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# Degradation of sodium *n*-butyl xanthate by vacuum UV-ozone (VUV/O<sub>3</sub>) in comparison with ozone and VUV photolysis

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## ABSTRACT

Sodium *n*-butyl xanthate (SBX) is widely used as a collector in the flotation of sulfide minerals. Residual SBX and its byproducts in the flotation effluents may cause environmental pollution. The degradation of SBX by a vacuum UV-ozone (VUV/O<sub>3</sub>) in comparison with ozone and VUV photolysis was studied. The effects of the pH and ozone dosage were investigated. The SBX was almost completely degraded within 5 min by both the O<sub>3</sub> and VUV/O<sub>3</sub> processes, whereas the removal of COD became less efficient compared to SBX removal. The COD removal and sulfur mineralization ratio in the VUV/O<sub>3</sub> increased by 30.4–41.6% and 16.2–23.3%, respectively, compared to the ozonation. The large ozone dosage enhanced the mineralization of SBX, but resulted in low ozone consumption ratio. However, the ozone consumption ratio increased by 17.3–45.1% while involving VUV irradiation in the ozonation. The concentrations of formed sulfur byproducts (CS<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>) were measured. The rapid conversion of CS<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> ions was observed, showing the effective mineralization of sulfur byproducts in the O<sub>3</sub> and VUV/O<sub>3</sub> processes. The enhancements of the SBX mineralization and ozone consumption ratio by involving VUV radiation with ozone were discussed, and the decomposition pathway of SBX was proposed.

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## 1. Introduction

Alkyl xanthates are widely used as collectors in the froth flotation of sulfide minerals. The estimated xanthate consumption is over 60,000 tons per year because 50–300 g xanthates are required per ton of ore (Somasundaran and Moudgil, 1988). Some xanthates enter into foam products, but xanthates remained in the flotation effluents may have serious environmental consequences. The xanthates are toxic for biota (Sun and Forsling, 1997) and harmful to nervous system and livers of both human and animals (Zhao et al., 2006). Carbon disulfide (CS<sub>2</sub>), one degradation byproduct, has been classified as a hazardous air pollutant under Title III of the 1990 Clean Air Act Amendment (CAAA) of the United States (Hugler et al., 1999). Therefore, the mineral processing industry is

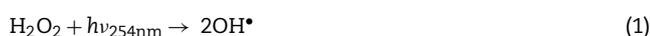
under the increasing pressure to eliminate the discharged organic flotation reagents. Currently, some techniques such as coagulation–precipitation (Kong et al., 2011) and biological treatment (Cheng et al., 2012) are used to remove organic reagents from flotation wastewaters. However, these methods have both advantages and disadvantages. For example, the biological treatment usually requires a long duration. In addition, the growth of bacteria may be retarded by presenting the xanthates (Natarajan and Prakasan, 2013). Therefore, it is urgent to develop new methods to effectively remove organic flotation reagents from the effluents.

Recently, advanced oxidation processes (AOPs) are studied to decompose alkyl xanthates using ozone (Liu et al., 2015), Fenton's reagent (Chen and Du, 2014), photocatalysis (Xiao and Ouyang, 2011), electrolysis and photoelectrooxidation

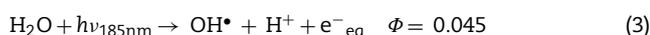
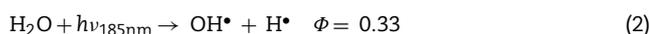
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(Molina et al., 2013). For instance, by combining an ozonator and a flotator, sodium *n*-butyl xanthate was efficiently removed with the diminishing of COD and the generation of  $\text{SO}_4^{2-}$  ions (Liu et al., 2015). Although the ozonation exhibits high efficiency in removing organic flotation reagents, a large energy consumption is required for  $\text{O}_3$  generation (Abbasi et al., 2015), and the low mineralization of byproducts appears due to the selectivity of oxidation (Beltrán and Alvarez, 1996; Chu et al., 2008). Additionally, various AOPs have been applied to remove alkyl xanthates, whereas the degradation pathways of xanthates are rarely mentioned.

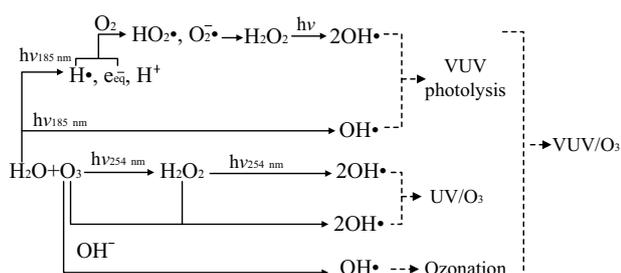
Previous studies demonstrated that the combined UV/ $\text{O}_3$  process was more effective in removing synthetic organic pollutants compared to ozone alone (Amat et al., 2005; Gottschalk et al., 2000; Umar et al., 2013). However, due to a low molar absorption coefficient ( $18.6 \text{ M}^{-1} \text{ cm}^{-1}$ ) of  $\text{H}_2\text{O}_2$  at 254 nm, the generation of hydroxyl radicals ( $\text{OH}^\bullet$ ) (Eq. (1)) is limited in the UV/ $\text{O}_3$  process.



In the past two decades, the vacuum-UV (VUV) lamps, emitting about 10% radiation at 185 nm and 80–90% radiation at 254 nm, have been produced by covering low-pressure Hg lamps with quartz glass (Oppenländer, 2003). The VUV radiation at 185 nm can photolyze water to form  $\text{OH}^\bullet$  (Eqs. (2) and (3)), hydrogen radicals ( $\text{H}^\bullet$ ) and hydrated electrons ( $e_{\text{aq}}^-$ ) (Gonzalez et al., 2004). The  $\text{OH}^\bullet$  can also be generated via the complex interactions among  $\text{H}^\bullet$ ,  $e_{\text{aq}}^-$ , dissolved  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  (Imoberdorf and Mohseni, 2012). Due to direct photolysis of water by 185 nm VUV radiation, the combined VUV (185 + 254 nm) and ozone (VUV/ $\text{O}_3$ ) process has the most  $\text{OH}^\bullet$  generation pathways compared to the ozonation, VUV photolysis and UV/ $\text{O}_3$  process, as shown in Fig. 1. Several studies proved that the VUV/ $\text{O}_3$  was the most effective in degrading organic pollutants among these oxidation processes (Echigo et al., 1996; Ratpukdi et al., 2010). However, to the best of our knowledge, the application of the VUV/ $\text{O}_3$  process for removing organic flotation reagents has never been investigated.



This work investigated the degradation of sodium *n*-butyl xanthate (SBX) by the VUV/ $\text{O}_3$  process in comparison with the ozonation and VUV photolysis. The effects of solution pH and ozone dosage were studied. The degradation performances including the SBX removal, mineralization and ozone consumption ratio were compared among three processes. The



**Fig. 1** – Comparison of hydroxyl radical generation pathways in the ozonation, VUV photolysis, UV/ $\text{O}_3$  and VUV/ $\text{O}_3$  processes.

concentrations of generated carbon disulfide ( $\text{CS}_2$ ) and sulfate ( $\text{SO}_4^{2-}$ ) were monitored to exhibit the evolution of sulfur byproducts. The enhancements of the SBX mineralization and ozone consumption ratio were discussed, and the decomposition pathway of SBX was proposed in the VUV/ $\text{O}_3$  system.

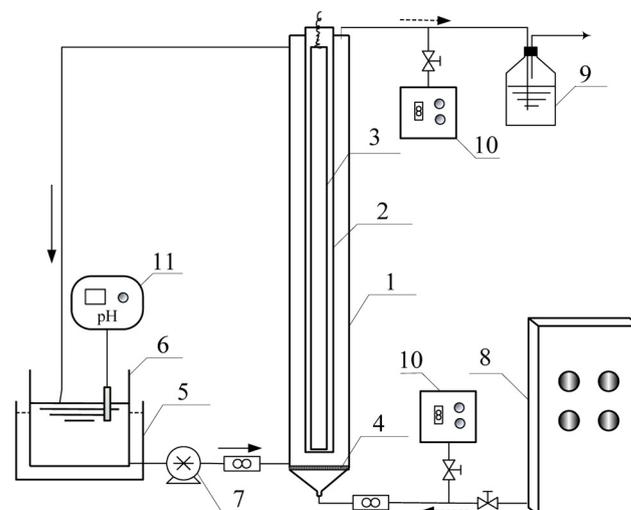
## 2. Experimental

### 2.1. Reagents

Sodium *n*-butyl xanthate (SBX) was purchased from Zhuzhou mineral processing reagent plant, Hunan Province, China. The SBX used in this work was further purified with a recrystallization method. The deionized water was used in the experiments.

### 2.2. Experimental setup and procedures

Fig. 2 showed a diagram of vacuum UV-ozone (VUV/ $\text{O}_3$ ),  $\text{O}_3$  and VUV photolysis experimental systems. The VUV lamp (23 W, Guangdong Cnlight Co., China) was an ozone-generating low-pressure Hg lamp with major emission (ca. 90%) at 254 nm and minor emission (ca. 10%) at 185 nm. All the experiments were conducted in a bubble-column, semi-batch reactor (internal diameter 45 mm, height 700 mm) made of borosilicate glass. A quartz tube (external diameter 30 mm) was mounted in the axial position to house a VUV lamp leaving an effective reaction volume of 0.62 L. The reactor was equipped with an inlet at the bottom and an outlet at the top, connected to a SBX solution tank and peristaltic pump (WT600-1F, Longer-Pump, China) to assist water recirculation. The hydraulic retention time of the solution in the reactor was ca. 20 s. The SBX solution was kept at ca. 25 °C with a water bath. Ozone was produced by an ozone generator (CF-YG10, Beijing Shanmeishuimei Environmental Engineering Co., China). An ozone gas stream (0.4–3.0 L/min) entered into the reactor via a porous gas distributor. The output gas passed through a KI adsorption solution to eliminate residual  $\text{O}_3$ . The ozone dosage ranging from 14.7 to 125.9 mg/min was controlled by changing the gas flow rate.



**Fig. 2** – The schematic diagram of the VUV/ $\text{O}_3$ ,  $\text{O}_3$  and VUV photolysis systems: (1) ozonation reactor, (2) quartz tube, (3) VUV/UV lamp, (4) porous gas distributor, (5) water bath, (6) SBX solution tank, (7) recirculation pump, (8) ozone generator, (9) KI adsorption solution, (10) gas sampler, (11) pH meter.

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