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Degradation of ethyl xanthate in flotation residues by hydrogen peroxide

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Abstract: The degradation behavior of ethyl xanthate (EX) salt was the most widely used collector in sulfide mineral flotation and emission of flotation tailings with residual EX was harmful to environment. In this work, hydrogen peroxide (H_2O_2) was investigated by UV-visible spectroscopy (UV/Vis) at different pH values from 3 to 12. For pH value from 5 to 12, EX was oxidized into ethyl per xanthate (EPX) by H_2O_2. Then EPX was further oxidized into thiosulfate (TS) salt rather than ethyl thiocarbonate (ETC) and this step was the reaction-limited step. Then depending on pH values, TS was degraded into sulphate and carbonate salts (pH>7) or elemental sulfur (pH<7). The kinetics data show that the degradation rate of EX increases with increasing the H_2O_2 concentration and is independent on the pH values. Without H_2O_2, EX is hydrolyzed to carbon disulfide fast at pH value <3.0, but the reaction of hydrolysis is undetectable at pH value >3.0 during test time.

Key words: ethyl-xanthate; thiosulfate; hydrogen peroxide; UV-visible spectroscopy

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1 Introduction

Xanthate is one of the most common organic-sulphur-based collectors (e.g., xanthates, and dithiocarbamates) which are widely used in the froth flotation of sulphide minerals as well as in the production of viscose rayon and pesticides [1−2]. However, the residual xanthate and its by-products in wastewater tailings are not allowed to dispose into environmental streams due to both strong nasty smells and being toxic to biological systems [3−6]. In recent years, especially with increasing effort on environment protection from community and governments, many methods have been developed to remove the xanthate and its by-products from wastewater tailings, such as chemical precipitation [7], chemical oxidation [8−11], adsorption [12−13], and biodegradation [3, 14−15].

Especially on the oxidation process, there are many studies that investigate the reaction kinetics and identify the degradation process and by-products for the last over 50 years [8, 16−19], as shown in Table 1. For exposing into air without any oxidation, the xanthate is hydrolyzed into carbon disulfide (CS_2) in the acidic solution with very fast reaction rate as

$$\mathrm{ROCS_2^- + H^+ \longrightarrow ROH + CS_2} \tag{1}$$

where R represents an aliphatic hydrocarbon chain, with most common type of ethyl xanthate (EX) salt. However, this auto-oxidation by air is relatively slow in the base condition (pH>7) in most flotation tailings [16−17, 20]. To increase the degradation rate of xanthate, several oxidizing reagents such as hydrogen peroxide (H_2O_2) or Fenton's reagent are used to oxidize the xanthate solution [8, 10, 19]. In the report by SILVESTER et al [8] and HAO et al [19], they proposed the general degradation of EX by H_2O_2 in base condition with pH value of 8−12 as

$$\underset{\text{(EX)}}{\mathrm{C_2H_5OCS_2^-}} \xrightarrow{\mathrm{H_2O_2}} \underset{\text{(EPX)}}{\mathrm{C_2H_5OCS_2O^-}} \xrightarrow{\mathrm{H_2O_2}} \underset{\text{(ETC)}}{\mathrm{C_2H_5OCSO^-}} + \mathrm{SO_4^{2-}} \tag{2}$$

In their tests, they also reported other degradation reaction paths and observed the unidentified species I3 but did not provide further analysis on it. Furthermore, there is no report on the degradation mechanism of EX by H_2O_2 in the acidic system until now even the acidic condition has been used to process EX waste tailings [11, 21]. In summary, due to the complex behavior of xanthate degradation, the unified mechanism of xanthate degradation remains unclear, which will result in the arbitrary treatment of residual xanthate in the tailings.

In this work, the degradation behavior of EX in homogeneous solution was studied by UV-visible spectroscopy (UV/Vis) with or without H_2O_2 at initial pH range from 3.0 to 12.0 without pH value controlled during test. The novel intermediate during H_2O_2 oxidation was identified and new mechanism was proposed. The

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Table 1 UV/Vis feature peaks of EX and its main degradation by-products

Chemical	Formula*	Abbreviation	Wavelength/nm	Coefficient of extinction, ε/($L\cdot mol^{-1}\cdot cm^{-1}$)
Ethyl xanthate	$C_2H_5OCS_2^-$	EX	226 301	8750 17500
Ethyl perxanthate	$C_2H_5OCS_2O^-$	EPX	347	10420
Ethyl thiocarbonate	$C_2H_5OCSO^-$	ETC	223.5	12200−13300
Dixanthogen	$(C_2H_5OCS_2)_2$	$(EX)_2$	238 283	17800 8600
Ethanol	C_2H_5OH	Et	192	—
Thiosulfate	$S_2O_3^{2-}$	TS	215	—
Carbon disulfide	CS_2	CS_2	206.5	60000−70000

* All anions are neutral by cation sodium, Na^+.

effect of pH value and concentration of H_2O_2 on degradation kinetics of EX was also discussed.

2 Materials and methods

2.1 Materials

The solid powder of sodium ethyl xanthate (SEX) was purchased from Qingdao Ruchang Mining Industry CO., Ltd. (China). It was purified by recrystallization from ethanol solution. The result of this recrystallization is to remove the non-crystal impurities. Then the concentrated SEX solution of 400 mg/L (2.8 mmol/L) was made by dissolving purified solid into deionization (DI) water in laboratory. The hydrogen peroxide (H_2O_2) was purchased from Shanghai Lingfeng Chemical Reagent CO., Ltd. (China). Other chemicals involved in the tests were of analytical grade.

2.2 Experimental methodology

The degradation tests of EX solution (total volume of 100 mL) without or with H_2O_2 were conducted using a 200 mL plastic beaker with magnetic stirrer at temperature of (25±1) °C with thermal couple control, as shown in Fig. 1. The test solutions of EX were prepared by diluting the bulk concentrated solution with various folders (10−80), which will be explained in section 3.1. The concentration of H_2O_2 was calculated based on EX mole concentration with various ratios from 1 up to 16. The test duration was 240 min.

In this test, the initial pH before adding H_2O_2 was adjusted by manual addition of NaOH (0.05 mol/L) or H_2SO_4 (0.05 mol/L) solution and was not adjusted during tests. The reported pH value at 0 min was the value measured after adding H_2O_2. The pH of the solution was recorded by Mettler Toledo pH meter made by Shanghai Ruosull Technology (China). Aqueous samples were taken at various time for analysis of the xanthate concentration and by-products by measuring the optical absorbance using a Thermo Herios UV-visible spectroscopy. The ion chromatography (IC) with model Dionex ICS-3000 was used to analyze the composition of reaction residues.

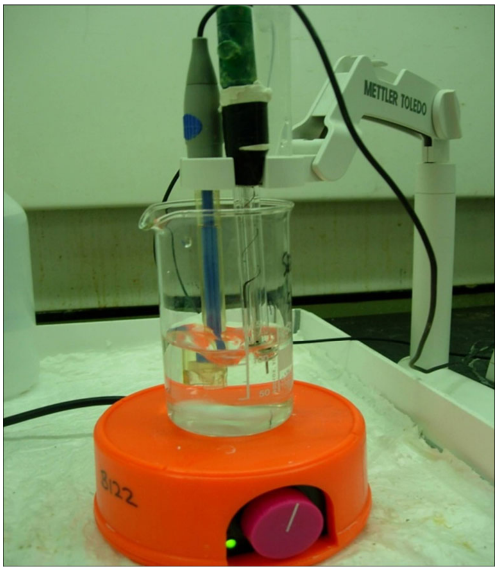

Fig. 1 Equipment setting-up for degradation of EX

3 Results and discussion

3.1 Calibration of EX concentration for UV/Vis measurement

In order to obtain optimal UV/Vis absorbance profile, the batch of EX solutions by diluting bulk concentrations (400 mg/L) with different times was measured by UV/Vis. Based on the theory of UV/Vis absorption spectrometry [22], the correlation between the UV absorbance value, A, and transmittance, T, can be described as $A=-\lg(T)$. So when A is 2.0, T is only 1%. As shown in Fig. 2, the quality of UV/Vis curves of 10 and 20 times is poor and no single absorbance peak could be observed as their absorbance peaks are higher than 2. For solution of 30 times and above, the absorbance peak of EX is lower than 2 at wavelength of 226 nm and 301 nm. Furthermore, only when the concentration is below the critical concentration, the linear relationship between absorbance value and concentration follows the Beer-Lambert law as

$$A=-\lg(I/I_0)=\varepsilon\cdot c\cdot L \tag{3}$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L is the path length through the sample (0.01 m), ε is coefficient of extinction and c is the mole concentration of the absorbed species [23].

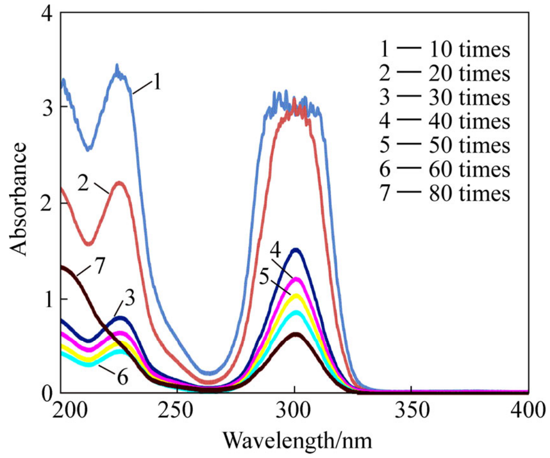

Fig. 2 UV/Vis spectra of EX solutions with different dilution folders

As shown in Fig. 3, there is the strong linear relationship between absorbance value and diluting concentration larger than 40 times. Therefore, in the following tests, to obtain good UV/Vis absorbance curves, the initial concentration of EX solution will be 10 mg/L (40 times, 0.7 mmol/L).

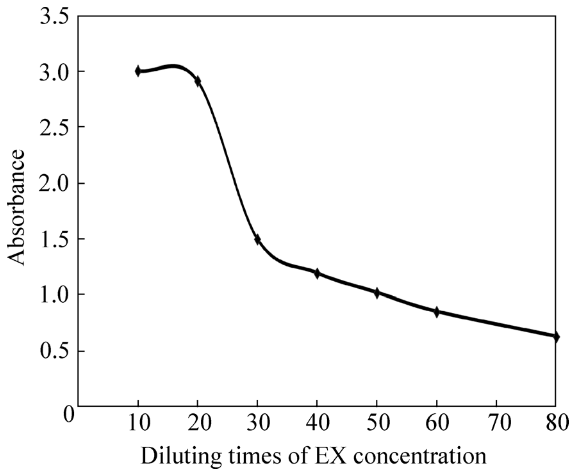

Fig. 3 Absorbance at 301 nm of EX solutions with different dilution times

3.2 Degradation of EX without H_2O_2

The automatic degradation of EX without H_2O_2 as a function of pH value was studied by UV/Vis for 4 h. As shown in Fig. 4 the EX concentration remains unchanged in investigated time for pH≥5. However, for pH value of 3, the degradation of EX is significantly increased. For less than 2 h, absorbance value of EX at 301 nm is almost decayed into less than 0.1 in comparison with value of 1.05 at the initial stage. In all tests, the pH values of solution remain constant after 20 min, as shown in Fig. 5. This may indicate that the dissolved oxygen in the solution has limited impact on this process and the concentration of proton will be the main factor on the rate determining step. As shown in Fig. 6, we observe the increased concentration of CS_2 in the first 10 min, and then the significant drop at wavelength of 206.5 nm.

As mentioned by other reports [16−17, 20], in the acidic solution, the EX is hydrolyzed into CS_2 by

$$C_2H_5OCS_2^- + H^+ \longrightarrow C_2H_5OH + CS_2 \tag{4}$$

This reaction follows a first order kinetic mechanism based on the equation below:

$$\frac{d(C_{EX})}{dt} = -kC_{EX} \tag{5}$$

where C_{EX} is the mole concentration of the absorbed species, t is the sampling time and k is reaction rate constant. Combining Eqs. (3) and (5), we could obtain the linear relationship between the log value of absorbance ln$A$ and time t. By re-plotting the data in Fig. 4 for pH value of 3.0, we calculate the reaction rate constant from slope of linear fitting of ln$A$−t and its value is 0.035.

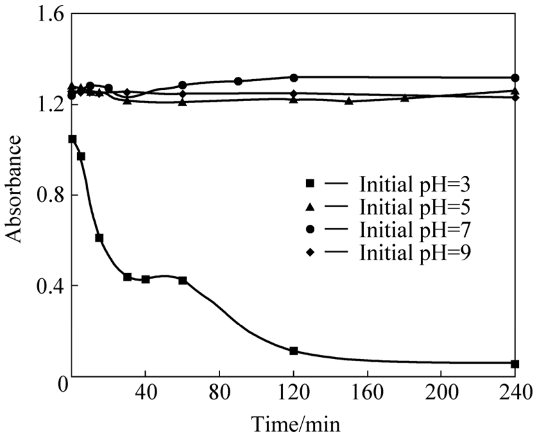

Fig. 4 Absorbance at 301 nm of EX solutions at different initial pH values

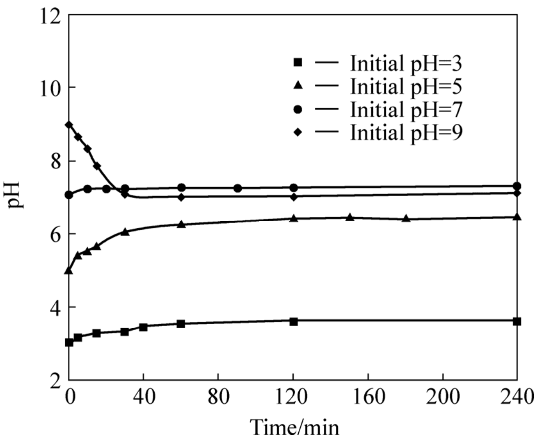

Fig. 5 pH values of EX solutions without oxidant at different initial pH values

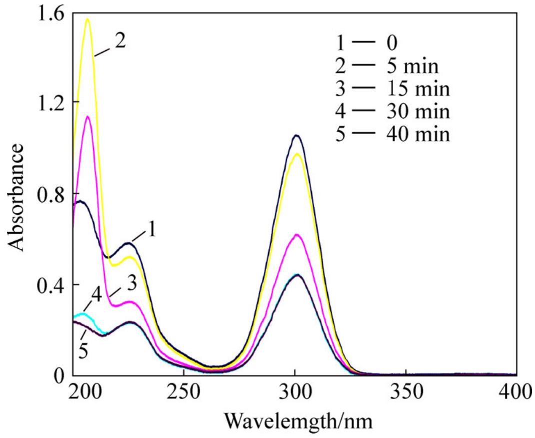

Fig. 6 Ultraviolet spectra of EX solutions with various time at initial pH=3

3.3 Degradation of EX with H_2O_2 at various pH values

The tests were conducted at various pH values (5, 7, 9 and 12) and H_2O_2 concentrations. The concentration of H_2O_2 was calculated based on the mole ratio of EX solution from 1:1 to 1:16. As the EX mole solution is 0.7 mmol/L with solution volume of 100 mL, the corresponding mole concentrations of H_2O_2 are 0.07 mmol/L, 0.28 mmol/L, 0.56 mmol/L and 1.12 mmol/L. During the tests, we did not use the buffer solution to control the pH value but monitored the change of pH values. For most cases, the pH values of system decease to be less than 7 after H_2O_2 adding in less than 30 min, as shown in Fig. 7.

The first test was conducted at initial pH=9 with c(EX): $c(H_2O_2)$ of 1. The results of UV/Vis spectra shown in Fig. 8 indicate that the EX is gradually oxidized to EPX from the deceasing values at 301 nm. The EPX concentration increases at the first 30 min then follows the slow decreasing trend for 4 h. On the contrary, we do not observe the absorbance peak of ETC at 223.5 nm reported by previous reports [8, 18−19]. However, a peak at wavelength of 215 nm appears after 10 min and then follows the similar degradation trend of EPX.

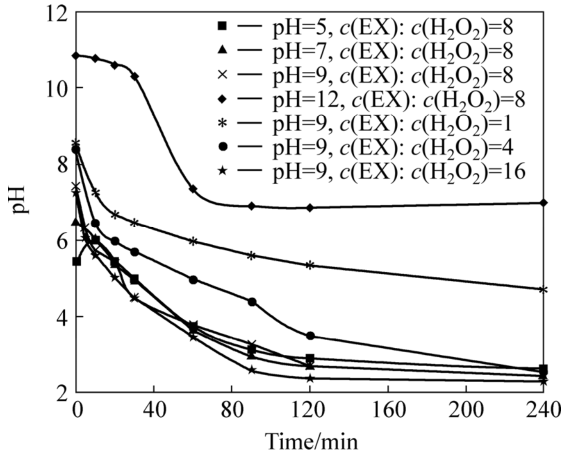

Fig. 7 pH values of EX solutions under different initial conditions

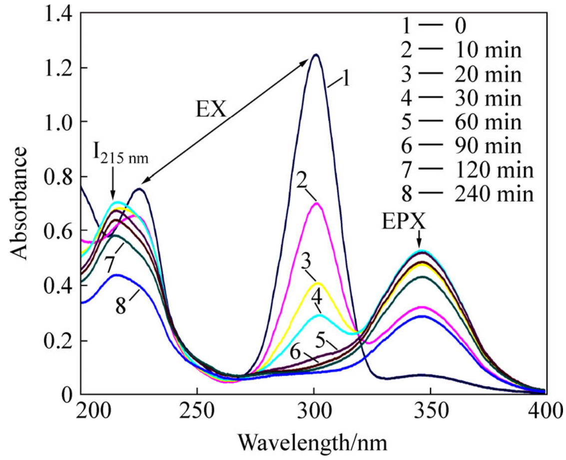

Fig. 8 UV/Vis spectra of EX solutions at various time at initial pH=9 with c(EX): $c(H_2O_2)$=1:1

To identify the products of I_{215nm}, 0.2 mL of the sample at 30 min was taken for IC measurement. As shown in Fig. 9, for separation curve, there is the thiosulfate adsorption peak for the sample. The UV/Vis spectrum of the 0.05 mmol/L pure sodium thiosulfate was also measured, as shown in Fig. 10. There is only one feature peak at wavelength of 215 nm, which corresponds to the adsorption peak in the tests at 215 nm. These evidences could confirm that the thiosulfate is not impurity from original solutions but the intermediate product of degradation of EPX during oxidation.

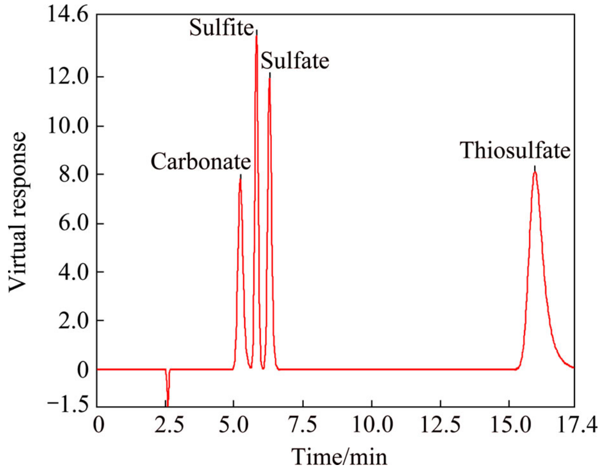

Fig. 9 Separation of carbonate, sulphite, sulphate and thiosulfate from 0.2 mL solution sampling at 30 min by ion chromatography

To enhance the degradation rate of EX, the concentration of H_2O_2 was increased from 4 to 16 folders. As shown in Fig. 11, at rate of 8, the absorbance values of EX and its degrading by-products are less than 0.1 after 4 h. Interestingly, during the test, the solution was

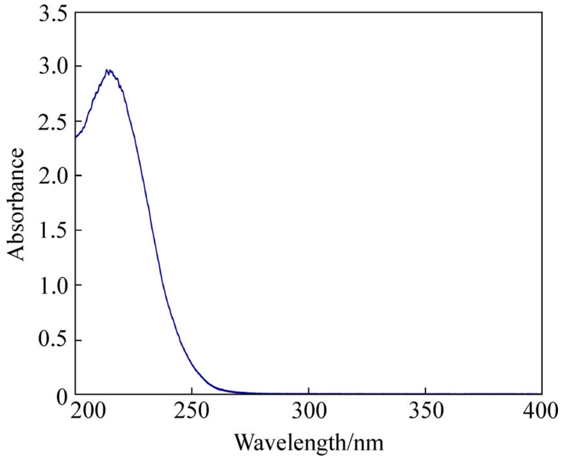

Fig. 10 UV/Vis spectrum of pure sodium thiosulfate (0.05 mmol/L) solutions

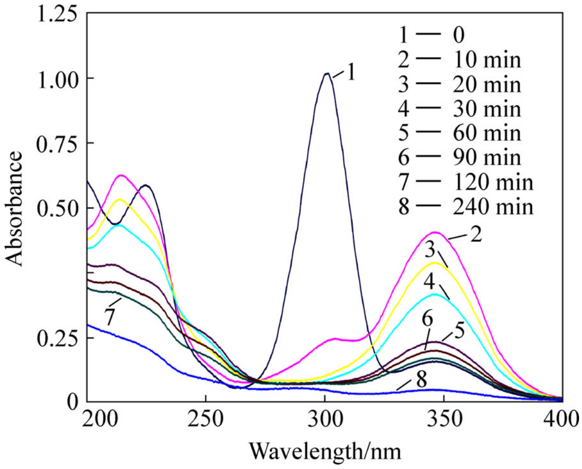

Fig. 11 UV/Vis spectra of EX solutions at various time at initial pH=9 with of c(EX): $c(H_2O_2)$=1:8

changed to be cloudy after 30 min when pH was less than 6. This cloudy solution kept the same state for the rest of time, as shown in Fig. 12(a). To verify the cloudy product, the solution was filtrated and dried at room temperature for analysis. Based on the data of atomic absorption spectroscopy of solid sample, it is identified as elemental sulfur.

Even by changing the initial pH values for 5 and 7, the solutions were also cloudy after 30 min. Only when increasing the initial pH value at 12, the solution was clear for the whole test time, as shown in Fig. 12(b). As shown in Fig. 13, the UV/Vis spectra of solution at pH=12 are similar with the trend in Fig. 11. As shown in Fig. 7, the pH value of system decreases to 7 at the first 40 min then almost keeps constant in the rest of time for initial pH=12. However, for other tests, the pH values of solutions change to be less than 7 in less than 30 min.

In summarizing all the data and analysis above, we propose that the EX has the new degradation mechanism at oxidation of hydrogen peroxide as

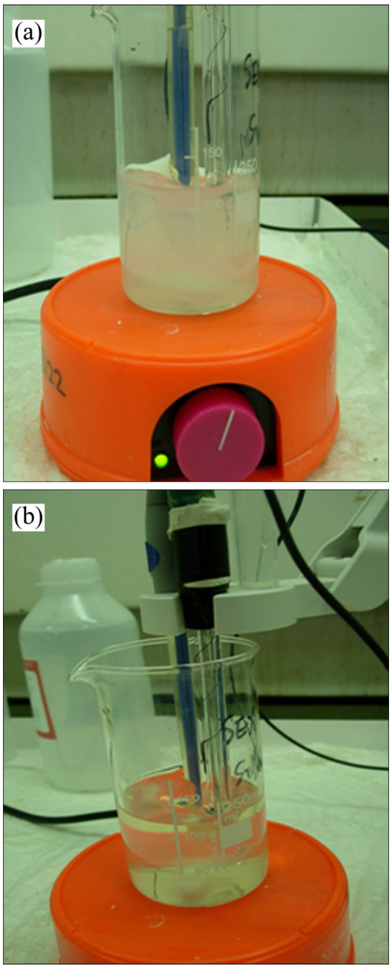

Fig. 12 Photos of EX solution after 4 h test under conditions of initial pH value of 9 (a) and initial pH value of 12 (b)

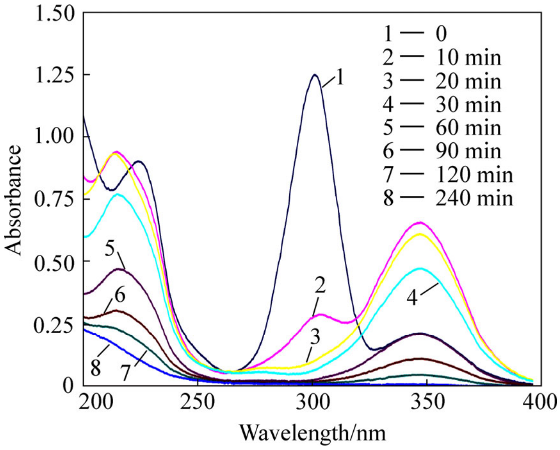

Fig. 13 UV/Vis spectra of EX solutions at various time at initial pH=12 with c(EX): $c(H_2O_2)$=1:8

$$\begin{aligned}
&\underset{\text{(EX)}}{C_2H_5OCS_2^-} \xrightarrow{H_2O_2} \underset{\text{(EPX)}}{C_2H_5OCS_2O^-} \xrightarrow{H_2O_2} \\
&\quad S_2O_3^{2-}+CO_3^{2-} \\
&S_2O_3^{2-} \xrightarrow[\text{pH>7}]{H_2O_2} SO_4^{2-} \\
&S_2O_3^{2-} \xrightarrow[\text{pH<7}]{H^+} SO_2+S
\end{aligned} \tag{6}$$

We also investigate the effect of pH values and concentration of H_2O_2 on kinetics of degradation of EX. As shown in Fig. 14, the absorbance peaks of 301 nm for EX is almost reduced to minimum in less than 20 min. The absorbance peaks of 347 nm for EPX shows the increasing trend with maximum value at the first 10 min then decreases with time, as shown in Fig. 15. By linear fitting the log value of absorbance at 301 nm and 347 nm with time based on Eq. (5), we could obtain the rate constant of EX and EPX degradation as a function of pH values and H_2O_2 concentration.

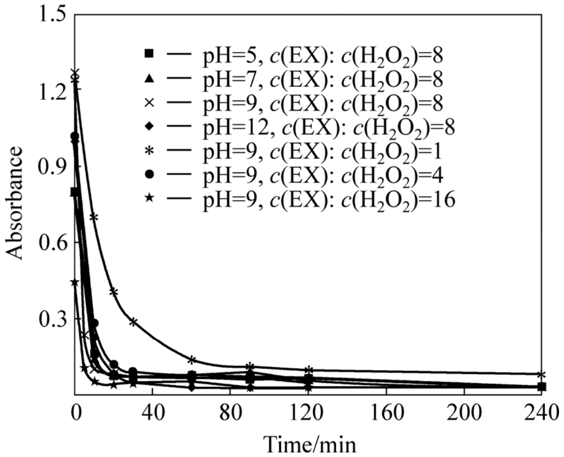

Fig. 14 Absorbance at 301 nm of EX solutions under different initial conditions

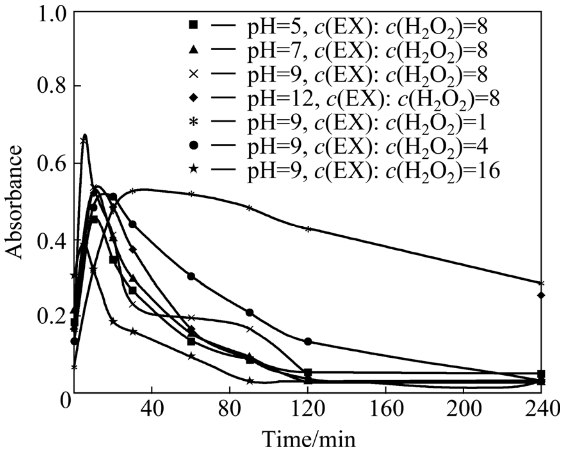

Fig. 15 Absorbance at 347 nm of EX solutions at different initial conditions

The test data show that pH values have limited effect on the degradation kinetics of both EX and EPX by H_2O_2 based on the values of Table 2. However, the concentration of H_2O_2 has significant effect on the degradation kinetics of both EX and EPX, as shown in Table 2.

With the increasing H_2O_2 concentration, the degradation rate of both EX and EPX is almost linearly increased. The kinetics of degradation of EX with various pH values and H_2O_2 concentrations shows that the concentration of H_2O_2 is significant linearly correlated with K_{EX} (r^2=0.899, p=0.016) and K_{EPX} (r^2=0.992, p=0.001) under the optimized pH values. Based on the test results, the recommended concentration of H_2O_2 is 8 times that of EX solution if requiring complete oxidation in 4 h.

Table 2 Rate constants of degradation of EX and EPX under various conditions of UV/Vis feature peaks of EX and its main degradation by-products

Condition	K_{EX}	K_{EPX}
pH=9, c(EX): $c(H_2O_2)$=1:1	0.049	0.003
pH=9, c(EX): $c(H_2O_2)$=1:4	0.107	0.013
pH=9, c(EX): $c(H_2O_2)$=1:8	0.125	0.021
pH=9, c(EX): $c(H_2O_2)$=1:16	0.204	0.048
pH=5, c(EX): $c(H_2O_2)$=1:8	0.116	0.023
pH=7, c(EX): $c(H_2O_2)$=1:8	0.113	0.024
pH=12, c(EX): $c(H_2O_2)$=1:8	0.098	0.024

In comparison with degradation of EX solution without H_2O_2, the rate of process is almost unchangeable for testing 4 h with pH≥5 but significantly increases when pH=3. However, the rate value of 0.0035 is still lower than the value of 0.049 at the lowest concentration of H_2O_2 in the test.

As discussed in the introduction, to enhance the kinetics of EX oxidation by H_2O_2, some iron salts such as ferric sulfate or ferrous sulfate can be added into solution to make highly reactive hydroxyl radicals based on Fenton's Reagent theory [6, 10−11]. Some other oxidants such as NaOCl and $KMnO_4$ may also be the promising candidates and this will be investigated in the future.

4 Conclusions

1) Degradation of ethyl xanthate (EX) salt by hydrogen peroxide with different initial pH values shows that the thiosulfate salt is the main by-product from degradation of EPX at various pH values. Then, under different pH values, thiosulfate salt could be further decomposed into elemental sulfur (pH<7) or sulfate and carbonate salts (pH>7). Based on the new by-products, the novel degradation mechanism is also proposed to explain the results.

2) The effects of initial pH values and H_2O_2 concentrations on kinetics of degradation of EX are investigated. The results reveal that H_2O_2 concentrations have significant effect on degradation while initial pH values have limited effect on degradation. Together, this research provides a new understanding on oxidation process of removal of flotation residuals by hydrogen peroxide.

References

[1] CHEN J H, ZHAO C H, GONG Z Q. Research on the photocatalytic removal of *N*-butyl and isobutyl xanthates in the TiO_2 suspension system [C]// 4th International Conference on Separation Science and Technology (ICSST-04). Nanning, China: Frontiers on Separation Science and Technology, 2004: 1010−1018.

[2] National Industrial Chemicals Notification and assessmentscheme. Sodium ethyl xanthate. Priority existing chemical No 5 [R]. Canberra, Australia: Australian Government Publishing Service, 1995: 1−66.

[3] CHEN Shao-hua, GONG Wen-qi, MEI Guang-jun, CHEN Xiao-dong, YAN Heng-zhen. Evaluation of biodegradability of alkyl xanthates flotation collecters [J]. Journal of Central South University (Science and Technology), 2011, 42(2): 546−554. (in Chinese)

[4] SHU Sheng-hui, YANG Yong-feng, ZHANG Zhi. Treatment methods and research progress in xanthate-removal from effluent of flotation operation [J]. Multipurpose Utilization of Mineral Resources, 2009, (4): 35−36.

[5] DUAN Hai-xia, LIU Jiong-tian, LANG Xian-ming, WANG Jing-cheng. Study development of interior xanthate wastwater treatment [J]. Mining and Metallurgy, 2009, 18(4): 80−82.

[6] AI Guang-hua, WEI Zong-wu. Study on flotation reagents prevention and control of ecological environmental pollution [J]. Environmental Protection of Xinjiang, 2008, 30(2): 31−34.

[7] MIELCZARSKI J. The role of impurities of sphalerite in the adsorption of ethyl xanthate and its flotation [J]. International Journal of Mineral Processing, 1986, 16(3/4): 179−194.

[8] SILVESTER E, TRUCCOLO D, FU Ping-hao. Kinetics and mechanism of the oxidation of ethyl xanthate and ethyl thiocarbonate by hydrogen peroxide [J]. J Chem Soc Perkin Trans, 2002, 2(9): 1562−1571.

[9] FAGADAR-COSMA G, TARANU I, FAGADAR-COSMA E. Electrochemical oxidation of sodium ethyl xanthate in aqueous solutions [J]. Rev Roum Chim, 2003, 48(2): 131−136.

[10] XU Jin, SUN Shui-yu, ZHANG Ping, CAI He-shan. Degradation of remainder xanthate in flotation wastewater by fenton reagent [J]. Environmental Protection of Chemical Industry, 2005, 25(2): 125−127.

[11] JI Hong-an. Study on using ozone to resolve xanthate and pine oil in the mineral wastewater [J]. Gansu Metallurgy, 2008, 30(3): 70−72. (in Chinese)

[12] VUCINIC D R, LAZIC P M, ROSIC A A. Ethyl xanthate adsorption and adsorption kinetics on lead-modified galena and sphalerite under flotation conditions [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006, 279(1/2/3): 96−104.

[13] CHENG Wei, ZHANG Qin, MA Wen-qiang. A research on removal of xanthate from floatation wastewater with activated carbon [J]. Acta Mineralogica Sinica, 2010, 30(2): 262−267.

[14] CHEN S H, GONG W Q, MEI G J, ZHOU Q, BAI C P, XU N. Primary biodegradation of sulfide mineral flotation collectors [J]. Miner Eng, 2011, 24(8): 953−955.

[15] CHOCKALINGAM E, SUBRAMANIAN S, NATARAJAN K A. Studies on biodegradation of organic flotation collectors using *Bacillus polymyxa* [J]. Hydrometallurgy, 2003, 71(1/2): 249−256.

[16] IWASAKI I, COOKE S R B. The decomposition of xanthate in acid solution [J]. J Am Chem Soc, 1958, 80(2): 285−288.

[17] IWASAKI I, COOKE S R B. Dissociation constant of xanthic acid as determined by spectrophotometric method [J]. J Phys Chem, 1959, 63(8): 1321−1322.

[18] FINKELSTEIN N P. Kinetic and thermodynamic aspects of the interaction between potassium ethyl xanthate and oxygen in aqueous solution [J]. Trans Inst Min Metall, 1967, 76: 51−59.

[19] HAO F P, SILVESTER E, SENIOR G D. Spectroscopic characterization of ethyl xanthate oxidation products and analysis by ion interaction chromatography [J]. Anal Chem, 2000, 72(20): 4836−4845.

[20] SUN Z, FORSLING W. The degradation kinetics of ethyl-xanthate as a function of pH in aqueous solution [J]. Mineral Engineering, 1997, 10(4): 389−400.

[21] AI Guang-hua, WANG Yong, TAO Xiu-xiang, CHEN Yu-lin. Removal of xanthate in flotation wastewater by ultrasound and fenton reagent [C]// Electric Technology and Civil Engineering (ICETCE), 2011 International Conference on. Lushan, China: IEEE, 2001: 6106−6110.

[22] RUBINSON K A, RUBINSON J F. Contemporary instrumental analysis [M]. Upper Saddle River, NJ: Prentice Hall, 2000: 653−662.

[23] MIURA Y, KAWAOI A. Determination of thiosulfate, thiocyanate and polythionates in a mixture by ion-pair chromatography with ultraviolet absorbance detection [J]. Journal of Chromatography A, 2000, 884(1/2): 81−87.

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