Ultrasonic-assisted ozone degradation of organic pollutants in industrial sulfuric acid

Tian Wang\textsuperscript{a,b,c}, Thiquynhxuan Le\textsuperscript{a,b,e}, Jue Hu\textsuperscript{a,b,c}, Annavarapu V. Ravindra\textsuperscript{d}, Haoran Xv\textsuperscript{a,b,c}, Libo Zhang\textsuperscript{a,b,c}, Shixing Wang\textsuperscript{a,b,c}, Shaohua Yin\textsuperscript{a,b,c}

\textsuperscript{a} State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, Yunnan, China
\textsuperscript{b} Key Laboratory of Unconventional Metallurgy, Kunming University of Science and Technology, Kunming 650093, Yunnan, China
\textsuperscript{c} Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, Yunnan, China
\textsuperscript{d} Department of Physics and Nanotechnology, SRM Institute of Science and Technology, Kattankulathur, Tamilnadu 603203, India

Keywords:
Industrial sulfuric acid
Ozone
Ultrasound
Decolorization
Organic pollutants

ABSTRACT

In this work, a combination of ozone (O\textsubscript{3}) and ultrasound (US) has been firstly used to decolorize black concentrated sulfuric acid with high organic content. The effect of different reaction factors on the transparency, extent of decolorization, H\textsubscript{2}SO\textsubscript{4} mass fraction, and organic pollutants removal is studied. In addition, the systematic interaction between ultrasound and ozone on the decolorization process is reviewed through comparative experiments of O\textsubscript{3}, US and US/O\textsubscript{3}. A sulfuric acid product that meets the requirements for first-class products in national standards, with an extent of decolorization of 74.07\%, transparency of 70 mm, and a mass fraction of 98.04\%, is obtained under the optimized conditions. Under the same conditions, it has been established that the treatment time can be saved by 25\% using the US/O\textsubscript{3} process compared to using O\textsubscript{3}. Further, the production of oxidative free radicals (•OH) in a concentrated sulfuric acid system is enhanced using the US/O\textsubscript{3} process compared with O\textsubscript{3}. In addition, the degree of effectiveness of different oxidizing components on the decolorization process is revealed by adding different free radical shielding agents when the US/O\textsubscript{3} process is used.

1. Introduction

Sulfur dioxide (SO\textsubscript{2}), which is one of the major harmful gases causing air pollution, is inevitably produced in the smelting process of metals such as zinc, lead, copper, nickel, and steel [1,2]. The preparation of industrial byproduct sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) from sulfur dioxide by flue gas desulfurization is an important way to realize the comprehensive recovery of sulfur resources and environmental emission in the metal smelting industry, which has great economic and social benefits [3]. In 2020, the production of sulfuric acid from smelting flue gas in China was 38.59 million tons, accounting for 39.1\% of China’s total production of sulfuric acid [4]. The H\textsubscript{2}SO\textsubscript{4} mass fraction, transparency, chromaticity, and impurity content (ash, iron, arsenic, lead, and mercury) are the main indicators for judging the quality of industrial sulfuric acid [5]. Under normal circumstances, the color of industrial concentrated sulfuric acid is light yellow and analytically pure concentrated sulfuric acid is colorless and transparent. However, the concentrated sulfuric acid produced from the flue gas of the metal smelting process often turns black, resulting in the product chromaticity not meeting the chromaticity requirements for industrial sulfuric acid, thereby reducing the product quality. Compared with qualified sulfuric acid products, sulfuric acid with excessive chromaticity has the problem of low selling price and is even good-for-nothing, causing great economic losses to the smelting company. Also, sulfuric acid is a highly corrosive and dangerous product. Therefore, excessive storage of sulfuric acid will have potential safety hazards and even cause smelting companies to face production cuts and shutdowns. Therefore, it is necessary to develop effective methods to remove color pollutants from sulfuric acid products and improve their quality.

The possible reasons for the excessive chromaticity of industrial sulfuric acid products are organic pollutants [6,7], nitrogen oxides [8,9], and metal impurities [9,10], of which organic pollutants are considered to be the primary cause. In metal smelting processes, organic pollutants introduced by metal minerals, fuels or flotation agents, which
are not completely removed in the purification system, enter sulfuric acid products. For industrial sulfuric acid with high organic content, although the high-temperature pyrolysis method can effectively remove organic pollutants and produce high-quality fresh sulfuric acid, its application is limited due to huge equipment and operating costs [11]. At the same time, the extraction and adsorption methods [12,13] have several shortcomings, such as poor removal effect, large amount of adsorbent and low reuse efficiency. The oxidation method has become the most commonly used decolorization method for industrial sulfuric acid due to its high removal efficiency, low cost, and simple operation. The organics in sulfuric acid with excessive chromaticity should be degraded to H₂O, CO₂, and other colourless small molecules through oxidation. Hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄), and oxygen (O₂) are usually used as oxidants in the decolorization of industrial sulfuric acid, but these oxidants often have shortcomings such as long decolorization time (6–12 h) and insufficient oxidation capacity when dealing with refractory organic pollutants [14,15]. In addition, new impurities of manganese and potassium ions are introduced into the sulfuric acid product when KMnO₄ is used as an oxidant and the H₂SO₄ mass fraction is reduced due to 70% water content in H₂O₂ oxidized, thereby affecting the purity of the product. Ozone is widely used in the decolorization of various wastewaters because it has a higher oxidation capacity than that of other oxidants, such as H₂O₂, KMnO₄, and O₂ [16,17]. The degradation of organic pollutants by ozone is based on the direct oxidation of ozone molecules and the indirect oxidation of free radicals, including hydroxyl radicals (•OH) and superoxide radicals (•O₂⁻) [18]. However, due to the low dissolution rate and poor mass transfer rate of ozone in solution, the utilization rate of ozone is low, resulting in the poor degradation effect of ozone alone on refractory organic pollutants. Wei et al. [19] successfully decolorized the industrial sulfuric acid produced by molybdenum smelting flue gas from black to light yellow by using ozone as the oxidant, but the decolorization time was approximately 5 h.

To overcome these shortcomings, an effective method combining ultrasound and ozone has been developed for water treatment in recent decades. Ultrasound, a mechanical wave with a cavitation effect and mechanical stirring effect, has been reported to improve the degradation efficiency of organic pollutants in aqueous solution by ozone [20]. Joshi et al. [21] studied the treatment of leachate generated from municipal solid waste using different approaches and found that the combination of ozone and ultrasound resulted in 24.5% COD removal in 60 min, which was much higher than only ultrasound (6% COD removal) or only ozone treatment (7.5% COD removal). Jawale et al. [22] also reported that the kinetic rate constant of 0.5 × 10⁻⁶ min⁻¹ using only ozone for the degradation of triazophos from wastewater significantly increased to 29.3 × 10⁻³ min⁻¹ when ozone was combined with ultrasound. The combined technology of ultrasound and ozone has been applied at the commercial level. A hybrid advanced oxidation reactor based on combined cavitation and ozonation, described as the Ozonix reactor, has been reported to be successfully used for treating recycled fluids at commercial sites in 750 oil and natural gas wells around the United States [23]. Based upon actual field results with commercial customers in the oil and gas business, the Ozonix reactor resulted in an effective treatment of the frac water, giving much better results compared to the chemical treatments. The enhancement effect of ultrasound is mainly explained by the cavitation effect of ultrasound promoting ozone decomposition to produce free radicals and increasing the volumetric mass transfer coefficient of ozone in aqueous solution [24,25]. Zhang et al. [26] used a mathematical model to calculate the self-decomposition rate constant of ozone in an aqueous solution with or without ultrasound and found that ultrasound could strengthen the self-decomposition rate of ozone and facilitate the formation of hydroxyl radicals by ozone. Weavers [27] experimentally certified that ultrasound could crush O₃-containing bubbles with a diameter of 0.5 to 1.0 cm into “microbubbles” with a diameter of 0.2 to 0.3 μm in aqueous solution, increasing the total reaction surface area by 10³ to 10⁴ times. However, the combined technology of ultrasound and ozone is mainly used in aqueous solution.

To our knowledge, the combined technology of ozone (O₃) and ultrasound (US) has never been reported for removing organic pollutants in concentrated sulfuric acid medium with low water content and high viscosity. In this work, the decolorization effect of US/O₃ on black industrial sulfuric acid with high organic content was studied to improve the product quality. The research contents included revealing the causes for the excessive chromaticity of sulfuric acid and discussing the effects of different reaction factors such as ultrasound power, temperature, treatment time and ozone gas flow, on the decolorization process. Furthermore, the effects of O₃ and US/O₃ processes were compared, and the enhancement mechanism of ultrasound on ozone oxidation was revealed.

2. Experimental

2.1. Materials

Black sulfuric acid with a H₂SO₄ mass fraction of 98.3%, TOC of 129.95 mg/L, and COD of 799.18 mg/L was produced from the flue gas desulfurization process of a lead–zinc smelting company in Yunnan, China. Ag₂SO₄ (AR grade), HgSO₄ (AR grade), Fe(NH₄)₂(SO₄)₂·6H₂O (AR grade), and (NH₄)₂SO₄ (AR grade) were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., China. O₂ gas (99.99%) and SO₂ gas (~99%) were obtained from Kunming Gas Plant, China. Tert-butyl alcohol (AR grade, 99%) was obtained from Chengdu Institute of the Joint Chemical Reagent, China. Superoxide dismutase SOD (AR grade, 99%) was obtained from Shanghai Yuanye Biological Technology Co. Ltd., China.

2.2. Experimental procedure

A schematic diagram of the US/O₃ system is shown in Fig. 1a. Ultrasonic equipment with a low frequency of 20 kHz and a maximum power of 1200 W developed in house by Kunming University of Key Laboratory of Unconventional Metallurgy, Ministry of Education was used in this study (Fig. 1b). The ultrasonic equipment has three main components: (1) ultrasonic transducer, (2) ultrasonic generator, and (3) closed decolorization tank. The cylindrical ultrasonic transducer (Φ82 mm × 330 mm) was made of special engineering plastics with corrosion resistance to concentrated sulfuric acid. During the experiments, the white cylindrical area (Φ80 mm × 190 mm) of the transducer that generates ultrasound was completely immersed in concentrated sulfuric acid. Ultrasound was emitted radially from the ultrasonic transducer and the ultrasonic radiation area was large, resulting in a very uniform ultrasonic field in sulfuric acid. The ultrasonic output power could be adjusted by controlling the electric current of the ultrasonic generator. The closed decolorization tank was made of high borosilicate glass (Φ150 mm × 300 mm), and the base and top plates were made of polytetrafluoroethylene.

Ozone was produced from pure oxygen through an ozone generator (Model JW-30A, Xuzhou Jiuzhouhong Ozone Equipment Manufacturing Co., Ltd.). During the experiments, ozone was continuously bubbled with a suitable flow rate controlled by adjusting the glass rotameter and then dispersed into black sulfuric acid through a diffusion aerator.

The closed decolorization tank was kept in a water bath, and then 3 L of black sulfuric acid was slowly injected into the decolorization tank. To ensure safety, the amount of sulfuric acid treated in each experiment was controlled to 3 L, although the maximum amount of sulfuric acid that could be injected into the decolorization tank was 4 L each time. The reaction temperature was controlled by adjusting the temperature of the water bath. After the sulfuric acid reached the set temperature, ozone was fed into the sulfuric acid and ultrasonic irradiation was carried out in combination with ozonation. During the experiment, the actual temperature of sulfuric acid was often 2–4 °C higher than the set
The temperature due to the application of ultrasound, so the stability of temperature should be ensured by adjusting the temperature of the water bath. Moreover, the results of our previous work indicated that increasing the stirring rate was beneficial to the decolorization effect, but after the stirring rate reached 800 r/min, the decolorization effect did not significantly improve with increasing stirring rate. Therefore, a mechanical stirrer with a stirring rate of 800 rpm was used to enhance the contact between ozone and sulfuric acid in the reactor during the experiment. Sulfuric acid samples were collected from the decolorization tank at various treatment times to analyse the transparency, chromaticity, \( \text{H}_2\text{SO}_4 \) mass fraction, and COD. The effect of different reaction temperatures, treatment times, ozone gas flows, and ultrasonic powers on the decolorization process was studied.

### 2.3. Analytical methods

The transparency, chromaticity, and \( \text{H}_2\text{SO}_4 \) mass fraction of the sulfuric acid product were analysed in accordance with the Chinese national standard [5]. Specifically, the \( \text{H}_2\text{SO}_4 \) mass fraction was analysed by titration. The transparency was obtained by the liquid height that can clearly distinguish the black-and-white checkerboard under light. The chromaticity of the sample was tested by the visual colorimetric method and the sample whose chromaticity was not darker than the standard chromaticity was regarded as a qualified product. The operating conditions for these examinations are described in the Supplementary material. The removal effect of organic pollutants in sulfuric acid was determined by chemical oxygen demand (COD) variation. COD was determined using the closed reflux titrimetric method based on standard approaches [28].

Black sulfuric acid and analytically pure sulfuric acid were mixed uniformly in different volume ratios and a series of sulfuric acids with different chromaticities between black and colorless were prepared, as shown in Fig. 2. In this study, the chromaticity of black sulfuric acid and analytically pure sulfuric acid were set to 100 and 0, respectively. The chromaticity of different sulfuric acid samples prepared was obtained according to the volume ratio of black sulfuric acid and analytically pure sulfuric acid. The chromaticity of the sulfuric acid sample obtained during the decolorization process was then obtained by comparing with the chromaticity of the sulfuric acid sample prepared as stated above.

The extent of decolorization was calculated as follows. Extent of decolorization (\%) = \((A_0 - A_t)/A_0 \times 100\%\), where \(A_0\) and \(A_t\) are the chromaticity of black sulfuric acid and the samples obtained under different decolorization times, respectively. Based on the above methods, the corresponding extent of decolorization of standard chromaticity in the Chinese national standard is 70%. In other words, the sample with an extent of decolorization greater than or equal to 70% is considered as the qualified product.

The content of metal ion impurities was analysed by the ICP-AES method. Some information on the ICP-AES measurements is provided in the Supplementary material. Total organic carbon (TOC) was
measured with a TOC analyser (Elementar, Vario TOC). To investigate the degradation efficiency of the organic pollutants, sulfuric acid samples with different decolorization times were investigated by UV–Vis spectrophotometry (Shimadzu, UV-3600). The generation of •OH during the reaction was characterized by electron paramagnetic resonance spectroscopy (EPR) using 5,5-dimethyl-1-pyrroline (DMPO) as the spin trapping agent.

3. Results and discussion

3.1. Reason for the excessive chromaticity of sulfuric acid

A comparison of the quality parameters of black sulfuric acid and the quality indexes of industrial sulfuric acid with first-class quality in the Chinese national standard is given in Table S1 in the Supplementary material. In addition to transparency and chromaticity, other indicators in black sulfuric acid meet the quality requirements for first-class products in China’s national standard.

3.1.1. Metal impurities

The contents of metal impurities in black sulfuric acid and analytically pure sulfuric acid were detected, and the results are presented in Table S2 in the Supplementary material. As shown in Table S2, the contents of Al, Fe, and Zn in black sulfuric acid are higher than those in analytically pure sulfuric acid. Among the three metal impurities, only Fe impurity may be the cause of the excessive chromaticity of industrial sulfuric acid [9,29]. However, the Fe content in black acid meets the requirements of the national standard for iron content, and the difference between the Fe contents in black sulfuric acid and analytically pure sulfuric acid is small and can be ignored. Therefore, the influence of metal impurities can be ignored.

3.1.2. Nitrogen oxides

Nitrogen oxides (N\(_2\)O\(_x\)) are also considered to be one of the reasons for the excessive chromaticity of industrial sulfuric acid [9,30,31]. Nitrogen oxides mainly exist in the form of nitrate in concentrated sulfuric acid. When sulfuric acid contains nitrogen oxide impurities, sulfuric acid reacts with iron to preferentially form a red compound salt of sulfuric acid. When sulfuric acid contains nitrogen oxide impurities, sulfuric acid reacts with iron to form a red compound salt of sulfuric acid. When sulfuric acid contains nitrogen oxide impurities, sulfuric acid reacts with iron to form a red compound salt of sulfuric acid.

\[
2Fe + H_2SO_4 + 2HNO_3 = Fe_2(NO_3)_3SO_4 + 2H_2↑ \quad (1)
\]

SO\(_2\) has been reported to effectively remove nitrogen oxides from sulfuric acid (Reaction (1)) [32]. In addition, Xiao et al. [33] reported that adding ammonium sulfate ([NH\(_4\)]\(_2\)SO\(_4\)) to industrial sulfuric acid could convert nitrate into nitrogen via Reactions (2) & (3).

\[
5SO_2 + 4H_2O + 2NO_3^- = 5SO_4^{2-} + N_2 + 8H^+↑ \quad (2)
\]

\[
5(NH_4)_2SO_4 + 6NO_3^- = 5SO_4^{2-} + 8N_2 + 4H^+ + 18H_2O \quad (3)
\]

In this work, the nitrate content (calculated as N) in black sulfuric acid is found to be 0.00357%, indicating the existence of nitrogen oxides. SO\(_2\) and (NH\(_4\))\(_2\)SO\(_4\) were used as removing agents to eliminate nitrogen oxides from sulfuric acid. Specifically, SO\(_2\) with a flow rate of 2 L/h was bubbled into 300 mL black sulfuric acid under a stirring rate of 1200 RPM at a reaction temperature of 60 °C. In another experiment, excessive (NH\(_4\))\(_2\)SO\(_4\) (1 g/L) was added to black sulfuric acid under stirring at 1200 RPM and a reaction temperature of 60 °C. The samples were removed after 1, 2, 3, and 4 h and compared with black sulfuric acid for chromaticity. The results (Fig. 3a and 3b) show that both the transparency and chromaticity of sulfuric acid did not change significantly under the action of SO\(_2\) or (NH\(_4\))\(_2\)SO\(_4\). However, the nitrate content in black sulfuric acid decreased from 0.00357% to 0.0011% or 0.0017% after 4 h of treatment with SO\(_2\) or (NH\(_4\))\(_2\)SO\(_4\), respectively. The above results show that nitrogen oxides are not the main reason for the excessive chromaticity of industrial sulfuric acid.

3.1.3. Organic pollutants

Ozone with a flow rate of 1.2 L/h was bubbled into 300 mL black sulfuric acid to remove organic pollutants under stirring at 1200 RPM and a reaction temperature of 60 °C. The chromaticity of sulfuric acid samples with different ozone oxidation times is shown in Fig. 4. 1\(^a\), 2\(^b\), 3\(^c\), and 4\(^d\), respectively, correspond to black sulfuric acid, sample after ozonation for 15 min, sample after ozonation for 60 min, and analytically pure sulfuric acid. Also, the TOC results of different samples are listed in Table 1.

Fig. 4. Chromaticity of different sulfuric acid samples. 1\(^a\) Black sulfuric acid, 2\(^b\) after 15 min of ozonation, 3\(^c\) after 60 min of ozonation, and 4\(^d\) Analytical pure sulfuric acid.
As the oxidation reaction progresses, the TOC value of sulfuric acid gradually decreases, while the decolorization effect is manifested with a significant reduction in chromaticity. Therefore, it is confirmed that organic pollutants are the main reason for the excessive chromaticity of sulfuric acid. Also, taking into the consideration the actual production process of the lead–zinc smelting company, it is proposed that the formation of organic pollutants may be caused by raw coal fuel [10]. The organic pollutants enter the flue gas system as a consequence of incomplete combustion of raw coal. And, if the organic pollutants are not completely removed in the purification system of the desulfurization process they enter the sulfuric acid product, resulting in the blackening of the product.

3.2. Effect of different factors on the degradation efficiency of organic pollutants in black sulfuric acid

3.2.1. Effect of ultrasonic power

The decolorization process of sulfuric acid was carried out with different ultrasonic power densities (66.7, 133.3, 200, 266.7, and 333.3 W·L⁻¹) under an acid volume of 3 L, a reaction temperature of 60 °C, an ozone gas flow rate of 1.8 L/h, a stirring rate of 800 RPM and a treatment time of 4 h. The extent of decolorization, transparency, and H₂SO₄ mass fraction of sulfuric acid samples are shown in Fig. 5.

As the ultrasonic intensity increases from 66.7 to 200 W·L⁻¹, the extent of decolorization and transparency of sulfuric acid gradually increase. This is mainly because the increase in ultrasonic power density causes a higher ozone mass transfer efficiency [34], cavitation effect [35] and the formation of many free radicals [36,37]. When the ultrasound intensity continues to increase, the strengthening effect of ultrasound reaches the maximum effect in the sulfuric acid system and the amounts of free radicals generated and ozone dissolved in the sulfuric acid reach the saturation value. At this time, the extent of decolorization and transparency remain stable with increasing ultrasonic power density, as shown in Fig. 5. According to the literature [38], a low degradation effect of organic pollution with excessive ultrasonic density could be ascribed to increased coalescence odds of ozone bubbles and temperature. Therefore, the optimized ultrasonic power density is 200 W·L⁻¹ in our study.

The effective calorimetric power (Pcal) [39–41] was used to quantify the energy transfer efficiency of the sonochemical reactor in our work. 3 L of black concentrated sulfuric acid (equivalent to a sulfuric acid mass of 5.52 kg) was directly sonicated with an ultrasonic power density of 200 W·L⁻¹ (equivalent to an ultrasonic power of 600 W) without any cooling for 10 min. The temperature increase was recorded in 1 min intervals. The calorimetric calibration curve of ultrasound in concentrated sulfuric acid medium is shown in Fig. 6, and the heating rate (dT/dt) of sulfuric acid is obtained as 0.0534 (°C s⁻¹).

The specific heat capacity (Cp) of sulfuric acid medium is calculated at different temperatures using the following equation:

\[
C_P = 9.617 - 14.387x + 6.154x^2 + 1.860 \times 10^{-3} \times (T - 20)
\]

where \(x\) is the H₂SO₄ mass fraction of sulfuric acid and \(T\) is the temperature.

Herein, \(C_P\) was obtained as 1.421 kJ kg⁻¹ °C⁻¹ for concentrated sulfuric acid with a H₂SO₄ mass fraction of 0.983 and a temperature of 20 °C. The effective calorimetric power (Pcal) of ultrasound in concentrated sulfuric acid medium was calculated to be 0.4195 kJ s⁻¹, equivalent to 419.5 W. The result shows that the energy efficiency \(\eta\) of ultrasound in concentrated sulfuric acid medium is: \(\eta = \frac{P_{cal}}{P_{sonic}} \times 100\% = 69.81\%\)

In addition, under an ultrasonic power density of 200 W·L⁻¹, the extent of decolorization and transparency of the sulfuric acid sample treated at 60 °C for 4 h with an ozone gas flow rate of 1.8 L/h are as high as 98.2% and 86.8 mm, respectively, which are far better than those requirements in China’s national standard (decolorization of ≥ 70% and transparency of ≥ 50 mm). Therefore, it is necessary to study the influence of temperature, decolorization time and ozone gas flow rate on the decolorization effect in detail to shorten the time and reduce the ozone flow and temperature as much as possible.

3.2.2. Effect of reaction temperature

The decolorization of black sulfuric acid in the US/O₃ system was carried out at different reaction temperatures (20, 30, 40, 50, 60, and 70 °C) for a specific time and for different times (0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 h) at a specific temperature under an acid volume of 3 L, ozone flow rate of 1.8 L/h, ultrasonic power density of 200 W·L⁻¹, and stirring rate of 800 RPM. Fig. 7 shows the effect of the reaction temperature on decolorization efficiency.

Under the action of ultrasound, an increase in temperature can promote the degradation of organic pollutants by ozone, resulting in an

---

**Fig. 5.** Effect of ultrasonic power density (3 L sulfuric acid, 800 RPM stirring rate, 60 °C reaction temperature, 1.8 L/h ozone gas flow, 4 h treatment time).

**Fig. 6.** Calorimetric calibration curve of ultrasound in concentrated sulfuric acid medium (3 L sulfuric acid, 200 W·L⁻¹ ultrasonic power density).
increase in the extent of decolorization and transparency, as shown in Fig. 7a and 7b. The dissolution and mass transfer process of ozone are suppressed at low temperatures due to the higher viscosity of sulfuric acid and diffusion resistance [42]. As the temperature increases from 20 to 60 °C, the viscosity of 98% concentrated sulfuric acid rapidly decreases from $25.8 \times 10^{-3}$ to $8.7 \times 10^{-3}$ Pa·s and then decreases to $5.7 \times 10^{-3}$ Pa·s at 75 °C [43]. In a less viscous sulfuric acid, the mass transfer of ozone is enhanced, and the reaction between ozone molecules and chromogenic groups of organic molecules is more comprehensive. In addition, an increase in temperature can accelerate the conversion of O$_3$ to OH$^\cdot$, thereby enhancing the degradation rate of organic pollutants [24]. At the same time, a rising temperature can reduce the half-life and solubility of ozone in the liquid phase [44,45]. Although these effects of temperature are contradictory, it can be seen from Fig. 7 that the advantages of increasing temperature circumvent the disadvantages for the decolorization of the concentrated sulfuric acid system. As a result, the extent of decolorization and transparency of sulfuric acid increase significantly from 85 to 94% and from 76 to 85 mm, respectively, as the temperature rises from 20 to 60 °C. Then, the extent of decolorization and transparency increase at a slow rate when the temperature is increased to 70 °C.

The H$_2$SO$_4$ mass fraction is nearly maintained during the whole decolorization process (Fig. 7c), which is explained by the fact that the decolorization reaction is carried out in a closed decolorization tank to avoid the influence of water vapor in the water bath and air on the concentration of sulfuric acid. The H$_2$SO$_4$ mass fraction is 98.1% after decolorization at 60 °C for 2 h. However, the H$_2$SO$_4$ mass fraction decreases slightly to 97.8% after decolorization at 70 °C for 4 h. The possible reason is that more small molecular organic pollutants formed from the destruction of macromolecular organic pollutants are further oxidized to produce water and CO$_2$ when the treatment time is extended to 4 h, resulting in a slight decrease in the H$_2$SO$_4$ mass fraction. In addition, more water vapor formed from the water bath at 70 °C, which may be absorbed by concentrated sulfuric acid the sampling observation port during the sampling process. The chromaticity of the samples after different reaction temperatures for 2 h is shown in Fig. 7d. The result shows that the chromaticity of the sample obtained after decolorization at 60 °C for 2 h is lower than the standard chromaticity, reaching the chromaticity of the first-class product.

### 3.2.3. Effect of ozone gas flow rate

The decolorization of black sulfuric acid in the US/O$_3$ system was carried out at different ozone gas flow rates (0.8, 1.0, 1.2, 1.5, 1.8, 2.0, 5.0, and 10.0 L/h) and for different times (0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 h) under an acid volume of 3 L, a reaction temperature of 60 °C, an ultrasonic power density of 200 W·L$^{-1}$, and a stirring rate of 800 RPM. Fig. 8 shows the effect of ozone gas flow rates on decolorization efficiency.

Increasing the ozone gas flow rate leads to an increase in the ozone content per unit volume of sulfuric acid per unit time. This forms strong turbulence in the sulfuric acid solvent and promotes the formation of cavitation bubbles under the action of ultrasound, which could
accelerate the mass transfer of ozone-sulfuric acid and enhance the degradation efficiency of organic compounds with chromogenic groups. Therefore, the extent of decolorization of sulfuric acid increases from 85 to 97%, while the transparency increases from 65 to 85 mm when the ozone gas flow rate increases from 0.8 to 1.8 L/h. Ozone with an appropriate flow rate is dispersed in sulfuric acid as microbubbles under the action of ultrasound. However, the excess gas flow promotes the formation of large ozone bubbles and forms an intense turbulence in sulfuric acid. The gas–liquid contact area of large bubbles is smaller than that of microbubbles and large bubbles easily overflow from the liquid phase under the action of intense turbulence, resulting in a short ozone–liquid contact time and a lower mass transfer rate [27,38]. It has been reported that excessive ozone flow is unfavorable to the degradation effect [46]. And the same phenomenon is observed in our work. The extent of decolorization and transparency (Fig. 8a and 8b) decrease due to the formation of large bubbles when the flow rate increases from 1.8 to 10 L/h (the difference in bubble size caused by flow is illustrated in Fig. S3 in the Supplementary material). The H$_2$SO$_4$ mass fraction of samples obtained after decolorization with different gas flow rates is maintained at ~98% (Fig. 8c), indicating that the ozone gas flow rate has little effect on the H$_2$SO$_4$ mass fraction during the sulfuric acid decolorization process, similar to the effect of reaction temperature. These results suggest that the most appropriate flow rate of ozone for the sulfuric acid decolorization process is 1.8 L/h under the operating conditions used in this study.

3.2.4. Effect of treatment time

The decolorization process of sulfuric acid was carried out for different times (0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 h) under an acid volume of 3 L, reaction temperature of 60 °C, ozone gas flow rate of 1.8 L/h, ultrasonic power density of 200 W·L$^{-1}$, and stirring rate of 800 RPM. The extent of decolorization, transparency, and H$_2$SO$_4$ mass fraction of sulfuric acid samples are shown in Fig. 8a-8c. The UV–Vis spectroscopy result is presented in Fig. 9.

As shown in Fig. 8a, prolonging the treatment time can enhance the probability of contact and reaction between ozone and organic pollutants due to the high concentration of organic pollutants in black sulfuric acid at the initial stage of the reaction, resulting in a significantly improved extent of decolorization from 0 to 73% after 2 h. Subsequently, the content of macromolecular organics containing chromogenic groups participating in the reaction decreases, leading to a slow increase in the extent of decolorization. The transparency increases slowly with prolonged treatment time contrary to the extent of decolorization. The increasing rate of transparency is significantly lower than the increasing rate of removal, especially within 1 h of reaction. The degradation of organic chromogenic groups that cause the excessive chromaticity of sulfuric acid and the transformation of organic pollutants from macromolecules to small molecules in the initial stage of decolorization, which leads to a significant increase in the extent of decolorization. However, the transparency of sulfuric acid is not significantly improved due to small molecules of organic pollutants still being present in sulfuric acid.

The UV–Vis spectra (Fig. 9) show that the absorption peak
diminishes sharply with prolonged reaction time and the chromaticity of the sulfuric acid raw material also significantly changes from black to colorless. This is due to the destruction and degradation of organic pollutants that cause the excessive chromaticity of sulfuric acid. In addition, a blue shift in the UV–Vis spectra of sulfuric acid is noticed and is more obvious with prolonged treatment time, which is caused by the destruction of chromophores by oxidative degradation [7].

3.3. The enhancement mechanism of the ultrasonic field

The effects of US alone, O3 alone, and US/O3 and different free radicals on the extent of decolorization and transparency of sulfuric acid were compared. The decolorization process of sulfuric acid was carried out at an acid volume of 3 L, a reaction temperature of 60 °C, an ultrasonic power density of 200 W L−1, an ozone gas flow rate of 1.8 L h−1, and a stirring rate of 800 RPM, and the results are shown in Fig. 10.

3.3.1. Comparison of effects of US alone, O3 alone, US/O3

From Fig. 10, US alone has little effect on the decolorization of sulfuric acid. The degradation of organic pollutants using US alone mainly depends on the generation of hydroxyl radicals during acoustic cavitation. Hydroxyl radicals are generated when ultrasound waves are transmitted through an aqueous solution (Reaction (5)) [47]. However, in the concentrated sulfuric acid system with low water content (<2 wt %), very few hydroxyl radicals are formed from water cavitation bubbles [48]. In addition, cavitation is difficult to achieve in highly viscous liquids using the US alone process [49,50]. Therefore, US alone has a poor degradation effect on organic pollutants in concentrated sulfuric acid with low water content and high viscosity.

\[ H_2O + US \rightarrow H + \cdot OH \]  

(5)

The extent of decolorization and transparency of samples in the US/O3 process are significantly higher than those obtained in the O3 alone process, as shown in Fig. 10. The quality of decolorized sulfuric acid met the requirements for first-class products in national standards after treating for 2 h with US/O3 or for 2.5 h with O3 alone. This result shows that under the same oxidation effect, the treatment time could be saved by 25% using the US/O3 process compared to using O3. This is because ultrasound can break O3 from large bubbles into microbubbles. The O3 bubbles in our experiment with and without ultrasound are shown in Fig. S4 in the Supplementary material. Compared with large bubbles, microbubbles increase the cavitation effect and further promote the generation of high temperature and high pressure when cavitation bubbles collapse instantaneously [51]. The presence of ultrasound can effectively improve the dissolved concentration of ozone in the liquid phase, reduce the resistance of ozone mass transfer and promote the chain reaction of ozone to form free radicals with stronger oxidizing ability (Reactions (6)-(8)) [18], resulting in a shortened treatment time.

\[ \cdot O_2 + O_3 \rightarrow O_2 + \cdot O_3 \]  

(6)

\[ \cdot O_3 \rightarrow O_2 + O^- \]  

(7)

\[ O^- + H_2O \rightarrow OH + OH^- \]  

(8)

The DMPO spin-trapping EPR technique was used to further verify the generation of •OH [52]. As shown in Fig. 11, the signal was not detected under the ultrasound system alone, which means that no hydroxyl radicals were generated in the ultrasound system alone. Under a separate ozone system, a quartet of weak signals with relative intensities of 1:2:2:1 were detected from the DMPO-•OH adducts during the reaction process [52]. In comparison, the ultrasound-assisted ozone system exhibited very strong DMPO-•OH signals, which were much stronger than those of single ozone system. This once again proves that the enhancement effect of ultrasound increases the number of hydroxyl...
radicals in the oxidation system with the participation of ozone. The DMPO-trapped EPR results confirm the importance of the enhancement effect of ultrasound, which is consistent with the results of other studies [52,53].

The COD results of sulfuric acid in the US/O₃ and O₃ processes are shown in Fig. 12. Fig. 12 shows that the oxidation reactions under US/O₃ and O₃ have three stages as follows. (i) Both the extent of decolorization and transparency increase rapidly from the beginning of the reaction to 1 h. At this time, the macromolecule organic pollutants that cause the colouring are broken to form more small colourless molecules, which leads to a significant decolorization effect of sulfuric acid and an increase in the COD value at this stage. (ii) When the treatment time is from 1 h to 2 h, the concentration of ozone and other oxidizing components in the solution gradually reaches the maximum, and the extent of decolorization and transparency continue to increase. The COD value at this stage drops significantly, proving that the rate of oxidation of small molecules into CO₂ is higher than that of larger molecules into small molecules. (iii) As the oxidation reaction continues, the concentration of degradable organic pollutants in sulfuric acid decreases. The extent of decolorization and transparency slowly increase, while the COD value slowly decreases due to the continuous action of the oxidizing components, and the oxidation effect slows down. However, the enhanced effect of ultrasound can promote the second stage of the reaction, thereby optimizing the reaction effect and saving time.

3.3.2. Effect of different oxidizing components in the US/O₃ process

In the US/O₃ process, the effect of different oxidizing components on the decolorization process was studied as shown in Fig. 10. The intermediate products (O₃²⁻, O²⁻) in Reactions (6)-(8) were reported to be in very small amounts in the liquid phase compared to •OH and •O₂ [18], so the influence of intermediate products (O₃²⁻, O²⁻) is ignored in our work. Herein, tert-butyl alcohol (TBA) was applied to determine the generation of •OH [54], and superoxide dismutase (SOD) was applied to determine the generation of •O₂ [55]. As shown in Fig. 10, whether SOD or TBA is added, the extent of decolorization and transparency of sulfuric acid are reduced. In addition, the order of the decolorization effect is US + O₃ > US + O₃ + SOD > US + O₃ + TBA, indicating that both •OH and •O₂ radicals play an oxidizing role in the decolorization process of sulfuric acid and that •OH plays a greater role than •O₂.

According to the decolorization effects of US + O₂, US + O₃ + SOD and US + O₃ + TBA in Fig. 10, the percentage of different oxidation components on the decolorization effect is calculated and shown in Fig. 13. As seen from Fig. 13, the order of the effects of different oxidation components in the decolorization process of black sulfuric acid is O₃ > •OH > •O₂. The redox potentials of •OH, O₂ and •O₂ are 2.8, 2.07 V and 0.89 V, respectively [56]. During the decolorization reaction, O₃ and •OH play a leading role in decolorization because of their strong oxidizing properties. Also, •OH can oxidize most organic pollutants due to its non-selective and higher redox potential, while O₂ is a selective oxidant and is generally suitable for oxidizing organics with electron-rich moieties [57,58]. It is worth noting, however, that the direct oxidation of O₃ still occupies a major position in the oxidation reaction process, not the hydroxyl radical. This is mainly because the generation of •OH is significantly less than that of ozone molecules in a concentrated sulfuric acid system with low water content, high viscosity, and high acidity [49]. Also note that the degree of effectiveness of •OH is higher at the beginning of the reaction and then decreases with the extension of the treatment time, while the influence of O₃ molecules on the extent of decolorization and transparency gradually increases. This is mainly because the content of organic pollutants in black sulfuric acid is high at the beginning of the reaction. At this time, the degradation effect of O₃ molecules on refractory macromolecular organics is poor, and the main role is to provide free radicals for the reaction system (such as reactions (6)-(8)). The •OH obtained by O₃ molecule decomposition is mainly responsible for breaking the refractory macromolecular organics into small molecule organics that are easily oxidized. Therefore, the degree of effectiveness of •OH is as high as 33% when the treatment time

![Fig. 11. EPR spectra of •OH formation from sulfuric acid in US/O₃ system.](image-url)

![Fig. 12. COD results of sulfuric acid (3 L sulfuric acid, 800 RPM stirring rate, 60°C reaction temperature, 1.8 L/h ozone gas flow, 4 h treatment time.) in (a) US/O₃ (200 W L⁻¹ ultrasonic power density) and (b) O₃ processes.](image-url)
is 0.5 h. As the treatment time increases, the content of small-molecule organic pollutants in black sulfuric acid increases. Both O₂ and OH can oxidize small molecular organic pollutants to CO₂, and there is a competition between O₂ and OH. However, because the half-life of O₃ molecules in the liquid phase is significantly longer than that of OH [59], the content of O₃ molecules in the liquid phase increases with the extension of treatment time. As a result, the effectiveness degrees of OH and O₃ in the extent of decolorization are 10.53% and 84.21%, respectively, when the treatment time is 4 h.

4. Conclusions

Sulfuric acid is a highly corrosive and dangerous product, and the excessive storage of black sulfuric acid will cause environmental pollution and safety hazards. In this study, the enhancement effect of ultrasound-assisted ozone to decolorize black industrial sulfuric acid and the enhancement mechanism of ultrasound were studied. Qualified ultrasound-assisted ozone to decolorize black industrial sulfuric acid pollution and safety hazards. In this study, the enhancement effect of excessive storage of black sulfuric acid will cause environmental

Acknowledgements

Funding: This work was financially supported by the “Zhihui Yunnan” program of Yunnan Provincial Science and Technology Department [202103AM140006]; Yunnan Fundamental Research Projects [202101BE070001-023].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2022.106043.

References

[1] X.K. Li, J.R. Han, Y. Liu, Z.H. Dou, T.A. Zhang, Summary of research progress on industrial flue gas desulfurization technology, Sep. Purif. Technol. 261 (2022) 119849, https://doi.org/10.1016/j.seppur.2021.119849.
[2] H.J. Tian, F.Q. Yuan, J.W. Xu, J. Chang, Q.J. Guo, Performance evaluation of a gypsum-based desulfurizer for sulfur recovery from the smelter off-gas: experimental analysis and thermodynamic performance, Energy Fuels. 32 (2) (2018) 2009–2018, https://doi.org/10.1021/acs.energyfuels.7b03276.
[3] S.X. Mei, Study on production process of sulfuric acid, Modern Chem. Res. 4 (2020) 105–106, https://doi.org/10.3969/j.issn.1672-8114.2020.04.049.
[4] K.C. Liao, M. Yang, Operation situation of China’s sulfuric acid industry in 2020 and development trend in 2021, Phosphate Compd. Fert. 36 (6) (2021) 1–5, https://doi.org/10.3969/j.issn.1007-6220.2021.06.002.
[5] Chinese national standard, GB/T 534-2014, sulphuric acid for industrials use. https://max.book118.com/html/2019/0404/5010232143002023.shtm, 2021 (accessed 13 September 2021).
[6] X.N. Cai, F. Shen, Y.J. Zhang, H.Y. Hu, Z.Q. Huang, Y.Z. Yin, X.T. Liang, Y.B. Qin, J. Liang, Mineralization of organics in hazardous waste sulfuric acid by natural manganese oxide ore and a combined MnO₂/activated carbon treatment to produce qualified manganese sulfate, J. Hazard. Mater. 366 (2019) 466–474, https://doi.org/10.1016/j.jhazmat.2018.12.021.
[7] Y.J. Zhang, T. Gan, H.Y. Hu, X.N. Cai, Z.Q. Huang, X.T. Liang, Y.Z. Yin, Y.B. Qin, Z. F. Feng, Effective treatment and utilization of hazardous waste sulfuric acid generated from alkaliolation by lignocellulose-ester-catalyzed oxidative degradation of organic pollutants, J. Hazard. Mater. 380 (2019), 120892, https://doi.org/10.1016/j.jhazmat.2019.120892.
[8] B.T. Dewey, A.H. Gelman, Color reactions of organic nitrogen compounds with selenious acid-sulfuric acid solution, Ind. Eng. Chem. Anal. Edit. 14 (4) (2002) 361–362, https://doi.org/10.1021/ie010194a29.
[9] Z.H. Wei, M.R. Ma, Y.M. Li, H.H. Chen, Root cause analysis and countermeasures of summer-seasonal redness in sulphuric acid by nickel-copper smelting gas sulphuric acid production, Sulphuric Acid Ind. 6 (2017) 13–15, https://doi.org/10.3969/j.issn.1002-1507.2017.06.004.
[10] M.J. Pei, Cause analysis and treatment of influencing chromaticity of industrial sulfuric acid, Chem. Prod. Technol. 15 (1) (2008) 53–58, https://doi.org/10.3969/j.issn.1006-6829.2008.01.016.
[11] D.F. Wang, B.D. Shav, A. Yang, Gasification of spent alkalylation sulfuric acid droplets in hot environments, AIChE J. 45 (1999) 1161–1168, https://doi.org/10.1002/aic.690450602.
[12] M. Asolf, S.A. Rachman, W.A. Nurwati, C. Ramayanti, Recovery of H₂SO₄ from spent acid waste using bentonite adsorbent, MATEC Web Conf. 101 (2017) 02007, https://doi.org/10.1051/matecconf/201710102007.
[13] D.F. Haghshehas, D. Darvishi, H. Rafieipour, E.K. Alamdari, A.A. Salaridini, A comparison between TEHA and Cyanex 923 on the separation and the recovery of sulfuric acid from aqueous solutions, Hydrometallurgy 97 (2009) 173–179, https://doi.org/10.1016/j.hydromet.2009.02.006.
[38] B. Wang, X.G.Y. Xiong, Y.Y. Shui, Z.Y. Huang, K. Tian, A systematic study of enhanced ozone mass transfer for ultrasound-assisted FTE hollow fiber membrane aeration process, Chem. Eng. J. 237 (2013) 678–688, https://doi.org/10.1016/j.cej.2013.09.188.

[39] R.A. Jouberti, Y. Yufal, L. Bowtell, V. Arvanitha, Energy characterisation of ultrasonic systems for industrial processes, Ultrasonics. 57 (2015) 18–30, https://doi.org/10.1016/j.ultras.2015.03.003.

[40] D. Meroni, R. Djellabi, M. Ashokkumar, C.L. Bianchi, D.C. Boffito, Sonoprocessing: from concepts to large-scale reactors, Chem. Rev. 122 (3) (2022) 3219–3258, https://doi.org/10.1021/acs.chemrev.1c00260.

[41] R.F. Contantine, A.M. Wilhelm, J. Berlan, H. Delmas, Power measurement in sonochemistry, Ultrason. Sonochem. 2 (1) (1995) 543–547, https://doi.org/10.1016/1074-5313(94)00010-P.

[42] J. Edeline, M. Ammann, T. Banas-Rausch, Microphysics of the aqueous bulk counts the water activity driven rate acceleration of bromide oxidation by ozone from 289-245 K, Environ. Sci.-Process Impacts. 21 (1) (2019) 63–73. https://doi.org/10.1039/c0em000417.

[43] Y.W. Sha, Z.B. Sun, K.S. Hong, E.H. Wei, Design handbook of sulfuric acid process—physical and chemical data, Ministry of Chemical Industry, Nanjing, 1990: 3 (3): Viscosity, 20-21.

[44] M. Mehrjouei, S. Müller, M. Möller, A review on photocatalytic ozonation used for the treatment of water and wastewater, Catal. En. 263 (2015) 209–219, https://doi.org/10.1016/j.cattod.2014.10.012.

[45] R.H. Huang, H.H. Yan, L.S. Li, D.Y. Deng, Y.H. Shu, Q.Y. Zhang, Catalytic activity of Fe/SBA15 for ozonation of dimethyl phthalate in aqueous solution, Appl. Catal. B-Environ. 106 (2011) 246–261, https://doi.org/10.1016/j.apcata.2011.05.041.

[46] I. Gultekin, N.H. Ince, Degradation of aryl-azo-naphthol dyes by ultrasound, ozone (and their combination: effect of alpha-substituents, Ultrason. Sonochem. 13 (2006) 208–214, https://doi.org/10.1016/j.ultsonch.2005.03.002.

[47] X.Y. Lu, W. Qin, J.L. Peng, H.D. Xu, D. Wang, Y. Cao, W. Zhang, J. Ma, A review on additives-assisted ultrasound for organic pollutants degradation, J. Hazard. Mater. 403 (2020), 123915, https://doi.org/10.1016/j.jhazmat.2020.123915.

[48] B. Wang, W. Shi, H. Zhang, H.Y. Ren, M.Y. Xiong, Promoting the ozone–liquid mass transfer through external physical fields and their applications in wastewater treatment: a review, J. Environ. Chem. Eng. 9 (2021), 106115, https://doi.org/10.1016/j.jece.2021.106115.

[49] H. Nazari-Mahroo, K. Pasandideh, H.A. Navid, R. Sadighi-Bonabi, How important is the liquid bulk viscosity effect on the dynamics of a single cavitation bubble, Ultrason. Sonochem. 49 (2018) 47–52, https://doi.org/10.1016/j.ultsonch.2018.07.013.

[50] C. Guo, J. Liu, X.H. Li, S.Q. Yang, Effect of cavitation bubble on the dispersion of magnetothermal polishing fluid under ultrasonic preparation, Ultrason. Sonochem. 79 (2021), 105782, https://doi.org/10.1016/j.ultsonch.2021.105782.

[51] X.G.Y. Xiong, B. Wang, W. Zhu, K. Tian, H. Zhang, A review on ultrasonic catalytic microbubbles ozonation processes: properties, hydroxyl radicals generation pathway and potential in application, Catalysts. 9 (3) (2018) 2–18, https://doi.org/10.3390/catal9030101.

[52] L. Zhao, W.C. Ma, J. Ma, G. Wen, Q.L. Liu, Relationship between acceleration of hydroxyl radical initiation and increase of multiple-ultrasonic field amount in the process of ultrasonic catalytic ozonation for degradation of nitrobenzene in aqueous solution, Ultrason. Sonochem. 22 (2015) 198–204, https://doi.org/10.1016/j.ultsonch.2014.10.014.

[53] W.Q. Guo, R.L. Cao, S.Y. Yang, S.Q. Ren, Sulfamethoxazole degradation by ultrasound/ozone oxidation process in water: kinetics, mechanisms, and pathways, Ultrason. Sonochem. 22 (2015) 182–187, https://doi.org/10.1016/j.ultsonch.2014.07.008.

[54] J.P. Xu, W.L. Qin, J.X. Yuan, L. Sun, F. Pan, D.S. Xia, Synergistic mechanism and degradation kinetics for atenolol elimination via integrated UV/ozone/ peroxynitrous oxide process, J. Hazard. Mater. 407 (2021), 124393, https://doi.org/10.1016/j.jhazmat.2021.124393.

[55] T.Q. Zhao, P. Li, C. Tai, J.P. She, Y.G. Yin, Y.A. Qi, G.C. Zhang, Efficient decolorization of typical azo dyes using low-frequency ultrasound in presence of carbonate and hydrogen peroxide, J. Hazard. Mater. 346 (2017) 42–51, https://doi.org/10.1016/j.jhazmat.2017.12.099.

[56] J.L. Wang, S.Z. Wang, Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism, Chem. Eng. J. 401 (2020), 126158, https://doi.org/10.1016/j.cej.2020.126158.

[57] P. Tao, C. Yang, H.H. Wang, Y.P. Zhao, X.M. Zhang, M.H. Shao, T.J. Sun, Synergistic effects of ultrasound-assisted ozonation on the formation of hydrogen peroxide, J. Environ. Chem. Eng. 9 (2021), 104905, https://doi.org/10.1016/j.jece.2021.104905.

[58] D.S. Babu, V. Srivastava, P.V. Nidheesh, M.S. Kumar, Detoxification of water and wastewater by advanced oxidation processes, Sci. Total Environ. 696 (2019), 133961, https://doi.org/10.1016/j.scitotenv.2019.133961.

[59] A. Phaniendra, B.D. Jastad, L. Periyasamy, Free radicals: properties, sources, targets, and their implication in various diseases, Indian J Clin. Biochem. 30 (2015) 11–26, https://doi.org/10.1007/s12291-014-0466-6.