



Key factors impacting treatment efficiency in actual copper mineral processing wastewater by ozonation

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ABSTRACT

Ozone advanced oxidation has been widely used in water treatment, but little research has been reported on the application of ozone to difficult-to-degrade mineral wastewater. In this paper, the effect of ozonation application in the treatment of copper mineral processing wastewater, which is difficult to be effectively treated by traditional processes due to its complex composition, was investigated. The effects of ozonation time, ozone concentration, temperature and pH on the degradation of organic compounds in the wastewater by ozonation were researched. It was found that the chemical oxygen demand (COD) of the wastewater could be reduced by 83.02% by ozonation under optimal treatment conditions. In addition, the mechanism of ozone degradation of the difficult-to-degrade wastewater was studied, and the reasons for the fluctuating variations of COD and ammonia nitrogen during ozonation treatment were explained.

Key words: ammonia nitrogen, chemical oxygen demand, copper mineral processing wastewater, ozone advanced oxidation, wastewater treatment

HIGHLIGHTS

- The mechanism of chemical oxygen demand (COD) and NH₃-N removal in actual copper mineral processing wastewater (CMPW) treated by ozone was analyzed.
- The effect of ozone-treating CMPW did not necessarily get better with the increase in temperature.
- Ozonation showed a better treatment effect on CMPW under alkaline conditions.
- COD concentration fell with ozonation time, then rose and finally fell.
- NH₃-N concentration rose and fell twice with ozonation time.

INTRODUCTION

Mineral processing wastewater contains many harmful components, which will cause pollution to surrounding water, air and soil if discharged directly. Therefore, mineral processing wastewater will be recycled in most cases. However, if the beneficiation wastewater is not effectively treated, it can cause great damage to the recovery and grade of valuable minerals during recycling (Farrokhpay & Zanin 2012; Li *et al.* 2021). In addition, the treatment of mineral processing wastewater is related to the development of the mineral industry (Jing *et al.* 2020), which in turn affects national political and economic policies. Therefore, the treatment of mineral processing wastewater is particularly important. At present, some technologies have been applied to the treatment of mineral processing wastewater and certain achievements have been made. For example, electrocoagulation was applied to the treatment of Pb/Zn sulfide mineral processing wastewater and the chemical oxygen demand (COD) was reduced from 424.29 to 72.9 mg/L (Jing *et al.* 2020). It was also reported the electrocoagulation could neutralize the pH of the wastewater from 2.83 and reduce the TSS content from 131.04 to 9.5 mg/L (Alam *et al.* 2021). The biological treatment of mine drainage using sulfate-reducing bacteria achieved a sulfate removal of 94.15 ± 1.76% (Vieira *et al.* 2021). In addition, there were some combined treatment methods. For example, an aquatic treatment pond of *Typha latifolia* Linn had

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been used to treat the Pb/Zn mine wastewater, the total suspended solids and COD of which were reduced by 99 and 55%, respectively (Lan *et al.* 1992). These methods had a certain treatment effect on the mineral processing wastewater, but the treated wastewater still could not meet the emission requirement. Therefore, more research was required to refine the treatment of mineral processing wastewater.

Ozone has been increasingly used in industrial wastewater treatment. It was found that ozone has good treatment effect on industrial wastewater and no secondary pollution is produced after ozone treatment (Chen *et al.* 2022). Ozone can produce a variety of free radicals in water, which has a significant effect on improving the removal of refractory organic matter (Konsowa 2003; Konsowa *et al.* 2010). Ozone starts advanced oxidation only when it decomposes to produce free radicals. And after degrading the dissolved organic matter in water, it was able to degrade the large organic matter gathered by tiny particles of organic matter (Indah Dianawati *et al.* 2018). This reflects the potential of ozonation in the application of the treatment of difficult-to-degrade organic matter. In this paper, ozonation was systematic studied apply to degrade organic matter in copper mineral processing wastewater (CMPW). The effects of the ozonation time, ozone concentration, temperature and pH on the degradation of the wastewater were explored. Finally, the mechanism of the removal of COD and ammonia nitrogen was discussed, which provided a basis for the future application of ozone in refractory industrial wastewater.

MATERIALS AND METHODS

The experimental process

The flow of 99.99% oxygen in the cylinder required for the reaction was regulated by the D07-19B flow controller (Beijing SevenStar Flow Co., Ltd) to enter the ozone generator, then oxygen was converted into ozone by the ozone generator, and finally ozone reacted with 500 mL of wastewater in the conical flask.

The detection method of COD and ammonia nitrogen used is an optical device 5B-6C (V8) multi-parameter water quality analyzer is used to obtain a specific wavelength of ultraviolet light, so that it is incident vertically through the water sample to be measured using electronic information technology to process the light signal intensity before and after the solution based on the Beer-Lambert law, and the relation model of absorbance and concentration was established to detect COD and ammonia nitrogen in this paper.

Experimental conditions

The experimental conditions used were laboratory temperature 294.65 K, temperature of copper mineral processing wastewater 296.15 K, pH 7, the initial COD 138.4 mg/L, the initial concentration of ammonia nitrogen 1.83 mg/L, ozone flow rate 70 L/h, ozone concentration 58.7 g/m³ (using INUSA MINI-HICON online concentration monitor to detect the gas-phase ozone concentration at the inlet), the volume of the CMPW: 500 mL, ozonation time (ozone) 7 min. If there are differences below, they will be explained separately.

Chemicals

The chemicals used were sulfuric acid (AP, Xilong Scientific Co., Ltd), sodium hydroxide (AP, Xilong Scientific Co., Ltd), potassium amyl xanthate (superior quality, JI AN Tianzhuo Flotation Reagent Co., Ltd), butylxanthate (superior quality, JI AN Tianzhuo Flotation Reagent Co., Ltd), ammonium dibutyl dithiophosphate (qualified product, JI AN Tianzhuo Flotation Reagent Co., Ltd), No. 2 oil (first-class product, JI AN Tianzhuo Flotation Reagent Co., Ltd), fulvic acid (purity $\geq 98\%$, Hefei Chisheng Biotechnology Co., Ltd) and humic acid (purity $\geq 97\%$, Hefei Chisheng Biotechnology Co., Ltd).

RESULTS

Effect of ozonation time

Ozonation time (time of ozone bubbled into water) can directly affect the effect of ozonation treatment of CMPW. Therefore, an experiment was carried out to treat 500 mL of CMPW by ozonation through a microporous aerator without using any other chemical reagents. The flow rate of ozone was 70 L/h, and the concentration of ozone was 58.7 g/m³. The variations of COD and ammonia nitrogen concentration under the different ozonation time was observed. The results are shown in Figure 1.

The COD and ammonia nitrogen showed different changes with the increase of the ozonation time. With the increase of ozonation time, the COD first decreased greatly, then raised slightly, and finally decreased slowly. Unlike the COD, the

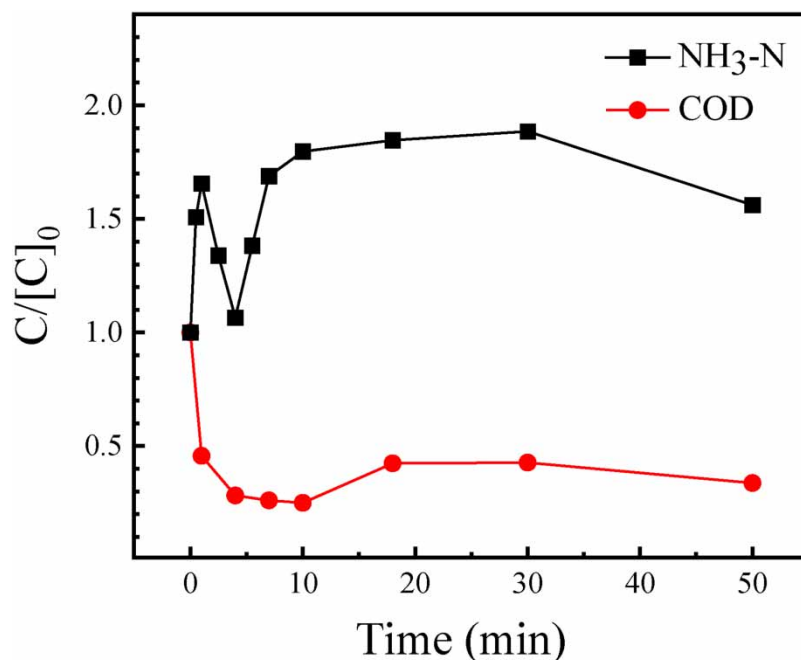


Figure 1 | Effect of aeration time on treatment effect ($T = 296.15$ K, $\text{pH} = 7$, $n = 58.7$ g/m³). (T = temperature of wastewater; t = time; n = concentration of ozone).

concentration of ammonia nitrogen raised sharply at start, then quickly dropped to near the initial concentration, soon raised again to the highest point and finally slowly dropped. The whole change process of the ammonia nitrogen concentration showed two uptrends with the increase of ozonation time (Figure 1). The COD (34.16 mg/L) was lower than the national emission standard class I-A (50 mg/L, GB 18918-2002) after ozonation, and the concentration of ammonia nitrogen was also lower than the national emission standard class I-A (5 mg/L, GB 18918-2002) after ozonation. The complex changes of COD and ammonia nitrogen show that the reaction process of ozone-treating CMPW is relatively complicated, which is worth research. The complex change process was explained in the discussion part.

Effect of ozone concentration

Studies have shown that the concentration of ozone can not only change the reaction type of the substances but also affect the reaction rate. Other studies also proved that the driving force for ozone transferring to the wastewater will increase as the concentration of ozone in the bubbles passed into the wastewater increases (Konsowa 2003). It is concluded that the higher the ozone concentration, the faster the reaction rate of the ozone molecules directly participated. For indirect reaction involving radicals produced by ozone decomposition, the reaction rate is also affected by the number of free radicals. However, generated radicals increase the probability of collision among the radicals at a high concentration, which makes the chance of recombination of ozone higher (Wu *et al.* 2010). Therefore, the effect of ozone concentration on the treatment effect of ozone-treating CMPW is worth exploring. In this paper, different gas sources were used to generate different concentrations of ozone from the ozone generator. The ozone concentration was 4.5 g/m³ when air was used as the gas source, while the ozone concentration was 58.7 g/m³ when oxygen was used as the gas source. The flow rate of both air and oxygen was 70 L/h. It should also be noted that the humidity of the air used as the air source during the experiment was higher, so the ozone concentration was lower than the ozone concentration generated by using the dried air source. The results are shown in Figure 2.

The COD showed a variation of increase slowly except a slight decrease at the beginning when the ozone concentration was 4.5 g/m³, and the final COD value was higher than the initial value. While the final COD value was much lower than its initial value when the ozone concentration was 58.7 g/m³ (Figure 2). The rising and falling sequences of the ammonia nitrogen concentration in the CMPW were opposite when the ozone concentrations are 4.5 and 58.7 g/m³ (Figure 2). The results further confirmed that the reaction of CMPW and ozone under different ozone concentrations was different.

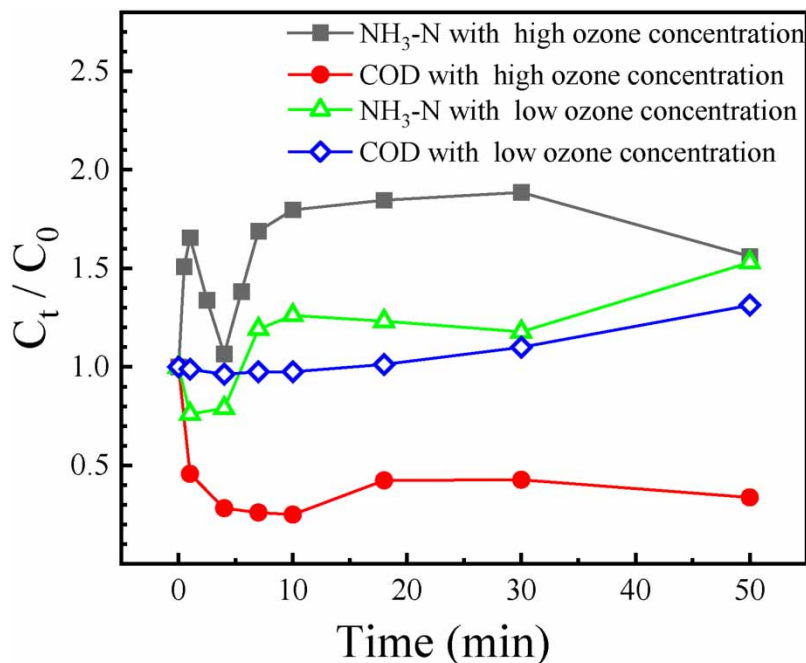


Figure 2 | Effect of ozone concentration on the treatment effect ($T = 296.15$ K, $\text{pH} = 7$).

Effect of temperature

Temperature is generally considered to be an important variable affecting the kinetics of reactions because it can accelerate the movement of molecules and thus improve the probability of collisions (Sotelo *et al.* 1987). The temperature not only changes the activation energy required for the reaction but also affects the solubility of the substance. The solubility of ozone in water decreases with the increase of temperature. However, when the water temperature rises, the rate of ozone decomposition increases, which improves the rate of radical generation. These two ways of temperature effect compensate for each other in the process of ozone-oxidizing substance (Ikeura *et al.* 2011). Some studies proved that the decomposition of ozone is very fast when the temperature is higher than 303.15 K while $\text{pH} = 8$ (Stachelin & Hoigne 1982), and other studies also proved that it has different effects on ozone to remove organic matter in different temperatures. Such as the optimal removal of UV254 and UV410 by ozone corresponding to the best temperature was 281.15–285.15 K, the best treatment temperature for coagulation effluent was about 281.15 K and the best treatment temperature for microfiltration effluent was 277.15–281.15 K (Li *et al.* 2016). Therefore, the effect of temperature on ozone-treating CMPW is very necessary. The range of water temperatures were set from 283.15 to 313.15 K in this paper based on the research of Li *et al.* (2016) and Sotelo *et al.* (1987). The results are shown in Figure 3.

The effect of ozone-treating CMPW did not necessarily get better with the increase of temperature, and the treatment effects at 303.15 and 313.15 K were slightly lower than 293.15 K (Figure 3). When the temperature was lower than 293.15 K in the experimental range, increasing the temperature would improve the reaction rate. However, when the temperature changed in the other range in the experiment, the increase of temperature would accelerate the rate of ozone escaping from the water. Thus, the ozone concentration in the liquid phase was decreased and the balance of the reaction was moved to the reverse direction which slowed the reaction rate of ozone and organic matter. Therefore, the COD of 303.15 K after the reaction was greater than 293.15 K. High temperatures can affect the properties of some flotation agents remaining in CMPW, such as xanthate, which is formed by the treatment of alcohol with carbon disulfide in the presence of an alkali at certain temperatures (288.15–308.15 K) (Wang 2016), so the curve showed a downward trend when the temperature was at 313.15 K. The result shows that the change of ammonia nitrogen was closely related to the organic matter in the CMPW (Figure 3).

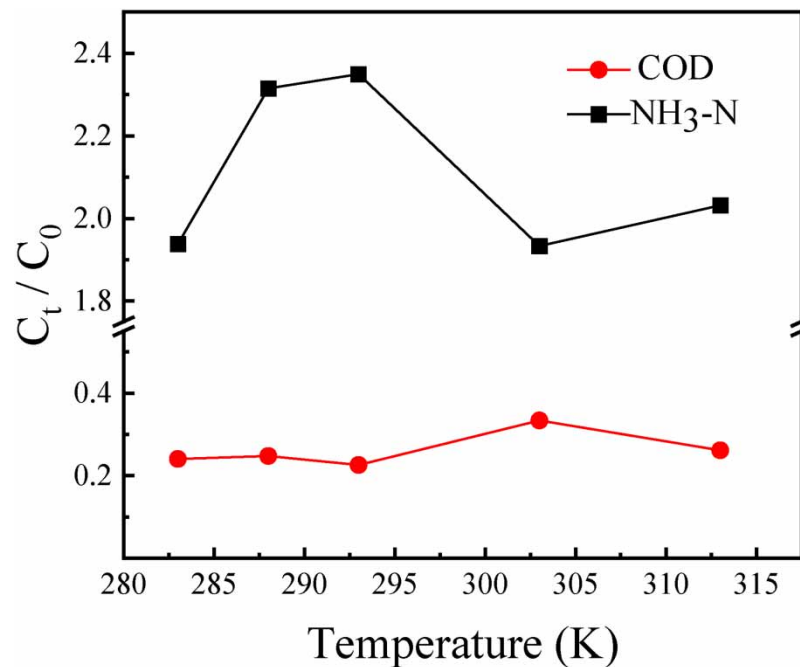


Figure 3 | Effect of temperature on the treatment effect ($\text{pH} = 7$, $n = 58.7 \text{ g/m}^3$, $t = 7 \text{ min}$).

Effect of pH

The oxidation ability of ozone has a certain relationship with the pH of the solution because different pH will affect the decomposition ability of ozone in the solution. Studies have proved that the decomposition rate of ozone will increase by about three times when the pH of the solution increases by one unit, and the physical and chemical properties of the organic matter in the solution are also closely related to the pH. The oxidation ability of ozone will be stronger when the pH of the solution is higher. Because when the pH is high, the ozone can produce highly reactive intermediates such as hydroxyl radicals, which is one of the strongest oxidants. In addition, studies have also found that when the pH of solution is lower than 7, the direct ozone decomposition and hydroxyl-induced decomposition are the main causes of ozone decomposition. The peroxy radicals $\cdot(\text{HO})_2$ (Sotelo *et al.* 1987) will be generated during the decomposition process due to the action of hydroxide ions when the pH of the solution is about 9. Moreover, the organic matter in the wastewater is oxidized by ozone to generate weak organic acids, and the pH of the solution will drop, which in turn affects the degradation rate constant of organic matter and reduces it (Konsowa 2003; Konsowa *et al.* 2010). The pH of wastewater can be controlled by artificial dosing. Therefore, it is of great significance to study the influence of pH on ozone-treating CMPW from the perspective of economic and practical value. In this paper, NaOH (AP) and H_2SO_4 (AP) are used to adjust the pH of CMPW (Jiang 2020). The results are shown in Figure 4.

Ozone showed a better treatment effect on CMPW under alkaline conditions (Figure 4). The degradation of organic matter in the CMPW will cause changes in the ammonia nitrogen concentration. The more organic matter is degraded by ozone, the greater the ammonia nitrogen concentration. But when the pH of the solution was greater than 7 (Jiang 2020), the content of $\text{NH}_3\text{-N}$ in the wastewater gradually increased, resulting in particle ammonia gas escaping from the water, which reduced the ammonia nitrogen concentration under alkaline conditions. The acid will degrade some substances that produce ammonia nitrogen in the mineral processing wastewater, which explains why the COD of wastewater under acidic conditions was lower than that under neutral conditions while the ammonia nitrogen concentration was not higher than under neutral conditions. In general, the treatment effect under acidic or alkaline conditions is better than the neutral conditions due to the complexity of CMPW. Furthermore, alkaline conditions show the best result.

Treatment effects

In order to study the best treatment efficiency of CMPW by ozonation, an experiment was conducted using the optimal parameters of the above-influencing factors. The results showed that the COD decreased from 138.4 to 23.5 mg/L and the

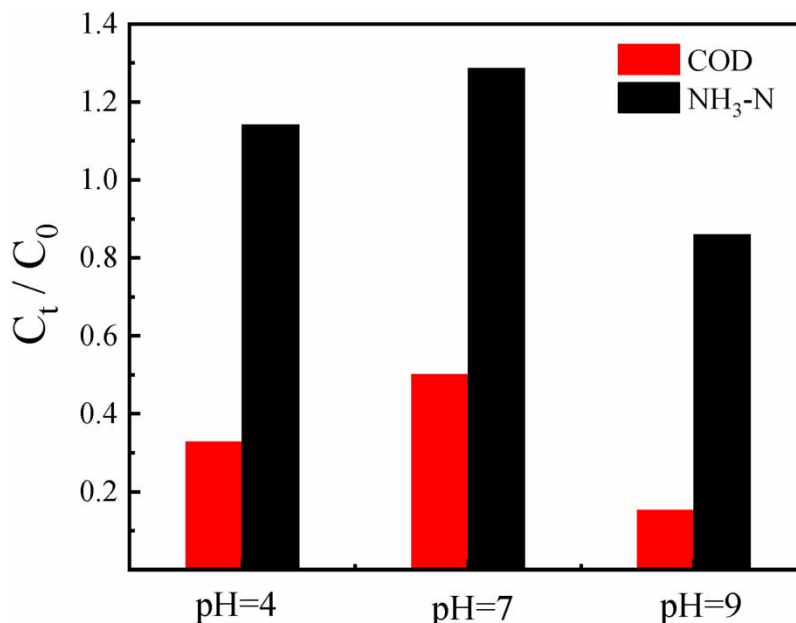


Figure 4 | The effect of pH on the treatment effect ($T = 296.15\text{ K}$, $n = 58.7\text{ g/m}^3$, $t = 7\text{ min}$).

ammonia nitrogen concentration increased from 1.83 to 2.33 mg/L ($T = 296.15\text{ K}$, $n = 58.7\text{ g/m}^3$, $t = 7\text{ min}$, pH = 9). The removal of COD in wastewater was up to about 83% under the best conditions. Although the ammonia nitrogen concentration raised slightly, it is far lower than the national emission standard. All experiments prove that ozone can be well applied to CMPW treatment. According to the calculation, the cost of the ozone treatment is 0.3 cents/L when this effect is achieved.

DISCUSSION

The nature of COD changes with ozonation time

Experimental results showed that the COD did not keep a constant decrease during the process of ozone-treating CMPW, which dropped sharply at first, then rebounded quickly and declined slowly at last (Figure 1). To find the reason for the COD rebound in the process of ozone-treating CMPW, the water samples of raw wastewater and wastewater aerated by ozone for 7, 18, and 50 min were tested by the three-dimensional fluorescence. The results are shown in Figure 5.

The Rayleigh scattering phenomenon is not analyzed here (Moriel *et al.* 2019). According to the corresponding analysis, the raw wastewater contains soluble microbial products-like (SMP) (Barker & Stuckey 1999) and humic acid-like (El Fallah *et al.* 2018). These two types of substances were degraded after 7 min of ozonation (Figure 5 and Table 1). The composition of SMP is very complex, which contains humic, fulvic acids, polysaccharides, proteins, nucleic acids, organic acids, amino acids, antibiotics, steroids, exocellular enzymes, siderophores, structural components of cells, and products of energy metabolism (Barker & Stuckey 1999). Not only that, the SMP produced by the anaerobic process also contains alkenes, alkanes, and aromatic hydrocarbons. Although the components of SMP are diverse, only the humus, polysaccharides and proteins are commonly present in various situations (Liu *et al.* 2002).

Due to the residual flotation, agents occupy a large proportion in the mineral processing wastewater. The water samples of butylxanthate, potassium amyl xanthate, foaming agent No. 2 oil (ROH), and ammonium dibutyl dithiophosphate were oxidized by ozone, respectively (The foaming agent No. 2 oil (ROH) cannot be dissolved in water, so it first dissolves in ethanol and then the COD and ammonia nitrogen data of ethanol are subtracted.) (Huang 2012). The results are shown in Figure 6.

Ozone has a significant degradation effect on each agent, and the COD of each agent solution has kept a downward trend with the increase of ozonation time (Figure 6). It proved that other substances cause the change in COD. Therefore, the experiment of ozonation for protein and humus in raw wastewater was carried out. The results are shown in Figure 7.

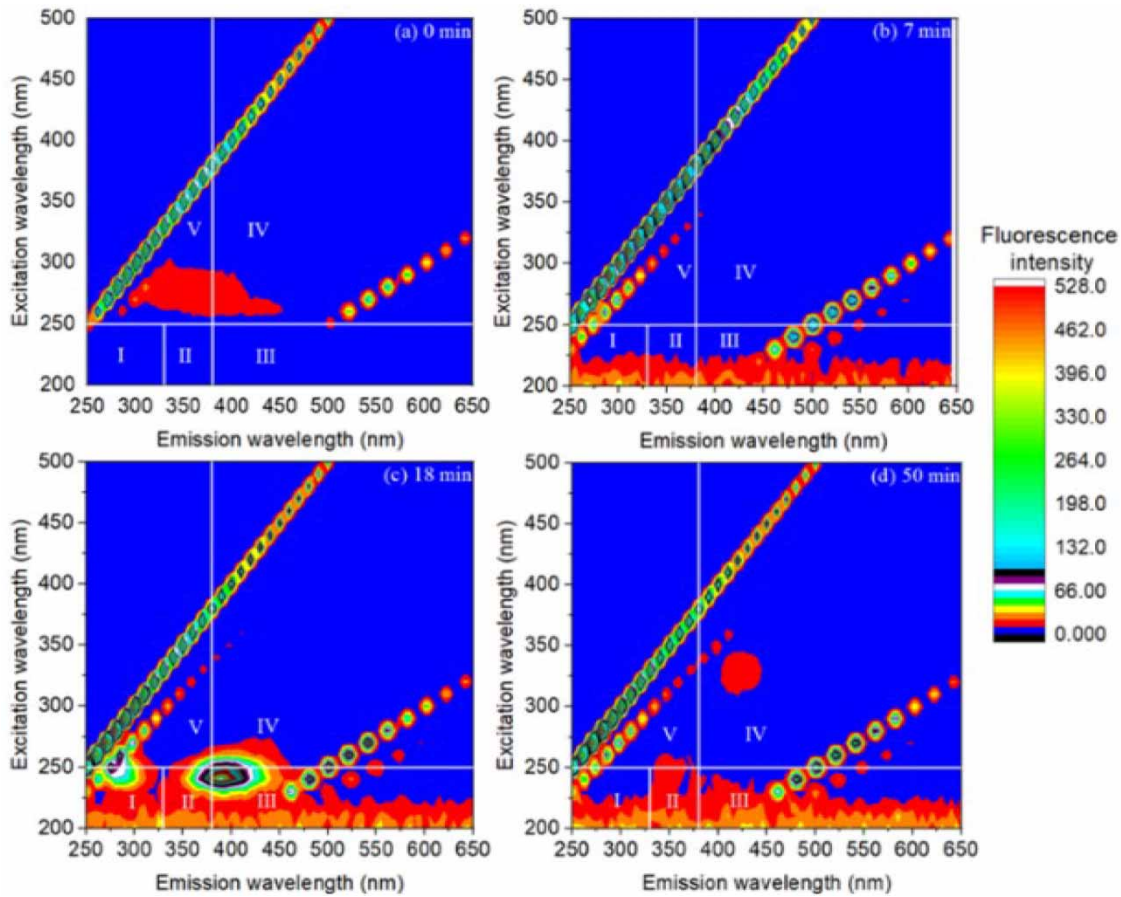


Figure 5 | The distribution of wastewater components at different aeration time.

Table 1 | Division of fluorescent region

Region	Range (Em/Ex)	Name
I	250 < Em < 330 nm, Ex < 250 nm	Tyrosine protein-like
II	330 < Em < 380 nm, Ex < 250 nm	Tryptophan protein-like
III	Em > 380 nm, Ex < 250 nm	Fulvic acid-like
IV	Em > 380 nm, Ex > 250 nm	Humic acid-like
V	Em < 380 nm, Ex > 250 nm	Soluble microbial product-like

The distribution of the different substances in the three-dimensional fluorescence spectrum is shown.

In the beginning, dissolved organic matter of IV and V regions and residual flotation agents in CMPW were oxidized and degraded by ozonation, which greatly reduced the COD. With continuous ozonation, some protein-like substances and humic acid-like (Figure 5(b) and 5(c)) in the wastewater were oxidized by strong oxidizing free radicals, which cause the COD in the CMPW that showed a slight raise (Figure 7). Finally, the COD showed a downward trend again after all small molecules were degraded. Furthermore, the COD of the humic acid solution did not change when ozonation was started, indicating that the nature of humic acid is relatively stable and wastewater-containing humic acid is difficult to be treated. With the increase of ozonation time, the concentration of ozone in the water increases, producing a lot of strong oxidizing free radicals. These free radicals can oxidize the humic acid in the solution, which proves again that the oxidizing ability of free radicals is higher than the ozone molecules.

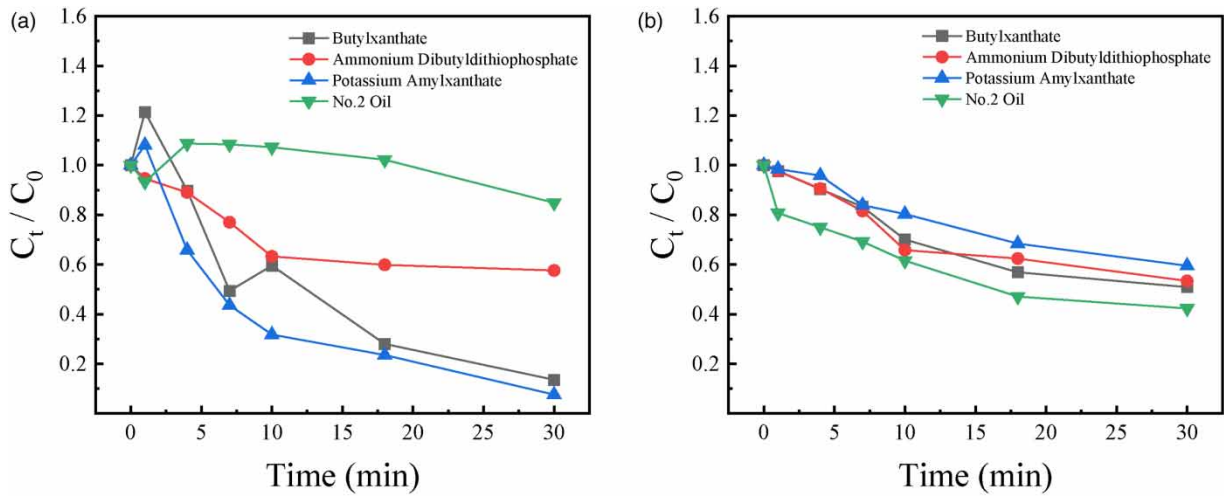


Figure 6 | The variations of $\text{NH}_3\text{-N}$ (a) and COD (b) with different agents.

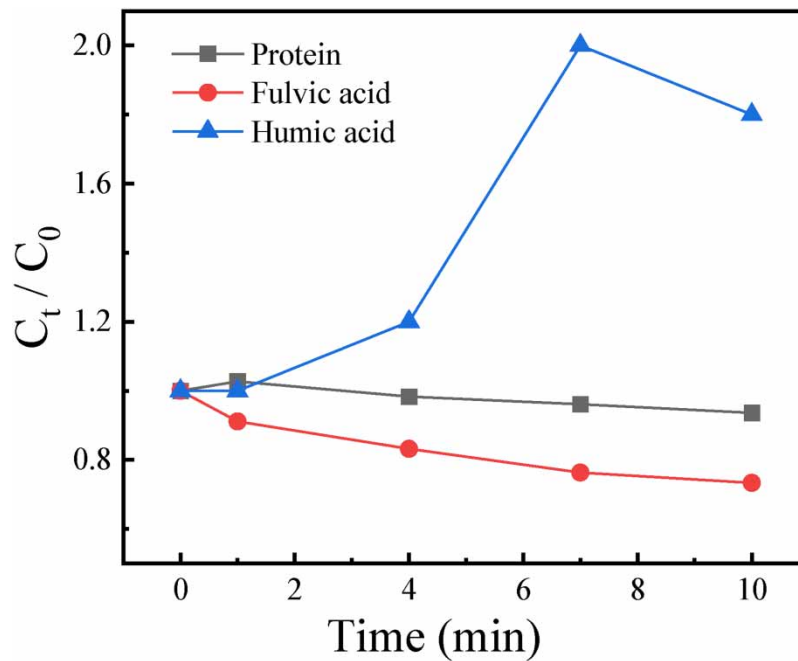


Figure 7 | The COD change of dissolved organic matter.

The nature of ammonia nitrogen changing with ozonation time

The ammonia nitrogen concentration showed a change of two uptrends and downtrends with the increase of ozonation time (Figure 1). The chemical stability of ammonia is stable, and the reaction rate between ammonia and ozone is slow. A large amount of $\text{NH}_3\text{-N}$ cannot be oxidized to $\text{NO}_2\text{-N}$. Moreover, nitrogenous organic matter can be oxidized into ammonia nitrogen by ozone (Wang *et al.* 2010), thereby increasing the concentration of ammonia nitrogen in wastewater. Dissolved organic nitrogen in the aquatic environment commonly occurs as amino acids, peptides and proteins and accounts for 0.5–10% (by mass) of the dissolved organic matter (Sharma & Graham 2010).

Firstly, the oxidation change of each agent was tested. It was found that the ammonia nitrogen concentration of the xanthate solution increased firstly and then decreased (Figure 6), and the rising time period was the same as the previous

experiment (Figure 1). The ozone oxidation experiment was carried out on the wastewater the residual xanthate is removed (natural solarization and acid decomposition methods) (Zeng *et al.* 2010). In the experiment, there were three water samples containing xanthate (flotation agents) (labeled 1, 2 and 3). Xanthate in water samples 1 and 2 was removed by natural exposure or acid decomposition, respectively, and no treatment was done on label 3. Then, under the same conditions, these three water samples were treated by ozone to study whether xanthate caused the increase of ammonia nitrogen concentration in the degradation process. The result is shown in Figure 8.

The xanthate was detected by a liquid chromatograph mass spectrometer (SCIEX QTOF system) (model: X-500R), and the results confirmed that the xanthate contained components such as $C_wH_xN_yO_z$ (w, x, y are natural numbers that are not zero, and z is a natural number that can be zero). The substance can generate an ammonia-like substance in the ozone oxidation process, which makes the concentration of ammonia nitrogen rise (Figure 8). Since other nitrogenous organic matter in the CMPW is relatively stable, ozone that passed into the wastewater will react with the generated ammonia nitrogen, resulting in a decrease in ammonia nitrogen concentration. These reasons resulted in the phenomenon that the ammonia nitrogen concentration increased and then decreased in the first stage. Then through experimental analysis, the ozone molecules at the beginning of the ozonation are directly consumed by easily oxidizable substances, so the concentration of hydroxyl in the solution is very low. The low hydroxyl concentrations are combined with the low reactivity of amines with hydroxyl at neutral pH (Buxton *et al.* 1988). The $\cdot OH$ from the decay of O_3 impossibly contributes to NH_4^+ formation. With the increase of ozonation time, the concentration of ozone in the wastewater increases, which produces many strong oxidizing free radicals with a stronger oxidizing ability. Previous studies have shown that $\cdot OH$ is driving the formation of amino acids NH_4^+ aspect plays an important role (Leitner *et al.* 2002). To study the mechanism of the nitrogenous organic matter oxidated by ozone in the CMPW, the nitrogenous organic matter in the CMPW was subjected to ozone oxidation treatment. The result is shown in Figure 9.

The ammonia nitrogen concentration of protein and fulvic acid solution increased firstly and then decreased with the increase of ozonation time (Figure 9). In addition, the protein-like substance and fulvic acid-like substance were produced during the process of ozone-treating CMPW (Figure 5(c)), which caused the concentration of ammonia nitrogen to rise in the second stage. Protein-like substances are gradually degraded by ozone. Firstly, the spatial structure of the protein is destroyed to form peptide chains, then the hydroxyl destroys the primary structure of the protein (Zhu *et al.* 2011). The peptide chains are decomposed into amino acids, which react with the hydroxyl radicals of ozone decomposition. Nitrate,

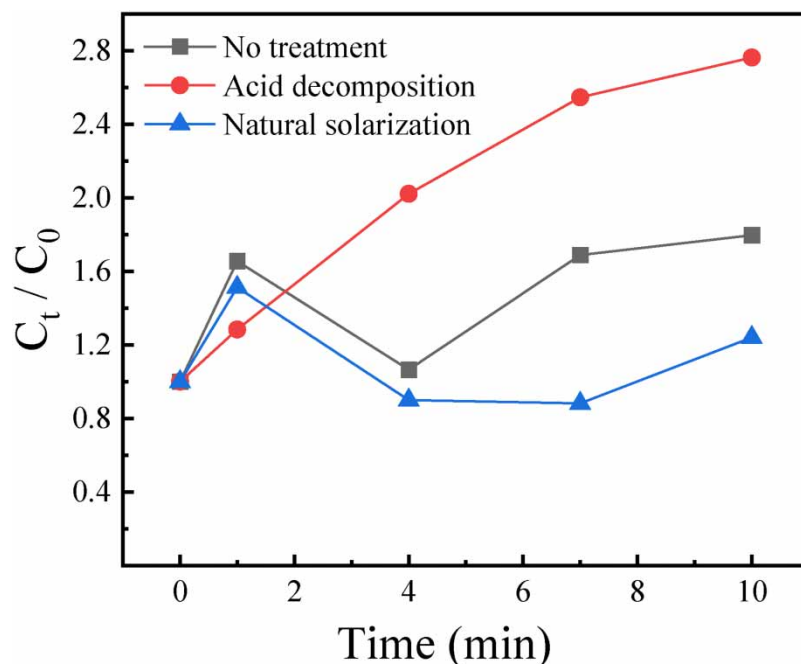


Figure 8 | The changes of ammonia nitrogen before and after removing xanthate.

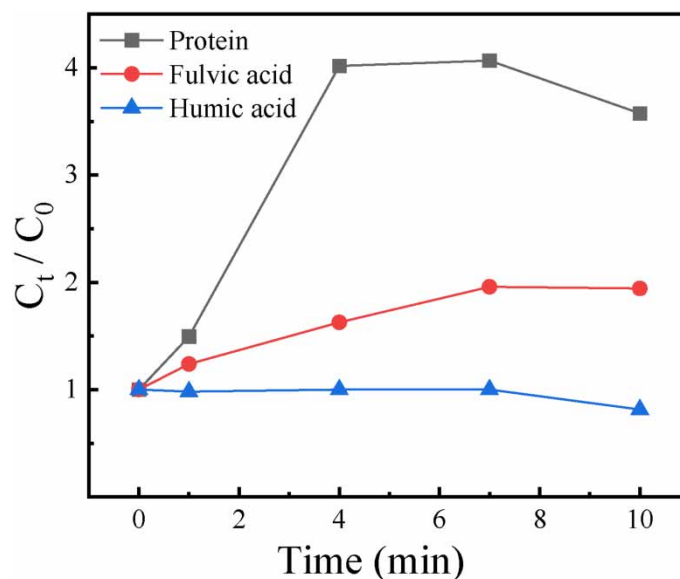


Figure 9 | The ammonia nitrogen changes of dissolved organic matter.

ammonia, carbonyl, and carboxylic acid are formed in this process (Sharma & Graham 2010), which increase the concentration of ammonia nitrogen in solution. Fulvic acid-like is oxidized by ozone to produce ammonia nitrogen, and fulvic acid-like is easily soluble in water. Therefore, fulvic acid-like needs to be degraded and removed. Finally, ozone or strong oxidizing free radicals will react with ammonia nitrogen when all substances are completely oxidized, which made the concentration of ammonia nitrogen that showed a last downward trend.

CONCLUSIONS

There have been many methods to treat copper mine wastewater, but none of them achieved good results. However, the ozone treatment of copper mine wastewater shows superiorities of high efficiency and without secondary pollution. The removal of COD reached to 83% in this paper. Meanwhile, other emission indicators such as metal ion concentration could meet the requirements of national emission standards in the experiments. Therefore, ozone advanced oxidation is a promising technology for mine wastewater treatment that will be continuously optimized and improved in the future.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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