX by MnO$_2$ could also be attributed to the fact that the adsorption of Mn$^{2+}$ by MnO$_2$ decreased the actual redox potential of MnO$_2$/Mn (II) (Zhang et al. 2008; Lin et al. 2009a; Lu et al. 2011; Remucale & Ginder-Vogel 2014; Liao et al. 2016). However, the presence of Mg$^{2+}$ and Ca$^{2+}$ co-solutes caused only a slight decrease in removal efficiency of AX, indicating that Mg$^{2+}$ and Ca$^{2+}$ have weak sorption affinities on the MnO$_2$ surface. For example, the removal rate of AX in 90 min only decreases by 2.64% or 1.01% on the presence of 0.05M of Ca$^{2+}$ or Mg$^{2+}$, respectively.

**Effect of coexisting HA on AX removal**

HA, as natural organic matter mostly found in water, is another factor that may affect the oxidative efficiency of MnO$_2$. In this study, the effect of coexisting HA on AX degradation by MnO$_2$ is shown in Figure 5.

It can be seen that the inhibitory effect of HA at both 0.1 and 1 mg/L was insignificant, only with 1.85% and 4.08% reduction within 90 min, respectively, while the inhibitory effect was found to be significant when the HA concentration was 10 mg/L. And these findings are in agreement with those reported in previous studies (Klausen et al. 1997; Lu et al. 2011). The effect of HA on the degradation of AX by MnO$_2$ is twofold. First, HA could facilitate the removal of AX by MnO$_2$, due to the complexation of HA with Mn$^{2+}$ as the oxidative reaction progressed. Second, HA has been reported to possibly react with MnO$_2$ (Sunda & Kieber 1994), due to the competition oxidation between HA and AX for MnO$_2$ surface active sites, the reaction rate of AX oxidation by MnO$_2$ decreased significantly.

**Recyclability of MnO$_2$**

To find out about the recyclability of the prepared MnO$_2$, the efficiency of the recycled MnO$_2$ as the oxidant was investigated. The MnO$_2$ was used in four consecutive cycles using fresh solutions under conditions of pH 5.0, 30 mg/L AX and 200 mg/L MnO$_2$ for 90 min. Between each experiment, the MnO$_2$ was removed by filtration and then washed in deionized water several times and dried under vacuum at 60°C.

The MnO$_2$ exhibited high activity in four-run tests. In the first run, the removal rate of AX was 98.47%. In the fourth run, only a slight decrease in removal rate was observed, and the removal rate was found to be 80%. The reduction in efficiency may be due to the blockage of active sites of MnO$_2$ making them unable to take part in the reaction (Mahamallik et al. 2013). Figure S1 (available with the online version of this paper) shows an SEM image of MnO$_2$ (a) and recycled MnO$_2$ (b). It can be seen that both MnO$_2$ and recycled MnO$_2$ particles are clearly seen to form spherical agglomerates. The results of the recycling tests indicate MnO$_2$ samples can maintain its spherulitic morphology after repeated use.

**FTIR analysis**

FTIR spectroscopy was used to analyze the changes on MnO$_2$ surface after reaction with AX. FTIR spectra of MnO$_2$ solids before reaction with AX are shown in Figure 6(a). The strong broad peak at 3,386 cm$^{-1}$ corresponds to the stretching vibration of the hydroxyl group in water and Mn-O-H molecules (Chen et al. 2011a, 2011b). The 1,623 and 1,106 cm$^{-1}$ bands were assigned to the bending vibrations of the hydroxyl groups of Mn-OH (Mahamallik et al. 2013), suggesting that MnO$_2$ in this study is a hydrous manganese oxide containing
numerous hydroxyl groups on the surface. The peak at 559 cm\(^{-1}\)/C0\(^{-1}\) represents the bending vibration of the O-Mn-O bond, indicating the presence of crystalline MnO\(_2\). Compared with the spectrum of MnO\(_2\) solids before reaction, new peaks occurred in the spectrum of MnO\(_2\) solids after reaction with AX (Figure 6(b)). The peaks at 1,060 and 594 cm\(^{-1}\)/C0\(^{-1}\) were assigned to the thiocarbonyl and carbon–sulfur groups of AX, respectively. Further, a band loss of Mn-O-H or a clear shift of the Mn-O-H band at 3,386 and 3,428 cm\(^{-1}\)/C0\(^{-1}\) indicates that numerous Mn-O-H groups on the MnO\(_2\) surface might be active sites for AX oxidation based on the FTIR result.

Reaction kinetics

A pseudo-first-order kinetic model was employed to fit the AX degradation kinetic:

\[
\ln \left( \frac{[AX]}{[AX]_0} \right) = -kt
\]

where \([AX]_0\) is the initial AX concentration, \([AX]\) is the AX concentration at time \(t\), and \(k\) is the reaction rate constant. It is proposed that the kinetics of AX degradation by MnO\(_2\) is a function of the initial AX concentration, MnO\(_2\) concentration, and pH value (Li et al. 2008; Wan et al. 2015). Thus, the improved parameter \(k\) can be expressed as:

\[
k = \frac{-r}{[AX]_0^{0.4573} [MnO_2]^{0.2034} [pH]^{0.1701}}
\]

where, \(n\), \(\alpha\) and \(\beta\) are the specific reaction orders, \(r\) is the initial degradation rate of AX, \([AX]\) and \([MnO_2]\) are the initial concentrations of AX and MnO\(_2\), respectively, and \([pH]\) is the reaction pH. Therefore, when plotting ln\(r\) against ln\([AX]\), ln\([MnO_2]\) and \([pH]\), the slope of the linearized curve would reflect the reaction order for \([AX]\), \([MnO_2]\) and \([pH]\), respectively. And the slope of the regression lines was found to be 0.4573, 0.2034, and –0.1701. From these results, Equation (2) can be rewritten as Equation (3):

\[
k = \frac{-r}{[AX]_0^{0.4573} [MnO_2]^{0.2034} [pH]^{0.1701}}
\]

CONCLUSIONS

This study showed that MnO\(_2\) has the ability to oxidize AX. The AX removal rates increased with an increase in the initial MnO\(_2\) concentration, but decreased with an increased pH. The presence of co-solute metal ions (Mn\(^{2+}\), Fe\(^{3+}\), Ca\(^{2+}\), Mg\(^{2+}\)) can reduce the AX degradation rates. The inhibitory effect of HA on the oxidation of AX was significant with increasing HA concentrations. Analysis of reaction kinetics showed that the reaction orders with respect to the initial AX concentration, MnO\(_2\) concentration and pH were 0.4573, 0.2034, and –0.1701, respectively. This study indicates that oxidation of AX by MnO\(_2\) may thus be an effective technology to treat xanthate in flotation wastewater.

ACKNOWLEDGEMENTS

This work was supported by the Fundamental Research Funds for the Central Universities, South-Central University for Nationalities (CZP17097, CZW15037), Natural Science Foundation of Hubei Province (2015CFC888).

REFERENCES


First received 9 May 2017; accepted in revised form 12 September 2017. Available online 26 September 2017.