UV\textsubscript{185}+254 nm photolysis of typical thiol collectors: decomposition efficiency, mineralization and formation of sulfur byproducts

Pingfeng Fu\textsuperscript{1,2}, Gen Li\textsuperscript{1}, Xiaoting Wu\textsuperscript{1}, Xiaofeng Lin\textsuperscript{1} and Bolan Lei\textsuperscript{1}

\textsuperscript{1}School of Civil and Resources Engineering, University of Science and Technology Beijing, Beijing 100083, People’s Republic of China
\textsuperscript{2}Key Laboratory of High-efficient Mining and Safety of Metal Mines, Ministry of Education, Beijing 100083, People’s Republic of China

The decomposition of toxic flotation reagents upon UV\textsubscript{185}+254 nm irradiation was attractive due to operational simplicity and no dosage of oxidants. In this work, the degradation of typical thiol collectors (potassium ethyl xanthate (PEX), sodium diethyl dithiocarbamate (SDD), O-isopropyl-N-ethyl thionocarbamate (IET) and dianilino dithiophosphoric acid (DDA)) was investigated by UV\textsubscript{185}+254 nm photolysis. The degradation efficiencies and mineralization extents of collectors were assessed. The formation of CS\textsubscript{2} and H\textsubscript{2}S byproducts was studied, and the mechanisms of collector degradation were proposed under UV\textsubscript{185}+254 nm irradiation. The PEX, SDD and IET were decomposed with nearly 100\% removal upon 75 min of UV\textsubscript{185}+254 nm irradiation. The decomposition rate constants decreased in the order SDD > PEX > IET > DDA, and the DDA was the refractory collector. After 120 min of UV\textsubscript{185}+254 nm irradiation, 15–45\% of carbon and 25–75\% of sulfur of collectors were completely mineralized, and the mineralization extent decreased in the order PEX > SDD > IET > DDA. The percentage of gaseous sulfur (CS\textsubscript{2} and H\textsubscript{2}S) ranged from 0.48 to 4.85\% for four collectors, showing the fraction of emitted sulfur byproducts was small. The aqueous CS\textsubscript{2} concentration increased in the first 10–20 min, and was decreased to a low level of 0.05–0.1 mg l\textsuperscript{-1} at 120 min. Two mechanisms, i.e. direct UV\textsubscript{254} nm photolysis and indirect oxidation with free radicals, were responsible for collector decomposition in the UV\textsubscript{185}+254 nm photolysis.

© 2019 The Authors. Published by the Royal Society under the terms of the Creative Commons Attribution License http://creativecommons.org/licenses/by/4.0/, which permits unrestricted use, provided the original author and source are credited.
1. Introduction

Froth flotation has become the most widely applied process for separating valuable minerals from ores in mines around the world. Thiol collectors, such as xanthates, dithiophosphates and dithiocarbamates, are important flotation reagents to render sulfide minerals hydrophobic and facilitate bubble attachments [1,2]. To achieve high recovery of non-ferrous metals, the dosage of collectors is frequently ranged from 30 to 300 g ton\(^{-1}\) (ore). Therefore, the consumption of thiol collectors becomes very large due to the extremely high amount of treated ores. Even in the 1980s, the global consumption of xanthates had reached above 52 000 tons per year [2]. Nevertheless, nearly 50% of collectors dosed in flotation circuits would be discharged in wastewaters after the mineral flotation [3]. Some collectors and their byproducts are found to be toxic to soil microbes, biota, animals and human beings [4–7]. Previously, the hazards of xanthate to frog embryos have been reviewed [7]. Accordingly, the discharge of collectors from mineral flotation may cause serious environmental pollution. Therefore, it has been of great concern to remove potentially toxic collectors from flotation wastewaters for the sustainable development of mining industry.

Recently, some processes have been developed to remove organic reagents from flotation wastewaters, including adsorption [8], chemical oxidation [9,10], ozonation [11,12] and biodegradation [13,14]. Chemical oxidation and ozonation have exhibited high efficiency in decomposing flotation reagents. But these processes need the dosage of chemical oxidants, such as sodium hypochlorite [9], persulfate [10], hydrogen peroxide [15] and ozone [11]. The usage of highly reactive oxidants in mines makes them less attractive and sometimes expensive. Since most of the mines are located far from industrial zones, there are potential risks associated with long distance transportation and storage of dangerous chemicals. The biodegradation is widely accepted as a low cost process in wastewater treatment. However, previous reports indicate that some flotation reagents are toxic to microbes, considerably reducing microbial activities in the biodegradation of flotation reagents [13,16].

Advanced oxidation processes (AOPs) involving ozone [10], Fenton’s reagent [17], hydrogen peroxide [15], persulfate [18,19] and photocatalyst [20–22] have been investigated to effectively degrade flotation collectors, pharmaceuticals and textile dyes. However, most of these studies only concerned the removal efficiencies of xanthates [11,12,15]. Up to now, research on the removal of other thiol collectors such as dithiophosphates and dithiocarbamates has been scarce. Because thiol collectors have different molecular structures [1,23], their decomposition behaviours by the same AOP method may differ. Additionally, the functional groups of all thiol collectors have sulfur atoms [1,23]. So, it is possible to generate toxic sulfur byproducts such as CS\(_2\) and H\(_2\)S, while organic sulfur of collectors is mineralized to sulfate. For example, the concentrations of aqueous CS\(_2\) were determined [29]. Moreover, the operation of UV185 nm photolysis has shown high oxidation capacity for pollutants, such as odour compounds [27], pharmaceuticals [28] and pesticides [29]. However, the operation of UV185 nm photolysis is much simpler than the UV254 nm/O\(_3\) and UV254 nm/TiO\(_2\) photocatalysis because no oxidant or catalyst is required. In terms of the practical treatment of flotation wastewaters, the transportation and storage of dangerous oxidants in mines can also be avoided if the UV185 nm photolysis is applied. Thus, it is quite necessary to assess the removal performances of flotation reagents by the UV185 nm photolysis. However, as far as we know, there is no report on the UV185 nm photolysis of organic flotation reagents.

\[
\begin{align*}
    H_2O + \text{hv}_{185nm} & \rightarrow \text{OH}^* + H^+ + e_{aq}^-; \\
    H_2O + \text{hv}_{185nm} & \rightarrow \text{OH}^* + H^*, \quad (1.1) \\
    2\text{OH}^* & \rightarrow H_2O_2, \quad (1.2) \\
    \text{H}^* + O_2 & \rightarrow \text{HO}_2^*, \quad (1.3)
\end{align*}
\]
HO₂• + H₂O ⇄ H₃O⁺ + O₂•⁻  \( \text{pK}_a = 4.8 \)

and

\[ 2\text{HO}_2• \rightarrow \text{O}_2 + \text{H}_2\text{O}. \]

In this work, the UV\(_{185+254}\) nm photolysis of thiol collectors is investigated by using a 40 W low-pressure Hg lamp, which emits about 10% radiation at 185 nm and 90% radiation at 254 nm. Four thiol collectors, potassium ethyl xanthate (PEX), sodium diethyl dithiocarbamate (SDD), O-isopropyl-N-ethyl thionocarbamate (IET) and dianilino dithiophosphoric acid (DDA), are selected as typical sulfide mineral collectors. The objectives of this work are (i) to assess the feasibility of decomposing thiol collectors by the UV\(_{185+254}\) nm photolysis, (ii) to determine the generation of CS₂ and H₂S byproducts, as well as (iii) to propose the collector decomposition mechanisms under UV\(_{185+254}\) nm irradiation. The mineralization of collectors is examined by measuring total organic carbon (TOC) and SO₄²⁻ concentrations. The amounts of gaseous CS₂ and H₂S, as well as the concentration of aqueous CS₂, were measured to study the generation of sulfur byproducts.

2. Material and methods

2.1. UV lamps and chemicals

Two types of low-pressure Hg lamps with electrical power of 40 W were purchased from Bright Star Light & Electricity Co., Ltd, Guangdong, China. The UV\(_{185+254}\) nm lamp transmitted both 185 nm VUV and 254 nm UV light through high-purity quartz glass, but the UV\(_{254}\) nm lamp only transmitted 254 nm UV light. The UV\(_{254}\) nm irradiation intensity of UV\(_{185+254}\) nm lamp was about 90% of UV\(_{254}\) nm lamp. The lamps had a length of 1199 mm and a diameter of 19 mm.

The PEX and SDD with analytical grade were purchased from Aladdin Chemical Reagent Co., Ltd, Shanghai, China. The industrial grade IET and DDA were purchased from Tieling Flotation Reagents Co., Ltd, Liaoning, China. Their molecular structures, molecular formulas and abbreviations are summarized in table 1. Other chemicals such as cupric acetate, lead acetate, diethylamine, triethanolamine, silver sulfate and mercury sulfate were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing, China. Deionized water was used in the degradation experiments.

| collector name | molecular structure | molecular formula | abbreviation |
|----------------|---------------------|-------------------|--------------|
| potassium ethyl xanthate | CH₃CH₂OOCSSK | C₂H₄OCSSK | PEX |
| sodium diethyl dithiocarbamate | CH₃CH₂NCS(NHCH₃)₂ | (C₆H₅NH)₂PSSH | DDA |
| O-isopropyl-N-ethyl thionocarbamate | H-C-O-C-N-CH₂-CH₃ | (CH₃)₂CHOCSNHCH₃ | IET |
| dianilino dithiophosphoric acid | | | |

Table 1. Collector name, molecular structure, molecular formula and abbreviation.
2.2. Experimental set-up and degradation procedures

All degradation experiments were conducted with a batch mode in a jacket glass reactor connected to a thermostatic bath. The schematic diagram of the experimental set-up is shown in figure 1. The cylindrical reactor, with 1240 mm height and 53 mm internal diameter, was installed at its axis with a quartz tube with a height of 1220 mm and outer diameter of 21 mm. The UV$_{185+254}$ nm or UV$_{254}$ nm lamp was inserted into the quartz tube. The optical distance from tube surface to the internal surface of the reactor was 16 mm. The air was continuously purged into the reactor through a porous glass plate with a flow rate of 1.67 l min$^{-1}$. The injected air stream not only provided dissolved oxygen for degradation reactions, but also stirred the collector solutions. The degradation experiments were conducted at 25 $\pm$ 2°C.

Prior to photolysis experiments, the collector (0.2 g) was dissolved in 2 l deionized water to prepare a PEX (SDD, IET or DDA) solution of 100 mg l$^{-1}$ concentration. The initial pH was adjusted to 7.0 $-$ 12.0 using 0.05 mol l$^{-1}$ NaOH or HCl solution. When the collector solution was introduced into the reactor purged with an air stream, the UV$_{185+254}$ nm or UV$_{254}$ nm lamp was turned on to carry out photolysis experiments. The irradiation time was controlled to be 120 min. Because CS$_2$, H$_2$S and other sulfur byproducts were emitted into gas phase, the emission gas was introduced into an activated carbon column to remove toxic byproducts. The aqueous samples were taken at designated intervals to determine the concentrations of collector, chemical oxygen demand (COD), TOC, CS$_2$ and SO$_4^{2-}$ ions.

2.3. Analysis and calculation

2.3.1. Determination of collector concentration, COD and TOC

The concentration of thiol collectors (PEX, SDD, IET and DDA) was determined by a UV–vis spectroscopic method [10,11,13,30]. The absorbance of collector solution was recorded by a UV–vis spectrophotometer (UV-5500PC, Shanghai Metash Instruments Co. Ltd, China). The COD was determined by the standard dichromate method (HJ/T 399-2007). The TOC of water samples was measured by using a Shimadzu TOC-V organic carbon analyzer. The carbon mineralization extent ($\gamma_c$) of the collector (PEX, SDD, IET and DDA) was calculated as the below equation

$$\gamma_c = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100\%,$$

where TOC$_0$ and TOC$_t$ (mg l$^{-1}$) were the TOC concentration at initial and time $t$, respectively.
2.3.2. Determination of concentrations of aqueous CS₂ and SO₄²⁻ ions

The aqueous CS₂ concentration was measured by a diethylamine cupric acetate spectrophotometric method (GB/T 15504-1995). Fifty millilitres of water sample were continuously purged by a 100 ml min⁻¹ N₂ stream for 1 h to volatilize CS₂, which was absorbed by a diethylamine and cupric acetate mixed liquid. Then the absorbance of absorption liquid was measured at 430 nm using dehydrated alcohol as a reference solution. The concentration of sulfate was determined by a barium chromate spectrophotometry method (HJ/T 342-2007). Because SO₄²⁻ ions, with the highest valence of sulfur, were the final oxidization product of organic sulfur in collectors, the sulfur mineralization extent (γₛ) of the collector was defined as the below equation [31]

\[ γₛ = \frac{M}{n \times 96} \times \frac{C_{SO₄²⁻}}{C_0} \times 100\% \]  

(2.2)

where \( M \) and \( n \) were the molecular weight and number of sulfur atom in the collector (PEX, SDD, IET or DDA), respectively, \( C_{SO₄²⁻} \) (mg l⁻¹) was the concentration of SO₄²⁻ ions at time \( t \), and \( C_0 \) (mg l⁻¹) was the initial concentration of the collector.

2.3.3. Measurement of the amount of gaseous CS₂ and H₂S

The amount of gaseous CS₂ emitted from the reactor for 120 min was measured by a diethylamine spectrophotometric method (GB/T 14680-93). By adding 5.0 mg cupric acetate, 2.5 ml diethylamine and 2.5 ml triethanolamine into a 500 ml volumetric flask, the CS₂ absorption liquid was prepared by diluting the mixture with dehydrated alcohol to 500 ml. As shown in figure 1, before the emission gas was introduced into CS₂ absorption liquid, it was first passed through a glass tube filled by absorbent cotton coated with lead acetate to remove H₂S. The amount of gaseous H₂S for 120 min was measured by a methylene blue spectrophotometric method (GB/T 11742-89). By adding 4.3 g cadmium sulfate, 0.30 g NaOH and 10.0 g polyvinyl alcohol ammonium phosphate into a 1000 ml volumetric flask, the H₂S absorption liquid was prepared by diluting the mixture with deionized water to 1000 ml.

3. Results and discussion

3.1. Effect of UV wavelength

The photolysis of thiol collectors (PEX, SDD, IET and DDA) upon UV₂⁵⁴ nm or UV₁₈₅⁺₂⁵⁴ nm irradiation is shown in figure 2. The removal efficiency of collectors and decomposition rate constants are summarized in table 2. In this work, overall kinetics of the collector degradation can be described by a simple pseudo-first-order rate law [32]. As shown in figure 2a and table 2, the removal efficiency of PEX and SDD at 75 min reached 97.93% and 99.16%, respectively, which was much higher than that (about 30%) of...
IET and DDA upon UV254 nm irradiation. In UV-irradiated solutions, the decomposition of pollutants is frequently initiated by excited molecules with absorbing UV irradiation [33]. Among four collectors, the PEX and SDD may have higher mole absorptivity of UV254 nm irradiation than IET and DDA, resulting in higher removal efficiencies. In most mines, residual flotation reagents are usually removed in tailing ponds by a natural degradation process involving sunlight and oxygen. As given in table 2, the half-life of IET and DDA was almost one order of magnitude larger than that of PEX and SDD. Therefore, it can reasonably be inferred that after the natural degradation, residual IET and DDA in tailing ponds would have higher concentrations than the PEX and SDD.

As exhibited in figure 2 and table 2, the removal efficiency of PEX and SDD had reached above 96% even at 20 min under UV185 + 254 nm irradiation. At 75 min, nearly 100% removal of PEX, SDD and IET was achieved, revealing that most thiol collectors could be effectively degraded by the UV185 + 254 nm photolysis without adding any oxidant. The decomposition rate constant (k_collector) of collectors upon UV185 + 254 nm irradiation decreased in the order k_SDD (0.2005 min⁻¹) > k_PEX (0.1565 min⁻¹) > k_IET (0.04485 min⁻¹) > k_DDA (0.00701 min⁻¹). As listed in table 2, the k_collector values for four collectors under UV185 + 254 nm irradiation were 1.60 ± 2.03 times higher than those achieved upon UV254 nm irradiation, showing the enhanced degradation of thiol collectors by the UV185 + 254 nm photolysis. However, the DDA, with very low k_collector value, can be considered as a refractory collector for the UV185 + 254 nm photolysis.

### Table 2. The removal efficiencies of collectors, decomposition rate constants (k_collector), half-lives (t₁/₂) and correlation coefficients (R²) in the degradation of thiol collectors under UV185 + 254 nm and UV254 nm irradiation, respectively.

| Collectors | UV irradiation | removal efficiency (%) | k_collector (min⁻¹) | t₁/₂ (min) | R² |
|------------|----------------|------------------------|---------------------|------------|----|
|            | UV185 + 254 nm | 20 min                 | 75 min              |            |    |
| PEX        | UV254 nm       | 96.51                  | 99.86               | 0.1565     | 4.43| 0.982 |
|            |                | 74.77                  | 97.93               | 0.06629    | 10.46| 0.989 |
| SDD        | UV185 + 254 nm | 98.45                  | 99.88               | 0.2005     | 3.02| 0.990 |
|            | UV254 nm       | 89.21                  | 99.16               | 0.1076     | 6.44| 0.992 |
| IET        | UV185 + 254 nm | 52.62                  | 99.08               | 0.04485    | 15.45| 0.986 |
|            | UV254 nm       | 6.25                   | 31.20               | 0.00447    | 155.07| 0.988 |
| DDA        | UV185 + 254 nm | 13.98                  | 43.26               | 0.00701    | 98.88| 0.998 |
|            | UV254 nm       | 11.31                  | 29.17               | 0.00438    | 158.25| 0.991 |

### 3.2. Effect of initial pH

The flotation of sulfide minerals is usually conducted in alkaline pulps. Thus, residual collectors are present in the flotation wastewaters at pH range from neutral to alkaline [34]. In this work, the effect of initial pH on the UV185 + 254 nm photolysis of PEX and DDA was investigated. As shown in figure 3, both the k_PEX and k_DDA values gradually decreased as initial pH rose. The decomposition rate constant (k_collector) of collectors upon UV185 + 254 nm irradiation decreased in the order k_SDD (0.2005 min⁻¹) > k_PEX (0.1565 min⁻¹) > k_IET (0.04485 min⁻¹) > k_DDA (0.00701 min⁻¹). As listed in table 2, the k_collector values for four collectors under UV185 + 254 nm irradiation were 1.60 ± 10.03 times higher than those achieved at pH 12.0, respectively. It suggests that the neutral pH can facilitate the decomposition of flotation collectors upon UV185 + 254 nm irradiation. In the previous studies, the higher decomposition efficiencies were also achieved at lower pH during the UV185 + 254 nm photolysis of 1,4-dioxane [30] and 4-tert-octylphenol [35].

Upon 185 nm VUV irradiation, the homolysis and photochemical ionization of H2O occur with the generation of OH• radicals (equations (1.1) and (1.2)), and OH• radicals (or HO2•) can recombine to form H2O2 (equations (1.3) and (1.6)) [25]. Under UV185 + 254 nm irradiation, H2O2 can be decomposed by absorbing UV254 nm light to form OH• radicals (equation (3.1)). Accordingly, OH• radicals and H2O2 are in equilibrium under UV irradiation offered by the UV185 + 254 nm lamp. On the other hand, the concentration of H2O2 is also dependent on the pH value of the reaction system. As given in equation (3.2), H2O2 itself is in equilibrium with OH⁻ anions [36]. Additionally, HO2• radicals are also in equilibrium with protons (equation (1.5)). According to equations (1.5), (1.6) and (3.2), it can be seen that high H⁺ concentration (i.e. low pH) promotes the equilibrium to form H2O2. In turn,
increased concentration of H₂O₂ results in the formation of more OH• radicals (equation (3.1)). This equilibrium consideration may explain why the k\\sub{PEX} and k\\sub{DDA} values were higher at the neutral pH under UV \textsubscript{185+254 nm} irradiation

\[ \text{H}_2\text{O}_2 + h\nu_{254\text{nm}} \rightarrow \text{OH}^{\bullet} + \text{OH}^{\bullet} \]  

(3.1)

and

\[ \text{H}_2\text{O}_2 + \text{OH}^{-} \leftrightarrow \text{H}_2\text{O} + \text{HO}_2^{-} \quad pK_a = 11.62. \]  

(3.2)

In addition, the equilibrium of carbonate may also influence the pH dependence of the collector decomposition. The mineralization of contaminants by UV-based AOPs results in the formation of CO₂, subsequently increasing the aqueous concentration of CO\textsubscript{3}\textsuperscript{2−} anions. According to the equilibrium of CO\textsubscript{3}\textsuperscript{2−} in water, HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} anions dominate the equilibrium approximately at neutral to weak basic pH (6 < pH < 10) and at strong basic pH (pH > 10), respectively. These carbonate species can scavenge OH• radicals. However, CO\textsubscript{3}\textsuperscript{2−} anions have a larger scavenging capacity than HCO\textsubscript{3}\textsuperscript{−} [37]. Thus, at higher initial pH, more OH• radicals would be scavenged by CO\textsubscript{3}\textsuperscript{2−} anions, resulting in lower decomposition rate constants of PEX and DDA.

3.3. The mineralization of thiol collectors

To investigate the mineralization of thiol collectors under UV \textsubscript{185+254 nm} irradiation, the concentrations of COD, TOC and SO\textsubscript{4}\textsuperscript{2−} ions were measured with the results shown in figure 4. For each collector, the relative concentrations of COD and TOC declined, and the SO\textsubscript{4}\textsuperscript{2−} concentration increased as the collector was decomposed. It suggested that the byproducts had been further degraded with the formation of CO₂ and SO\textsubscript{4}\textsuperscript{2−} ions under UV \textsubscript{185+254 nm} irradiation. As indicated in figure 4, the TOC was reduced just a bit while the evident decrease in COD was observed for each collector. Thus, the removal efficiency of COD was higher than the mineralization extent of carbon as given in table 3. By comparing the decomposition rate constants for collector and COD removal, as summarized in tables 2 and 3, the k\\sub{collectors} for each collector was 3−21 folds higher than the k\\sub{COD} value. It clearly indicated that only a small fraction of organic carbon in collectors was mineralized to CO₂ upon UV \textsubscript{185+254 nm} irradiation although nearly 100% removal of PEX, SDD and IET was achieved. For four collectors, the mineralization extent of carbon (\(\gamma_c\)) at 120 min increased in the order DDA < IET < SDD < PEX. In particular, the \(\gamma_c\) for the PEX was much higher than that for DDA, IET and SDD, indicating that the byproducts derived from PEX seemed to be readily decomposed by OH• radicals.

As shown in figure 4, the concentration of SO\textsubscript{4}\textsuperscript{2−} ions increased up to 90.36 mg l\textsuperscript{−1} for PEX, 64.79 mg l\textsuperscript{−1} for SDD, 26.90 mg l\textsuperscript{−1} for IET and 11.48 mg l\textsuperscript{−1} for DDA, respectively, under UV \textsubscript{185+254 nm} irradiation for 120 min. The SO\textsubscript{4}\textsuperscript{2−} ions were the final sulfur product in the oxidation of organic sulfur in thiol collectors [11,12,24]. The occurrence of SO\textsubscript{4}\textsuperscript{2−} ions with increased concentrations well demonstrated that organic sulfur of collectors could be completely mineralized [24]. As summarized in table 3, the mineralization extent of sulfur (\(\gamma_s\)) at 120 min had reached 74.83% for PEX, 57.69% for SDD, 41.19% for IET and
16.75% for DDA, respectively. Thiol collectors except for DDA had much higher \( g_s \) values than the \( g_c \), suggesting that the conversion of organic sulfur to SO\(_4^{2-}\) was more efficient than the mineralization of organic carbon to CO\(_2\). Considering \( g_c \) and \( g_s \) together, the mineralization extent of thiol collectors decreased in the order PEX, SDD, IET, DDA upon UV\(_{185+254}\) nm irradiation. In particular, the PEX and SDD had much larger extent of mineralization when compared with IET and DDA at the same degradation conditions.

### 3.4. Generation of CS\(_2\) and H\(_2\)S byproducts

Sulfur byproducts, such as carbon disulfide (CS\(_2\)), carbonyl sulfide (COS), hydrogen sulfide (H\(_2\)S), sulfite (SO\(_3^{2-}\)) and thiosulfate (S\(_2\)O\(_3^{2-}\)), were detected in the oxidation of xanthates by the AOPs [15,24,38–40]. Among these sulfur byproducts, the CS\(_2\), COS and H\(_2\)S are toxic and highly volatile contaminants [41].
For example, CS2 is considered as a hazard air pollutant under the Title III of the 1990 Clean Air Act Amendment (CAAA) of the USA [42]. Accordingly, while toxic sulfur byproducts are emitted from air purged flotation wastewaters into the atmosphere or indoor environment, it may pose a significant hazard to safety, health and the environment (SHE). However, to the best of our knowledge, no work is available in the literature on the quantitative determination of emitted CS2 and H2S in gas phase when thiol collectors are decomposed by the AOPs. For the aqueous CS2 byproduct, Fu et al. [11,24] had measured the CS2 concentration while degrading xanthates by the O3 and UV/O3 processes. However, the evolutions of aqueous CS2 byproduct has not yet been investigated during the degradation of thiol collectors, except for xanthates by the AOPs.

In this work, the amounts of gaseous CS2 and H2S emitted from air purged solutions were measured using the CS2 and H2S absorption liquids, respectively. As illustrated in figure 5, upon UV185+254 nm irradiation of 100 mg l⁻¹ collector solutions for 120 min, the amount of gaseous CS2 reached 1.405 mg for PEX, 3.784 mg for SDD, 0.154 mg for IET and 0.202 mg for DDA, respectively. The results indicated that the SDD and PEX released much larger amount of gaseous CS2 than IET and DDA. For the emission of H2S byproduct, gaseous H2S reached 0.0836 mg for PEX, 0.468 mg for SDD, 0.101 mg for IET and 0.0502 mg for DDA, respectively. Among four collectors, the SDD had released the largest amount of H2S into gas phase. For each collector, the amount of gaseous CS2 released was larger than that of H2S, and the trends became more evident for PEX and SDD. By considering CS2 and H2S together, the amount of gaseous sulfur byproducts released upon UV185+254 nm irradiation increased in the order IET/C25/DDA/PEX/SDD. According to these results, it could be seen that the release of gaseous sulfur byproducts was quite diverse due to their different molecular structures and sulfur contents of thiol collectors.

As mentioned above, the emitted CS2 and H2S are toxic gases. Thus, it is essential to indicate the percentage of gaseous sulfur to total sulfur in collectors. By assuming that no volatile sulfur byproducts except for CS2 and H2S are present in emission gas, the percentage of gaseous sulfur (βₘg) can be defined according to the below equation

\[
\beta_{mg} = \frac{m_1 \times (64/76) + m_2 \times (32/34)}{((n \times 32)/M) \times C_0 \times V} \times 100\% ,
\]  

(3.3)

where \(m_1\) and \(m_2\) (mg) were the amount of emitted CS2 and H2S into gas phase for 120 min, \(n\) was the number of S atom in collectors and \(V\) (l) was the volume of collector solutions. Thus, the \(\beta_{mg}\) values for four collectors are summarized in table 4. Except for the SDD, the \(\beta_{mg}\) for PEX, IET and DDA was very low, showing that only a small fraction of sulfur in thiol collector was released into emission gas in the UV185+254 nm photolysis. However, a previous study had estimated that 20.6% of total sulfur in \(n\)-butyl xanthate was released into gas phase after the oxidation by O3 [12]. These data were achieved by subtracting total sulfur in \(n\)-butyl xanthate with sulfur in SO₄²⁻ ions. Since other sulfur byproducts such as sulfite, thiosulfate as well as organic sulfur compounds would be also presented in aqueous solutions, 20.6% of sulfur released in gas phase might be overestimated by Yan et al. [12].

In this work, aqueous CS2 concentrations were also measured. As presented in figure 6, the CS2 concentration for each collector rapidly increased to its maximum value in the first 10–20 min, and
then gradually decreased to a low level under UV$_{185+254}$ nm irradiation. The measured maximum concentration of CS$_2$ was 0.37 mg l$^{-1}$ for PEX, 1.88 mg l$^{-1}$ for SDD, 0.18 mg l$^{-1}$ for IET and 0.15 mg l$^{-1}$ for DDA, respectively. It can be clearly seen that the decomposition of SDD can generate much more CS$_2$ in comparison to other collectors. Additionally, the order of maximum CS$_2$ concentration for four collectors was well consistent with that for the amount of gaseous CS$_2$ as shown in figure 5. As shown in figure 6, residual CS$_2$ concentrations for all collectors were decreased to a low level of 0.05–0.1 mg l$^{-1}$ after 120 min of UV$_{185+254}$ nm irradiation. By considering the remarkable increase in SO$_4^{2-}$ concentrations shown in figure 4, it can be reasonably inferred that most of CS$_2$ byproduct was converted to SO$_4^{2-}$ ions by OH$^\cdot$ radicals with the pathways as elucidated in our previous work \[24\].

As discussed above, the decomposition of SDD and PEX had generated a larger amount of CS$_2$ in comparison to IET and DDA. As summarized in table 1, both the sulfur content and molecular structure of thiol collectors are quite different from each other. Accordingly, the different sulfur contents and decomposition mechanisms caused by different molecular structures would be associated with the formation of sulfur byproducts under UV$_{185+254}$ nm irradiation. The sulfur contents of PEX, SDD, IET and DDA are 40.25%, 37.42%, 21.77% and 22.85%, respectively. The high sulfur contents of PEX and SDD may well elucidate their large amount of generated CS$_2$ byproduct. Additionally, the generation mechanisms of CS$_2$ from thiol collectors might also significantly influence its amount. However, up to now, the reports on the decomposition mechanisms of thiol collectors by the AOPs are scare. For the ozonation of xanthates, it is suggested that the attack on the C–O bond of xanthates by OH$^\cdot$ radicals and nucleophilic reactions occurring for the C=S bond of the −CSS$^-$ group could result in the generation of the CS$_2$ \[24,39\]. In this case, the C–O bond in the PEX and C–N bond in the SDD have high electron density, which may be preferentially attacked by OH$^\cdot$ radicals. Thus, the CS$_2$ may be generated from the PEX and SDD under UV$_{185+254}$ nm irradiation according to equations (3.4) and (3.5), respectively. As presented in table 1, the IET and DDA had molecular structures that were different to the PEX and SDD. The pathways of CS$_2$ generated from IET and DDA may be different from that for the PEX and SDD. In our future work, attention should be paid to elucidating the generation pathways of sulfur byproducts.

\[
\text{CH}_3\text{CH}_2\text{OCSSK} + \text{OH}^\cdot + 1/2\text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CS}_2 + \text{K}^+ + \text{O}_2^* \quad (3.4)
\]

and

\[
(\text{CH}_3\text{CH}_2)_2\text{NCSNa} + \text{OH}^\cdot + 1/2\text{O}_2 \rightarrow (\text{CH}_3\text{CH}_2)_2\text{NH} + \text{CS}_2 + \text{K}^+ + \text{O}_2^* \quad (3.5)
\]
3.5. The mechanisms of UV$_{185+254}$ nm photolysis of thiol collectors

As shown in figure 2 and table 2, thiol collectors could be degraded by both UV$_{254}$ nm and UV$_{185+254}$ nm photolysis, but with higher degradation rate constants under UV$_{185+254}$ nm irradiation. As mentioned above, free radicals such as OH• can be effectively generated in air purged water under 185 nm VUV irradiation as given in equations (1.1)–(1.6). OH• radicals, with an oxidation–reduction standard potential of 2.80 V, are non-selective and vigorous oxidants. The rate constants for OH• reacting with most organic compounds are within the range of $10^6$–$10^9$ l/(mol s) [43]. Therefore, under UV$_{185+254}$ nm irradiation, two degradation mechanisms as shown in figure 7, i.e. direct UV$_{254}$ nm photolysis and indirect oxidation with free radicals such as OH•, should be responsible for the decomposition of collectors [44].

Nevertheless, the contributions of UV$_{254}$ nm photolysis and indirect oxidation with free radicals to collector decomposition were quite dependent on molecular structures of thiol collectors. For the PEX, SDD and DDA, both UV$_{254}$ nm photolysis and indirect oxidation with free radicals had contributed greatly as the $k_{\text{collectors}}$ values under UV$_{185+254}$ nm irradiation were 1.60–2.63 times higher than those under UV$_{254}$ nm irradiation. But for the IET, the $k_{\text{IET}}$ for UV$_{185+254}$ nm photolysis was 10.03 times higher than that for UV$_{254}$ nm photolysis. This suggested that indirect oxidation with free radicals was the main mechanism for the UV$_{185+254}$ nm photolysis of IET.

4. Conclusion

Thiol collectors (PEX, SDD, IET and DDA) could be effectively degraded by the UV$_{185+254}$ nm photolysis without dosing any oxidant. The removal efficiencies of PEX, SDD and IET reached nearly 100% upon 75 min of UV$_{185+254}$ nm irradiation. The $k_{\text{collectors}}$ for four collectors decreased in the order $k_{\text{SDD}} > k_{\text{PEX}} > k_{\text{IET}} > k_{\text{DDA}}$. The DDA was the typical refractory flotation collector for UV$_{185+254}$ nm photolysis. In the UV$_{185+254}$ nm photolysis of the PEX and DDA, the $k_{\text{collectors}}$ values were decreased at high initial pH, indicating neutral pH of flotation wastewaters can facilitate the collector decomposition. After 120 min of UV$_{185+254}$ nm irradiation, the $\gamma_c$ and $\gamma_s$ for four collectors reached 15–45% and 25–75%, respectively, with the mineralization extent of PEX > SDD > IET > DDA. The effective degradation of thiol collectors was attained under UV$_{254}$ nm irradiation alone. Thus, two mechanisms, i.e. direct UV$_{254}$ nm photolysis and indirect oxidation with free radicals such as OH•, were responsible for the decomposition of collectors by the UV$_{185+254}$ nm photolysis.

After UV$_{185+254}$ nm irradiation for 120 min, the percentage of gaseous sulfur was 1.57% for PEX, 4.85% for SDD, 0.53% for IET and 0.48% for DDA, respectively, indicating that only a small fraction of sulfur in collectors was released into emission gas. For each collector, the amount of emitted CS$_2$ in gas phase was larger than that of H$_2$S. The aqueous CS$_2$ concentration increased rapidly in the first 10–20 min for each collector, and was then reduced to a low level of 0.05–0.1 mg l$^{-1}$ at 120 min under UV$_{185+254}$ nm irradiation.

Data accessibility. The datasets supporting this article have been uploaded as part of the electronic supplementary material.

Authors’ contributions. G.L. and X.W. set up the degradation system. G.L. and X.L. carried out the UV photolysis of thiol collectors. B.L. and X.W. measured the aqueous concentration of CS$_2$ and amount of emitted CS$_2$ and H$_2$S in gas phase. P.F., G.L. and X.L. contributed to analysis data and wrote the draft of the manuscript. Finally, P.F. revised the manuscript.
Matsushita T, Hirai S, Ishikawa T, Matsui Y, Shirasaki N. 2015 Decomposition of 1,4-dioxane by vacuum ultraviolet irradiation: study of economic feasibility and by-product formation. Process Saf. Environ. Prot. 94, 528 – 541. (doi:10.1016/j.psep.2014.11.005)

Zhang GS, He XX, Nadagouda MN, O’Shea KE, Dionysiou DD. 2015 The effect of basic pH and carbonate ion on the mechanism of photocatalytic destruction of cylindrospermopsin. Water Res. 73, 353 – 361. (doi:10.1016/j.watres.2015.01.011)

Shen Y, Nagaraj DR, Farinato R, Somasundaran P. 2016 Study of xanthate decomposition in aqueous solutions. Miner. Eng. 93, 10 – 15. (doi:10.1016/mineng.2016.04.004)

Liu RD, Sun W, Ouyang K, Zhang LM, Hu YH. 2015 Decomposition of sodium butyl xanthate (SBX) in aqueous solution by means of OOF: ozonator combined with flotator. Miner. Eng. 70, 222 – 227. (doi:10.1016/mineng.2014.09.020)

Chen XM, Hu YH, Peng H, Cao XE. 2015 Degradation of ethyl xanthate in flotation residues by hydrogen peroxide. J. Cent. South Univ. 22, 495 – 501. (doi:10.1007/s11771-015-2548-8)

Bartholomaeus AR, Haritos VS. 2005 Review of the toxicology of carbonyl sulfide, a new grain fumigant. Food Chem. Toxicol. 43, 1687 – 1701. (doi:10.1016/j.fct.2005.06.016)

Hugler W, Acosta C, Revah S. 1999 Biological removal of carbon disulfide from waste air streams. Environ. Prog. 18, 173 – 177. (doi:10.1002/ep.670180313)

Staehelin J, Hoigne J. 1982 Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. Environ. Sci. Technol. 16, 676 – 681. (doi:10.1021/ es00104a009)

Zoschke K, Bomick H, Worch E. 2014 Vacuum-UV radiation at 185 nm in water treatment—a review. Water Res. 52, 131 – 145. (doi:10.1016/j.watres.2013.12.034)