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Pretreatment of preserved fruits wastewater by a novel Fe(III)-catalyzed oxidation coupled with calcium oxide precipitation

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ABSTRACT

The high concentration of sulfite in preserved fruits wastewater is toxic to microorganisms, which tends to break down the biological treatment system and leads to poor effluent quality. In addition, the pH decreases constantly due to the presence of sulfite during biological treatment, even if it is repeatedly adjusted to neutral. Therefore, to ensure the stable and efficient operation of biological treatment, a novel pretreatment was proposed through transition metal ions catalyzed oxidation coupled with chemical precipitation. The results showed that Fe(III) ion achieved the best catalytic efficacy for the oxidation of sulfite which was attributed to the combination of complexation and free radical reaction. Under the optimal conditions (aeration rate = 0.10 L/min, Fe(III) dosage = 5 mmol/L), the sulfite removal was 80.1%, concomitant with 20.7% of chemical oxygen demand (COD) removal. Further, by calcium oxide precipitation, the sulfite was completely removed, COD decreased by 32.2% as well as BOD_5/COD increased to 0.96, ensuring pH stability and high biodegradability in subsequent biological treatments. These findings demonstrate that this pretreatment process has great potential for sulfite removal and provides an economical and practical approach to the treatment of preserved fruits wastewater.

Keywords: Preserved fruits wastewater; Sulfite; Catalytic oxidation; Fe(III) ion; Precipitation

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1. Introduction

As a food additive, sodium pyrosulfite ($Na_2S_2O_5$) is widely used as a preservative, bleach, and loosening agent in the food processing of fruits and vegetables. Especially in the preserved fruits processing industry, a large amount of $Na_2S_2O_5$ has been used to keep the preserved fruits bright, beautiful, and preserve. However, the residual $Na_2S_2O_5$ in food is required to be lower than 0.35 g/kg according to National Food Safety Standard for the Use of Food Additives (GB2760-2014) [1]. Therefore, large quantities of preserved fruits wastewater have been generated in the production process due to the washing of preserved fruits to reduce residual $Na_2S_2O_5$. Usually, $Na_2S_2O_5$ is hydrolyzed

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into hydrogen sulfite (HSO_3^-) after dissolution, resulting in a high concentration of sulfite and low pH in preserved fruits wastewater [2]. Sulfite acid is a dibasic acid with $pK_{a,1} = 1.81$, $pK_{a,2} = 6.91$ (ionization equilibrium constant at 25°C). According to the ionization equilibrium of sulfite, it is mainly present in the form of bisulfite ions when the pH of the solution is between 1.81 and 6.91 [3]. The pH value in preserved fruits wastewater is about 4, so the sulfite is mainly in the form of bisulfite. Sulfite can act as a reducing agent in the environment, so the oxidization of sulfite in wastewater leads to a continuous decline in pH in biological treatment even if pH is repeatedly adjusted to neutral. In addition, sulfite is a reactive and toxic compound that can damage proteins, nucleic acids, and lipids of living organisms [4]. In common biological wastewater treatment systems, the high concentration of sulfite may suddenly decrease the activity of activated sludge and biofilms, leading to the collapse of the wastewater treatment system and substandard effluent quality [5]. Therefore, it is necessary to oxidize and remove sulfite before the biological treatment of preserved fruits wastewater.

Generally, the oxidation rate of sulfite is very slow under direct aeration and can be promoted by strong oxidants such as hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), and ozone (O_3) [3,6–9]. Frank et al. [6] found that the oxidation rate constant of HSO_3^- was enhanced linearly with the increasing H_2O_2 concentration from 0 to 150 μmol/L. In addition, ozone significantly shortened the time of sulfite oxidation compared with air [7]. However, the use of these strong oxidants increases the cost of wastewater treatment and potentially arouses corrosive and toxic problems [8,9].

Besides, it has been reported that sulfite removal can be accelerated simply by transition metal ions, which activated sulfite to produce free radicals [10–13]. For example, Li et al. [11] indicated that Co(II) ion enhanced the reaction rate constant of magnesium sulfite about 6 times more than the control. However, these studies focused on the sulfite oxidation in liquids with no or low-level organic matters, such as simulated printing and dyeing wastewater, flue gas desulfurization absorbent solution, and cloud droplets [14,15], while almost no reports involved sulfite removal from organic-rich wastewater by transition metal ions. In recent years, sulfite and transition metals have been found to construct Fenton-like systems, and widely be used in the degradation of recalcitrant organic contaminants such as iohexol and azo dye [10,16,17]. These studies suggested that the mechanism of advanced oxidation removal of organic pollutants based on sulfites is similar to other advanced oxidation methods such as peroxymonosulfate, ultrasound, photocatalysis, etc., which are all oxidation removal of organic pollutants by highly reactive oxidising species ($SO_4^{\bullet-}$ and $^{\bullet}OH$, etc.) [18–21]. However, these studies mainly focused on the removal of organics, rather than the sulfite removal. In addition, the concentration of sulfite, which was used to produce sulfate radicals for the oxidation of refractory organic matters, has been consistently reported to be low [10,17]. Preserved fruits wastewater is characterized by high concentrations of both organic matters and sulfite. In this scenario, whether transition metal ions can catalyze sulfite oxidation is unclear. Thus, it is also worthwhile to investigate the influence of organic matters in preserved fruits wastewater on sulfite oxidation, organic matters removal as well as the mechanism of sulfite oxidation in preserved fruits wastewater.

Hitherto, the pretreatment of preserved fruits wastewater usually adopted Fenton oxidation followed by flocculation–sedimentation. This process has the disadvantages such as high chemical cost, poor safety, as well as large amounts of iron sludge generation. To this end, a novel pretreatment process for preserved fruits wastewater was proposed through transition metal ions catalyzed oxidation coupled with chemical precipitation, and the viability of this pretreatment was evaluated. Firstly, the most effective transition metal ion was screened. Subsequently, the effects of aeration rate, initial pH, catalyst dosage, organic matter concentration, and sulfite concentration on sulfite oxidation were investigated. The reaction mechanism of sulfite catalytic oxidation in the preserved fruits wastewater was also explored. Finally, the effectiveness and economics of the pretreatment of preserved fruits wastewater by the combination of catalytic oxidation and chemical precipitation was assessed. The present study provided a simple and economical approach for the pretreatment of preserved fruits wastewater before the biological treatment process.

2. Materials and methods

2.1. Preserved fruits wastewater

The preserved fruits wastewater used in this work was collected from the collection pool in Jinyuan preserved fruits factory wastewater treatment station, in Guangdong, China. After removing the large particles, the wastewater was stored at 4°C. The water quality indexes of the preserved fruits wastewater are shown in Table 1.

2.2. Chemical reagents

DTNB (5,5′-Dithiobis-(2-nitrobenzoic acid)), ethanol, sodium sulfite, disodium hydrogen phosphate, and potassium dihydrogen phosphate used to determine the concentration of sulfite and calcium oxide for neutralization were all from Shanghai Macklin Biochemical Co., Ltd., China. All chemicals were of analytical grade. The reagent purity is shown in Table S1. Ultrapure water for analysis was from an RO-DI system ® Laboratory water purification system (18.2 MΩ cm resistivity at 25°C).

2.3. Experimental procedure

2.3.1. Catalyst screening

In this study, four common transition metal ions $FeCl_3$, $CuCl_2$, $MnCl_2$, and $CoCl_2$ were used to screen suitable catalysts for sulfite oxidation in preserved fruits wastewater. The initial concentration of all the metal ions was 5 mmol/L. An experiment with no metal ions was set as control. All the screening experiments were conducted in cylindrical glass bottles with a working volume of 100 mL at a temperature of 25°C and a stirring speed of 300 rpm in duplicate. The water samples were taken at regular time intervals and filtrated by a 0.22 μm polyethersulfone membrane for further measurements.

Table 1
Water quality of raw and pre-treated preserved fruits wastewater

Parameter	Unit	Raw wastewater	After Fe(III) catalytic oxidation	After precipitation
pH		4.06 ± 0.03	2.12 ± 0.01	8.86 ± 0.01
COD	mg/L	8,285 ± 233	6,570 ± 85	5,615 ± 49
BOD_5	mg/L	6,578 ± 184	2,679 ± 33	5,393 ± 57
BOD_5/COD		0.79 ± 0.04	0.41 ± 0.00	0.96 ± 0.00
NH_4^+–N	mg/L	21.4 ± 1.3	14.7 ± 1.6	13.2 ± 2.4
TN	mg/L	108 ± 1.4	103 ± 3.5	94 ± 4.2
TP	mg/L	97.4 ± 1.3	108.6 ± 2.3	n.d.
Total Fe	mg/L	5.4 ± 0.1	287.9 ± 3.8	26.6 ± 2.3
Cl^-	mg/L	3,999.7 ± 7.1	4,623.0 ± 12.8	4,507.4 ± 5.9
SO_4^{2-}	mg/L	1,375 ± 35	1,975 ± 35	1,900 ± 0
SO_3^{2-}	mg/L	1,145.8 ± 9.0	228.0 ± 7.8	n.d.
Total phenols	mg/L	379.3 ± 3.3	260.4 ± 2.2	166.1 ± 6.5

Note: n.d. – not detected, the detection limit is 1.0 mg/L for TP and 0.2 mg/L for SO_3^{2-}.

2.3.2. Fe(III) ion catalytic oxidation condition

Batch experiments were conducted to investigate the effects of various factors on the catalytic oxidation of sulfite in preserved fruits wastewater with Fe(III) ion. The influencing factors included aeration rate (0–0.15 L/min), initial wastewater pH (4–8), Fe(III) dosage (1–9 mmol/L) as well as initial sulfite concentration (10–50 mmol/L). In addition, the effect of organic matters of preserved fruits wastewater on the catalytic oxidation of sulfite was also investigated. In this case, different concentrations of organic matters in wastewater were obtained by gradient dilution of preserved fruits wastewater, while the supplementation of sulfite and sulfate was used to keep their concentrations in line with the raw preserved fruits wastewater. All experiments were carried out in the cylindrical glass bottles described in section 2.3.1. To ensure the reproducibility, all the experiments were performed in duplicate. The water samples were taken at regular time intervals (up to 120 min), filtrated through a 0.22 μm polyethersulfone membrane, and used for further measurements.

2.3.3. Chemical precipitation

After the catalytic oxidation of preserved fruits wastewater, a chemical precipitation process was conducted to adjust pH and remove iron ions and sulfate as much as possible, so that the pre-treated preserved fruits wastewater was conducive to further biological treatment. Owing to this, calcium oxide (CaO) was added at varying dosages (0.6, 0.8, 1.0, 1.2, and 1.4 g/L) to the oxidized wastewater. Subsequently, the wastewater was mixed for 5 min at 450 rpm, followed by precipitation for 30 min. Then, the supernatant of the sample was collected to measure the quality of water.

2.4. Analytical methods

The pH value was determined using a PHS-25 pH meter (Shanghai Jingke Rex, China). Total phosphorus (TP), total nitrogen (TN), NH_4^+–N, chemical oxygen demand (COD), and sulfate (SO_4^{2-}) were determined using Hach reagents (Hach Co., USA). A metrohm883 ion chromatograph (Metrohm Co., Switzerland) was employed to quantify Cl^- concentration and verify SO_4^{2-} concentration.

The concentrations of dissolved Fe, Co, Mn, and Cu ions in wastewater were detected by inductively coupled optical plasma emission spectrometer Optima 8000DV (PerkinElmer Co., USA). The total phenols in preserved fruits wastewater were tested by a total phenols test kit using gallic acid as the standard (Solarbio, Beijing, China) [22].

Sulfite (SO_3^{2-}) was determined using a modified spectrophotometric method with DTNB [23,24]. Briefly, 0.5 mL of sample was added to a mixture containing 0.5 mL of EDTA (1 mmol/L), 1.5 mL of DTNB (1 mmol/L), and 2.5 mL of Na_2HPO_4/KH_2PO_4 buffer (pH = 7). After color reaction for 15 min, the mixed solution was measured at 412 nm with a UV-visible spectrophotometer.

The sulfite removal efficiency during the oxidation process was calculated using the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_t}{C_0} \tag{1}$$

where C_0 is the initial sulfite concentration, C_t is the sulfite concentration at t time.

2.5. Statistical analysis

Statistical analysis of data was carried out with 22 version of SPSS software. One-way analysis of variance (ANOVA) was performed to determine statistical significance ($p < 0.05$).

3. Results and discussion

3.1. Screening of metal ion catalysts for sulfite oxidation

The abatement of sulfite catalyzed by different transition metal ions over time in the preserved fruits wastewater is shown in Fig. 1. In the absence of a catalyst, sulfite was only reduced by 14.1% within 180 min, suggesting that the oxidation of sulfite in preserved fruits wastewater

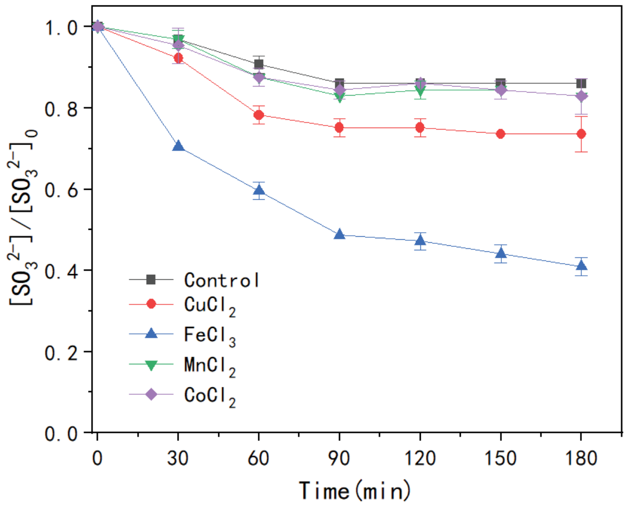

Fig. 1. Representation of the normalized concentration of sulfite ($[SO_3^{2-}]_0$ = 10 ± 2 mmol/L) as a function of time during the catalytic oxidation of sulfite using various metal ions as catalysts.

with air was very inefficient. Furthermore, $MnCl_2$ and $CoCl_2$ showed little catalytic oxidation of sulfite since the sulfite removal efficiencies were only 17.1%. The addition of $CuCl_2$ increased the removal of sulfite to 26.4%, but the fast removal stage occurred within 60 min and the sulfite concentration almost no longer decreased subsequently. In contrast, the concentration of sulfite continuously decreased in the system with $FeCl_3$ and did not reach a steady state within 180 min. In this case, the sulfite removal was 59.0% which was about 3 times higher compared with the system without a catalyst, representing the best activity for the catalytic oxidation of sulfite. Thus, $FeCl_3$ was the most suitable catalyst in this study.

The catalytic oxidation of sulfite by transition metal ions may be affected by pH. Co(II) and Cu(II) showed more obvious catalytic activity than other metals (Mn(II), Fe(II), and Fe(III)) at pH 8 [25]. However, the ability to induce sulfite autoxidation to produce free radicals was Fe(III) > Co(II) > Cu(II) > Mn(II) when pH was 7 [26]. Moreover, Fe(III) was reported to exhibit better activity of sulfite catalytic oxidation under acidic conditions [17]. In this work, the preserved fruits wastewater was acidic (Table 1), which was probably the reason why Fe(III) worked better. Our work showed that it is feasible to catalyze sulfite oxidation in preserved fruits wastewater by transition metal Fe(III) ion. Therefore, $FeCl_3$ was used as the catalyst for the subsequent experiments.

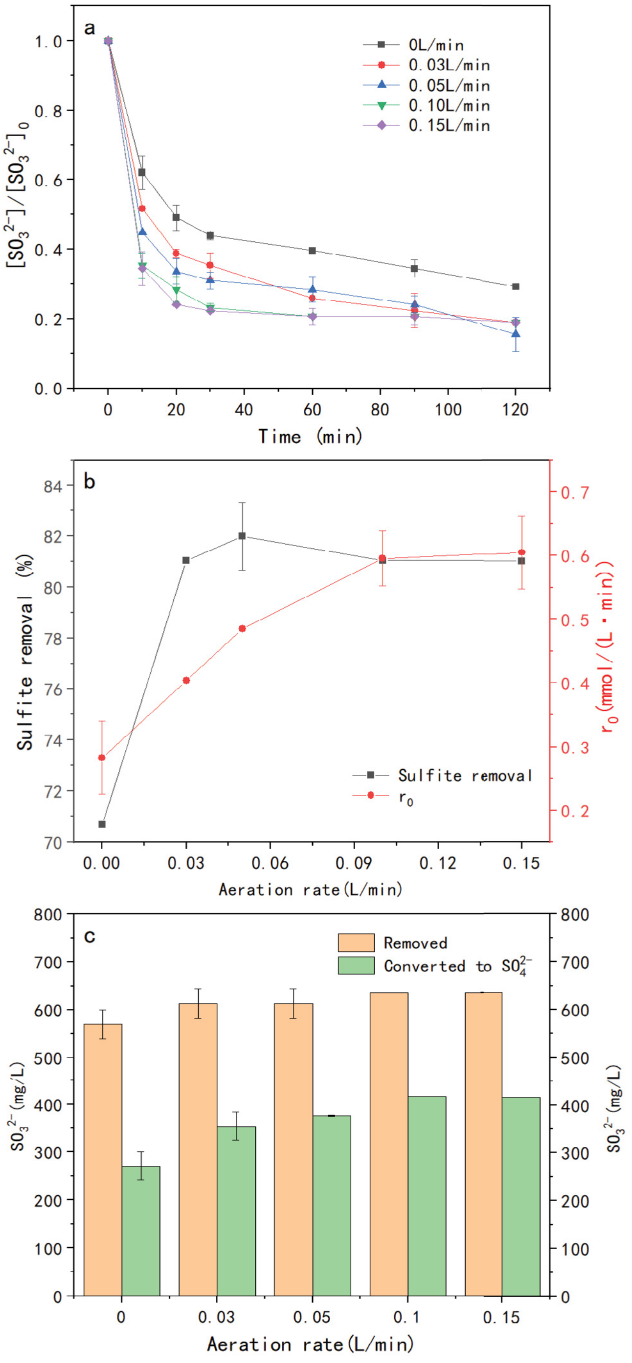

Fig. 2. Effect of aeration on sulfite catalytic oxidation. (a) Representation of the normalized concentration of sulfite ($[SO_3^{2-}]_0$ = 10 ± 2 mmol/L) as a function of time during the catalytic oxidation of sulfite at different air flow rates, (b) initial reaction rate (r_0) and sulfite removal at different air flow rates, and (c) comparison of the amounts of sulfite which were removed and converted to sulfate respectively at different air flow rates (operating conditions: 25°C, stirring speed 300 rpm, $FeCl_3$ dosage 5 mmol/L).

3.2. Factors influencing sulfite catalytic oxidation by Fe(III) ion

3.2.1. Effect of aeration rate on sulfite catalytic oxidation

Given that aeration can increase the mass transfer and dissolved oxygen, the effect of aeration on the sulfite catalytic oxidation process in preserved fruits wastewater was investigated. As can be seen in Fig. 2a, the sulfite in preserved fruits wastewater decreased sharply within the initial 20 min of the reaction and gradually tended to be flat afterward regardless of aeration. However, aeration significantly improved sulfite removal compared with the treatment without aeration. After 20 min of the reaction, the sulfite decreased by 50.9% in the non-aerated group while it decreased by more than 70% in the groups with 0.10 and 0.15 L/min of aeration rate.

In order to quantitatively compare the sulfite abatement under different aeration conditions, the initial oxidation rate (r_0) and the removal efficiency of sulfite were calculated (Fig. 2b). The r_0 was enhanced linearly from 0.28 to 0.59 mmol/(L·min) as the aeration rate rose from 0 to 0.1 L/min. When the aeration rate increased above 0.1 L/min, the r_0 did not increase evidently, suggesting that 0.1 L/min of aeration rate was sufficient for the oxidation reaction. Meanwhile, the removal of sulfite reached 81.0% in all the groups, except for the group without aeration in which the sulfite removal achieved 70.7%. Similar results had been reported by Barbosa Segundo et al. [27], where the removal rate of sulfite increased from 32.0% to 93.8% with increasing the rate of aeration from 0 to 0.5 L/min. In the heterogeneous transition metal catalyzed sulfite oxidation system, there was also a phenomenon that adequate aeration effectively improved the sulfite oxidation efficiency, indicating the importance of aeration to improve the oxidation efficiency [28].

It should be noted that in this study the removed sulfite was not fully oxidized to sulfate (Fig. 2c). This observation was parallel with a previous study in which only less than 46% of removed sulfite was converted into sulfate when industrial landfill leachate was treated with mixed transition metals (including Cr, Cu, Fe, Ni, and Zi) [27]. These results suggested that there was an intermediate valence state of sulfur in the process of sulfite catalytic oxidation to sulfate. It was reported that sulfite could be converted into dithionate ($S_2O_6^{2-}$) during Fe(III)-catalyzed S(IV) oxidation [29]. Moreover, $S_2O_6^{2-}$ is an inert component in an acidic solution and difficult to undergo redox reactions [30]. Thus, it was inferred that in this case approximately 45%–57% of the sulfite removed was converted to $S_2O_6^{2-}$ in the process of catalytic oxidation. Although the aeration rate had little effect on the amount of sulfite removed ($p > 0.05$), it significantly affected the amount of sulfite oxidized to sulfate ($p < 0.05$) (Fig. 2c). It remains desirable to convert sulfite to sulfate as much as possible to better satisfy the demand of subsequent chemical precipitation. Therefore, 0.1 L/min aeration rate was considered to be optimal for Fe(III)-catalyzed sulfite oxidation in the preserved fruits wastewater.

3.2.2. Effect of initial wastewater pH on sulfite catalytic oxidation

Fig. 3 represents the effect of initial pH (pH_0) on sulfite catalytic oxidation. When pH_0 was in the range of 4–6, sulfite rapidly decreased within 20 min and then slowly decreased to reach a plateau (Fig. 3a), and the sulfite removal rate (77.0%–81.5%) was not significantly different ($p > 0.05$) (Fig. 3b). While pH_0 was 8, the decline of sulfite became very slow, with the lowest sulfite removal rate (50.0%) in all the treated groups. Although the removal of sulfite (77.0%) at $pH_0 = 7$ was not significantly different ($p > 0.05$) from those under acidic conditions, the r_0 dramatically decreased to 0.24 mmol/(L·min) (Fig. 3b), which might be relative to the pH changes during the reaction (Fig. 3c). During the reaction process, the trend of sulfite removal was consistent with the pH decrease during the reaction. When the initial pH was acidic (pH 4–6), the pH of the wastewater dropped rapidly to the value between 2–3 within 20 min, corresponding to the rapid decrease of sulfite. When the initial pH was neutral ($pH_0 = 7$), the pH decreased stepwise with time, corresponding to a slow decline of sulfite until pH

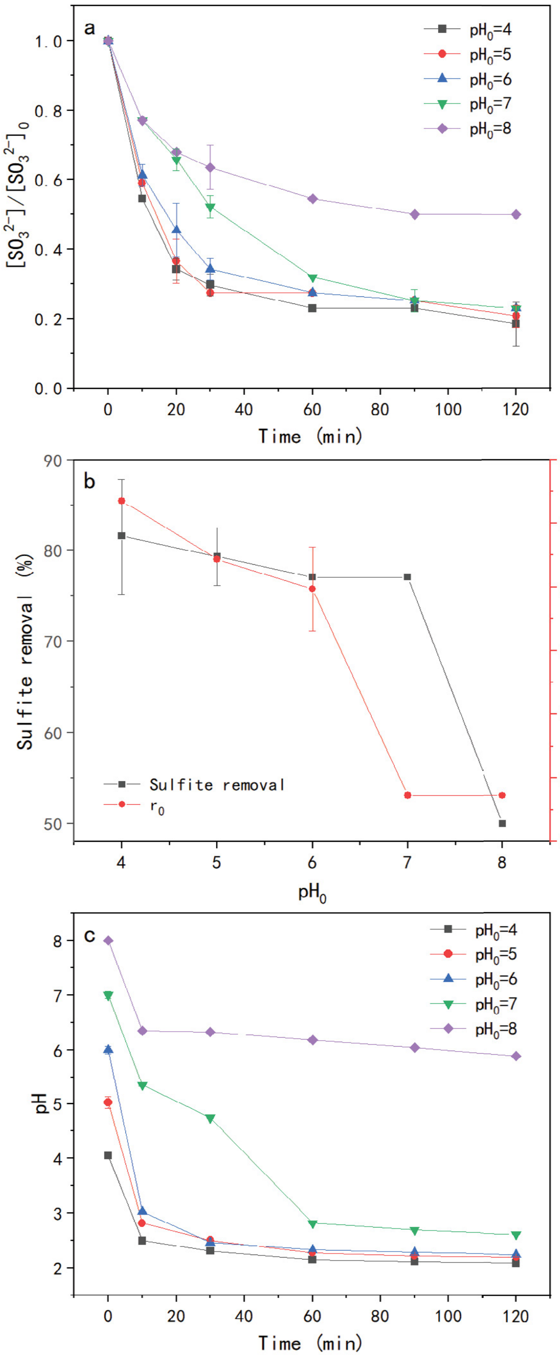

Fig. 3. Effect of pH_0 on sulfite catalytic oxidation. (a) Representation of the normalized concentration of sulfite ($[SO_3^{2-}]_0 = 10 \pm 2$ mmol/L) as a function of time during the catalytic oxidation of sulfite at different pH_0, (b) initial reaction rate (r_0) and sulfite removal at different pH_0, and (c) pH changes during sulfite catalytic oxidation at different pH_0 (operating conditions: 25°C, stirring speed 300 rpm, $FeCl_3$ dosage 5 mmol/L, aeration rate 0.10 L/min).

reached 2–3 in 60 min. However, when the initial pH was alkaline (pH_0 = 8), the pH of the wastewater decreased to 6 and almost no longer dropped, resulting in the stagnation of sulfite removal as well. Our results indicated that the reaction of Fe(III) with sulfite seemed more favorable at lower pH values, which agreed with previous studies [31,32]. This might be due to the precipitation of Fe(III) ions into ferric hydroxide when pH was above 5, and more precipitation would be produced with the increase of pH, which limited the concentration of Fe(III) ions in the reaction [33]. The drop in pH during catalytic oxidation reaction may have two major reasons. Firstly, due to the introduction of $FeCl_3$ which is a salt of a strong acid and weak base, hydrogen ions were produced after hydrolysis. Secondly, the oxidation of bisulfite released hydrogen ions. However, catalytic oxidation was unable to continue owing to the precipitation of Fe(III) ions under neutral or alkaline conditions, so hydrogen ions were not released anymore and the pH value stopped dropping.

Overall, the pH of the wastewater had a great influence on sulfite catalytic oxidation, and the Fe(III)-catalyzed sulfite oxidation was suitable to be carried out under acidic conditions. Considering the acidic characteristics of preserved fruits wastewater, thus, it is not necessary to adjust the initial pH in the further experiment.

3.2.3. Effect of Fe(III) dosage on sulfite catalytic oxidation

Fig. 4 shows the effect of Fe(III) ion dosage on sulfite catalytic oxidation. It was noticed that the removal efficiency of sulfite was significantly enhanced when the Fe(III) dosage was raised from 1 to 3 mmol/L (Fig. 4a). On the other hand, the r_0 raised from 0.08 to 0.39 mmol/(L·min) with increasing the Fe(III) dosage from 1 to 3 mmol/L, while it enhanced slowly as the Fe(III) dosage continued to rise to 9 mmol/L (Fig. 4b). Similarly, the removal of sulfite raised from 23.9% to 77.8% with increasing the Fe(III) dosage from 1 to 3 mmol/L, while kept stable as the Fe(III) dosage further increased (Fig. 4b). Contrary to our results, some research revealed that excellent sulfite catalytic oxidation could be achieved with only a relatively little amount of Fe(III). For instance, Zhou et al. [34] found that 1.5 mmol/L sodium sulfite was almost completely removed within 2 h using only 0.3 mmol/L of Fe(III). Yu et al. [35] suggested that 0.1 mmol/L of Fe(III) quickly consumed 1 mmol/L sodium sulfite within 1 h. This might be attributed to the complexes of certain reducing organics present in the preserved fruits wastewater with Fe(II) which was generated during the oxidation reaction. These reducing organics simultaneously acted as redox buffers and complexing agents, which prevented the Fe(II) from being oxidized back to the Fe(III), rendering the catalytic oxidation reaction unable to proceed [36]. It was considered that the catalytic oxidation efficiency was enhanced when the Fe(III) dosage exceeded the amounts of Fe(III) required for the complexation and redox buffering of these organics.

Although the removals of sulfite had no significant differences ($p > 0.05$) when Fe(III) dosage was in the range of 3–9 mmol/L, the production of sulfate increased significantly by 18.2% when Fe(III) dosage was raised from 3 to 5 mmol/L, and the sulfate no longer rose significantly when Fe(III) dosage increased further (Fig. 4c). Since more sulfate generation can facilitate subsequent chemical precipitation treatment, the optimum Fe(III) dosage was set as 5 mmol/L for Fe(III)-catalyzed sulfite oxidation in the preserved fruits wastewater.

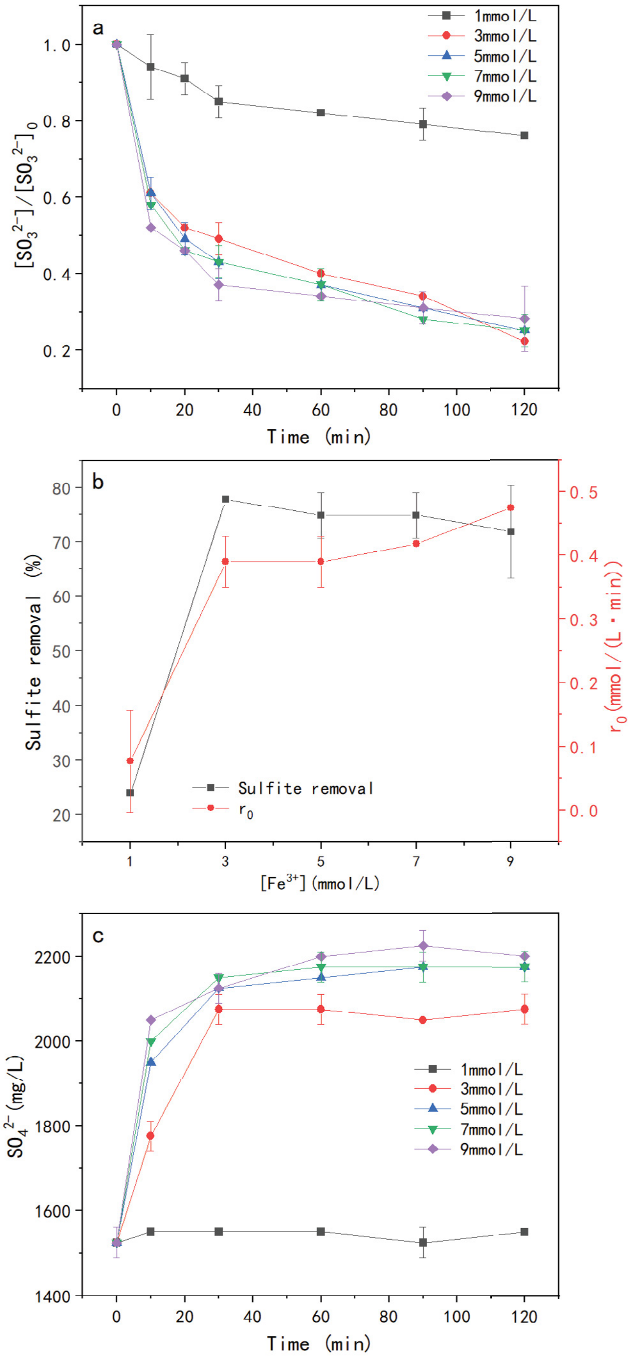

Fig. 4. Effect of Fe(III) ion dosage on sulfite catalytic oxidation. (a) Representation of the normalized concentration of sulfite ([SO_3^{2-}]$_0$ = 10 ± 2 mmol/L) as a function of time during the catalytic oxidation of sulfite at different Fe(III) dosage, (b) initial reaction rate (r_0) and sulfite removal at different Fe(III) ion dosage and (c) SO_4^{2-} concentration as a function of time at different Fe(III) ion dosage (operating conditions: 25°C, stirring speed 300 rpm, aeration rate 0.10 L/min).

3.2.4. Effect of organic matters on sulfite catalytic oxidation

From Fig. 5a, it can be seen that sulfites dramatically decreased in all treatments during the first 30 min and thereafter remained stable, although the organic matters in the wastewater from preserved fruits had a very obvious adverse effect on sulfite removal. The sulfite was completely removed when no organic matters (0%) present in the wastewater, but the sulfite removal linearly decreased down to 67.5% with the organic concentration increasing up to 100% (Fig. 5b). Correspondingly, the r_0 dropped from 0.91 to 0.45 mmol/(L·min) when the organic concentration in the wastewater increased from 0% to 100% (Fig. 5b). It was clear that both sulfite removal and r_0 were negatively correlated with the organic loading, indicating that organic matters in preserved fruits wastewater inhibited the activity of sulfite oxidation.

Previous reports have demonstrated that some organic compounds, such as carbamazepine, had no significant effect on sulfite oxidation, while others, such as gallic acid, catechin, and sobrerol, had inhibitory effects on the oxidation of sulfite, indicating that the sulfite oxidation was affected by the types of organic compounds [32,37–39]. In this study, the adverse effect of organic matters on Fe(III)-catalyzed sulfite oxidation may have two reasons: the complexation with Fe(II) ions and the capture of free radicals. The formation of Fe(III)-sulfite complex is an essential step to initiate the sulfite catalytic oxidation reaction and the cycles between Fe(III) and Fe(II) in the sulfite oxidation process [40]. Some natural organics such as citrate and catechol can form stable complexes with Fe(II), competing with Fe(III)-sulfite complex and thus inhibiting sulfite oxidation reaction [36]. Coincidentally, the preserved fruits wastewater inevitably contains citrate as sodium citrate is commonly used as a food additive in the process of preserving fruits. This reason was corresponding to the speculation in section 3.2.3. On the other hand, our results indicated that the preserved fruits wastewater also contained a large number of phenols (Table 1), which were reported as scavengers for free radicals such as hydroxide radicals and sulfate radicals, leading to the interruption of the chain reaction and the inhibition of the sulfite oxidation [32,39]. It can be concluded that there were some organic substances in the preserved fruits wastewater that hindered the oxidation of sulfite. Therefore, it was suggested that when the concentration of these organic substances is too high, some measures such as dilution can be used to alleviate the adverse effect on sulfite oxidation.

3.2.5. Effect of initial sulfite concentration on sulfite catalytic oxidation

Since variations in preserved fruits processing processes, season and fruit varieties can cause fluctuations in sulfite concentration in preserved fruits wastewater, it is necessary to determine the effect of different initial sulfite concentrations on sulfite oxidation catalyzed by Fe(III).

As can be seen in Fig. 6a, the sulfite in different treatment groups all showed a rapid decrease within 10 min, followed by a slow decrease, but the higher the initial sulfite concentration, the longer it took to decline to a stable concentration. Specifically, r_0 increased linearly from 0.36 to 3.33 mmol/(L·min) with the initial sulfite concentration increasing from 10 to 50 mmol/L (Fig. 6b), suggesting that sulfite concentration strongly affected the sulfite oxidation rate.

In this study, the reaction rate equation can be described as:

$$r = kC_{\text{sulfite}}^{\alpha} \tag{2}$$

Taking the logarithm on both sides, it follows:

$$\ln r = \ln k + \alpha \ln C_{\text{sulfite}} \tag{3}$$

where r is the sulfite oxidation rate (mmol/(L·min)), k is the reaction rate constant (min^{-1}), and α is the reaction order of sulfite.

Through linear fitting between ln r and $\ln_{C\text{sulfite}}$ (Fig. S1), it was obtained that the reaction order of sulfite was 1.4, and the reaction rate constant k was 0.015 min^{-1}.

Dong et al. [32] observed that the final residual sulfite concentration was independent of the initial sulfite

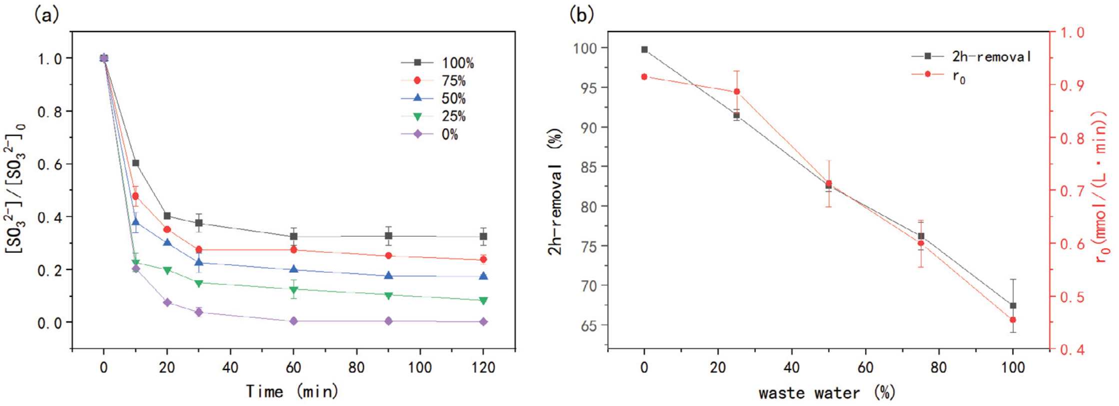

Fig. 5. Effect of organic concentration on sulfite catalytic oxidation. (a) Representation of the normalized concentration of sulfite ($[SO_3^{2-}]_0$ = 10 ± 2 mmol/L) as a function of time during the catalytic oxidation of sulfite with different organic concentrations, (b) initial reaction rate (r_0) and sulfite removal with different organic concentration (operating conditions: 25°C, stirring speed 300 rpm, $FeCl_3$ dosage 5 mmol/L, aeration rate 0.10 L/min).

concentrations (0.1–1.5 mmol/L) in Fe(III)–S(IV) Fenton-like system. Similarly, our results showed that the residual sulfite was in the range of 190 to 270 mg/L in all the treatment groups with marginal differences, which suggested that this catalytic system had very broad applicability to the initial sulfite concentration in preserved fruits wastewater.

3.3. Mechanism of sulfite catalytic oxidation by Fe(III) in preserved fruits wastewater

To date, Fe(III)-catalyzed sulfite oxidation has been recognized as a radical mechanism where the redox cycling of Fe(III) was fundamental (Fig. S2) [16,32,38]. In this process, the initiation step is the formation of a Fe(III)–S(IV) complex, which is decomposed spontaneously to produce Fe^{2+} and $SO_3^{\bullet -}$ (Fig. S3) [12,41]. The generated $SO_3^{\bullet -}$ is then reacted with dissolved O_2 to form $SO_5^{\bullet -}$ (Eq. 6), which in turn leads to the formation of other reactive oxysulphur intermediates including $SO_4^{\bullet -}$, $SO_3^{\bullet -}$ and HSO_5^- [42,43]. The reduced Fe(II) is subsequently oxidized to Fe(III) by reactive oxysulphur intermediates ($SO_5^{\bullet -}$ and HSO_5^-) [44,45].

In the radical mechanism, reactive oxidative species (such as $SO_4^{\bullet -}$ and $OH^{\bullet}$) were supposed to contribute to the sulfite oxidation in Fe(III)-catalyzed system. Methanol can quench $OH^{\bullet}$ and $SO_4^{\bullet -}$ because of its high reactivity to these two radicals ($7.8 \times 10^8 - 1.0 \times 10^9$ m^{-1}·s^{-1} for $OH^{\bullet}$ and $2.0 \times 10^6 - 2.5 \times 10^7$ m^{-1}·s^{-1} for $SO_4^{\bullet -}$) [42,46]. The second-order rate constant of tert-butanol with $OH^{\bullet}$ ($3.8 \times 10^8 - 7.6 \times 10^8$ m^{-1}·s^{-1}) is about 1000 times that of $SO_4^{\bullet -}$ ($4.0 \times 10^5 - 9.1 \times 10^5$ m^{-1}·s^{-1}) [42,46]. However, the reaction of alcohols with $SO_5^{\bullet -}$ is relatively inert since its rate is less than 1×10^3 m^{-1}·s^{-1} [42]. Therefore, the use of methanol and tert-butanol can distinguish the contribution of free radicals ($OH^{\bullet}$, $SO_4^{\bullet -}$ and $SO_5^{\bullet -}$) to sulfite oxidation. Interestingly when methanol and tert-butanol were added, respectively in the preserved fruits wastewater, no obvious inhibition occurred in the sulfite oxidation process (Fig. 7a and b). Hence, it was considered that the sulfite oxidation in preserved fruits wastewater was not mainly attributed to $OH^{\bullet}$ and $SO_4^{\bullet -}$, while $SO_5^{\bullet -}$ might be an important free radical involved in sulfite oxidation.

In our catalytic oxidation experiment (0.10 L/min aeration, 5 mmol/L Fe(III)), it was observed that the color of

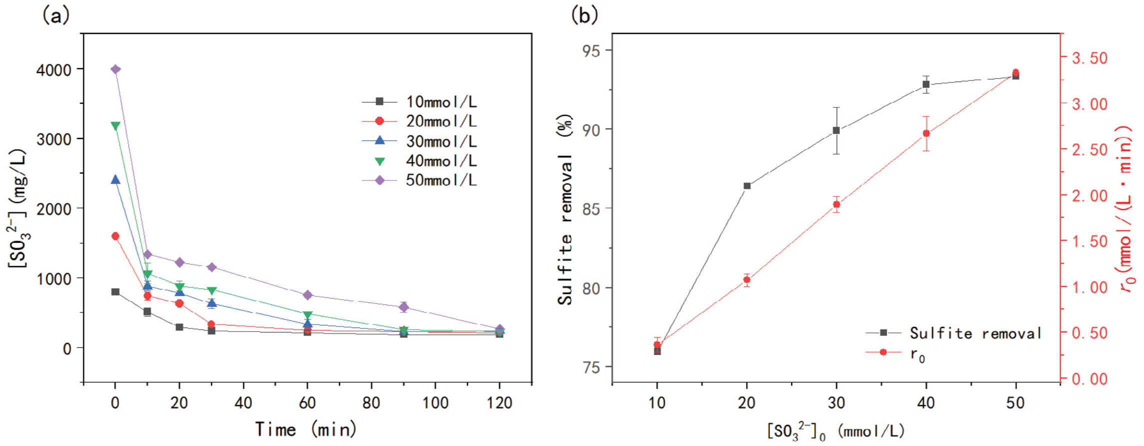

Fig. 6. Effect of initial sulfite concentration ($[SO_3^{2-}]_0$) on sulfite catalytic oxidation. (a) The abatement of sulfite concentration over time with different $[SO_3^{2-}]_0$, (b) initial reaction rate (r_0) and sulfite removal with different $[SO_3^{2-}]_0$ (operating conditions: 25°C, stirring speed 300 rpm, $FeCl_3$ dosage 5 mmol/L, aeration rate 0.10 L/min).

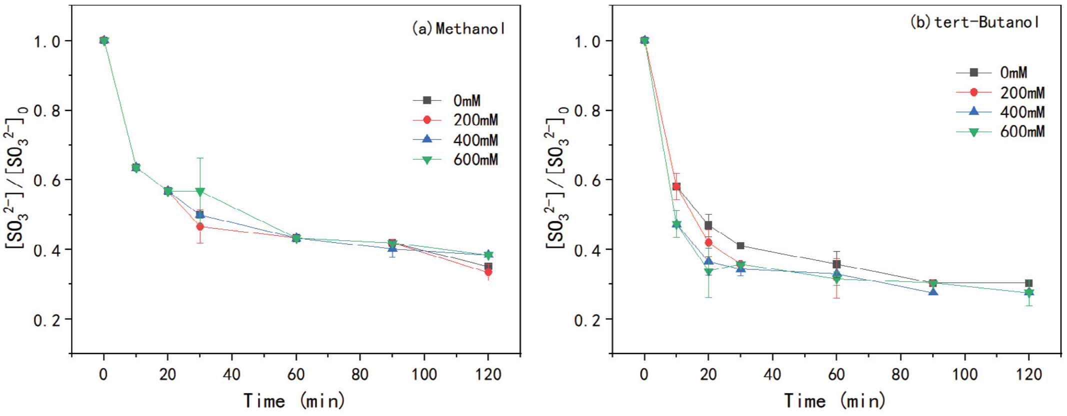

Fig. 7. Representation of the normalized concentration of sulfite ($[SO_3^{2-}]_0$ = 10 ± 2 mmol/L) as a function of time with different concentrations of free radical scavengers methanol (a) and tert-butanol (b).

the wastewater changed over time (Fig. S4), which was inferred to be caused by Fe(III)-sulfite complex [42,47]. Initially, Fe(III) ion combined with water molecules to form hydrated molecules, which then underwent a series of hydrolysis reactions and mainly existed in the form of $[\mathrm{Fe(OH)(H_2O)_5}]^{2+}$ [48]. Then stable octahedral metal hydrates cooperated with $\mathrm{HSO_3^-}$ to form a red O-bonded sulfo complex ($[\mathrm{Fe(OH)(H_2O)_5SO_3}]^{+}$) (Eq. 4), which explained the color change at the beginning stage in this study (Fig. S4b) [47,49]. Inside the complex, an electron migration from S(IV) to Fe(III) occurred, immediately followed by the bond scission to generate the $\mathrm{SO_3^{\bullet -}}$ radical and $[\mathrm{Fe(II)(H_2O)_6}]^{2+}$ (Fig. S3, Eq. 5) [12,29,41], which would be involved in the radical mechanism of Fe(III)-catalyzed sulfite oxidation aforesaid. Therefore, Fe(III)-catalyzed sulfite oxidation reaction in this study was supposed as a combination of complexation and free radical reaction.

According to the analysis aforesaid, the Fe(III)-catalyzed sulfite oxidation reaction in preserved fruits wastewater can be summarized into three stages: chain initiation, chain growth, and chain termination.

The formation of Fe(III)-sulfite complexes was the chain initiation stage including Eqs. (4) and (5) (Table 2), which were the rate-controlling steps in the overall sulfite catalytic oxidation reaction [41,49].

During the chain growth stages (Table 2), $\mathrm{SO_3^{\bullet -}}$ reacted with dissolved $\mathrm{O_2}$ to produce $\mathrm{SO_5^{\bullet -}}$ (Eq. 6) [43]. The obtained $\mathrm{SO_5^{\bullet -}}$ reacted with $\mathrm{HSO_3^-}$ to produce $\mathrm{SO_3^{\bullet -}}$ which were cycled to be involved in the reaction in Eq. 7 [42]. $\mathrm{SO_5^{\bullet -}}$ and $\mathrm{HSO_5^-}$ generated also oxidized Fe(II) back to Fe(III) (Eqs. (8) and (11)) [44,45], and Fe(III) could react with $\mathrm{HSO_3^-}$ again. Thus the cycle between Fe(III) and Fe(II) constantly occurred, ensuring that Eqs. (4) and (5) reacted continuously until $\mathrm{HSO_3^-}$ was depleted.

Subsequently, the production of $\mathrm{SO_4^{2-}}$ and $\mathrm{S_2O_6^{2-}}$ through Eqs. (10) and (11) represented the chain termination stage (Table 3) [29,50]. $\mathrm{SO_5^{\bullet -}}$ was able to react with $\mathrm{HSO_3^-}$ to generate $\mathrm{SO_4^{2-}}$ and $\mathrm{SO_4^{\bullet -}}$ (Eq. 12) [51]. However, the generated $\mathrm{SO_4^{\bullet -}}$ may be quickly quenched by organic matters present in the preserved fruits wastewater. As the reaction progressed, the $\mathrm{SO_4^{2-}}$ concentration was continually improved, and more and more Fe(III) ions formed complexes with $\mathrm{SO_4^{2-}}$ ions (Eq. 13), which decreased the accessibility of substrate to the catalyst so that the reaction rate accordingly decreased [52]. Since $[\mathrm{Fe(III)(OH)(H_2O)_5SO_3}]^{+}$ was gradually consumed during the sulfite catalytic oxidation, the color of the wastewater faded with time (Fig. S4b–d).

3.4. *Evaluation of the pretreatment of preserved fruits wastewater*

3.4.1. *Fe(III)-catalyzed oxidation of preserved fruits wastewater under optimum conditions*

The evaluation of Fe(III)-catalyzed oxidation of preserved fruits wastewater was conducted under optimum conditions (0.10 L/min aeration, 5 mmol/L Fe(III), unadjusted $\mathrm{pH_0}$).

Table 2
Proposed mechanism of Fe(III)-catalyzed sulfite oxidation in preserved fruits wastewater

No.	Reaction	Equilibrium constants (*K*) or rate constant (*k*)	References
	Chain initiation		
(Eq. 4)	$\left[\mathrm{Fe(III)(OH)(H_2O)_5}\right]^{2+} + \mathrm{HSO_3^-} \leftrightharpoons \left[\mathrm{Fe(III)(H_2O)_5SO_3}\right]^{+} + \mathrm{H_2O}$	$K = 600\ \mathrm{M^{-1}}$	[43]
(Eq. 5)	$\left[\mathrm{Fe(III)(H_2O)_5SO_3}\right]^{+} + \mathrm{H_2O} \rightarrow \left[\mathrm{Fe(II)(H_2O)_6}\right]^{2+} + \mathrm{SO_3^{\bullet -}}$	$k = 0.2\ \mathrm{s^{-1}}$	[12,25]
	Chain growth		
(Eq. 6)	$\mathrm{SO_3^{\bullet -}} + \mathrm{O_2} \rightarrow \mathrm{SO_5^{\bullet -}}$	$k = 2.5 \times 10^{9}\ \mathrm{M}^{-1\cdot s-}1$	[39]
(Eq. 7)	$\mathrm{SO_5^{\bullet -}} + \mathrm{HSO_3^-} \rightarrow \mathrm{HSO_5^-} + \mathrm{SO_3^{\bullet -}}$	$k = 3 \times 10^{5}\ \mathrm{M}^{-1\cdot s-}1$	[38]
(Eq. 8)	$\left[\mathrm{Fe(II)(H_2O)_6}\right]^{2+} + \mathrm{HSO_5^-} \rightarrow \mathrm{SO_4^{\bullet -}} + \mathrm{H_2O} + \left[\mathrm{Fe(III)(OH)(H_2O)_5}\right]^{2+}$	$k = 3 \times 10^{5}\ \mathrm{M^{-1}\cdot s^{-1}}$	[30,40]
(Eq. 9)	$\left[\mathrm{Fe(II)(H_2O)_6}\right]^{2+} + \mathrm{SO_5^{\bullet -}} \rightarrow \mathrm{HSO_5^-} + \left[\mathrm{Fe(III)(OH)(H_2O)_5}\right]^{2+}$	$k = 3.2 \times 10^{6}\ \mathrm{M^{-1}\cdot s^{-1}}$	[40,41]
	Chain termination		
(Eq. 10)	$\mathrm{HSO_5^-} + \mathrm{HSO_3^-} \rightarrow 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+}$	$k \approx 10^{7}\ \mathrm{M^{-2}\cdot s^{-1}}$	[46]
(Eq. 11)	$\mathrm{SO_3^{\bullet -}} + \mathrm{SO_3^{\bullet -}} \rightarrow \mathrm{S_2O_6^{2-}}$	$k = 1.8 \times 10^{8}\ \mathrm{M}^{-1\cdot s}–1$	[25]
(Eq. 12)	$\mathrm{SO_5^{\bullet -}} + \mathrm{HSO_3^-} \rightarrow \mathrm{SO_4^{2-}} + \mathrm{SO_4^{\bullet -}} + \mathrm{H^+}$	$k = 3.0 \times 10^{8}\ \mathrm{M^{-1}\cdot s^{-1}}$	[47]
(Eq. 13)	$\left[\mathrm{Fe(III)(OH)(H_2O)_5}\right]^{2+} + \mathrm{SO_4^{2-}} \leftrightharpoons \left[\mathrm{Fe(III)(OH)(H_2O)_5SO_4}\right]$	$K \approx 2.6 \times 10^{2}\ \mathrm{M^{-1}}$	[48]

Table 3
Cost comparison of preserved fruits wastewater pretreatment processes

Process	Pharmaceutical agents	Unit price (RMB/ton)	Dosage (kg/ton wastewater)	Pharmaceutical costs (RMB/ton wastewater)	Total cost of pharmaceutical agents (RMB/ton wastewater)
Fe(III)-catalyzed oxidation coupled with CaO precipitation	$FeCl_3$	2,000	0.81	1.62	1.99
	CaO	370	1.00	0.37	
Fenton with flocculation–sedimentation	$FeSO_4·7H_2O$	460	2.50	1.15	8.42
	H_2O_2 (27%)	800	6.80	5.44	
	NaOH	2,200	0.83	1.83	

It can be seen from Table 1 that SO_3^{2-} concentration decreased from 1,145.8 to 228.0 mg/L, suggesting that 80.1% of SO_3^{2-} was removed by Fe(III)-catalyzed oxidation. Meanwhile, COD dropped considerably from 8,285 to 6,570 mg/L (removed by 20.7%) (Table 1). Among them, the reduction of COD contributed by sulfite oxidation was not more than 153.0 mg/L, which only accounted for 8.9% of the total COD removal. This indicated that the Fe(III)-catalyzed oxidation achieved sulfite oxidation and partial organic pollutants degradation simultaneously, which was also reflected by the reduction of total phenols (removed by 31.3%) (Table 1).

In the advanced oxidation process, the active species $SO_4^{\bullet-}$, $^{\bullet}OH$, and $SO_4^{\bullet-}$ have been generally considered to play a major role in the degradation of organic pollutants [18–21]. The degradation of refractory organic compounds in the Fe(III)–S(IV) system has been reported elsewhere [32,53]. Active species $SO_4^{\bullet-}$ and $^{\bullet}OH$ were believed to play a substantial role in carbamazepine degradation [32], while $SO_4^{\bullet-}$ and $SO_5^{\bullet-}$ were considered to be the main contributor to the removal of aniline [53]. Moreover, reaction intermediates like $SO_4^{\bullet-}$, $SO_5^{\bullet-}$, as well as Fe(IV) were reported to play important roles in the degradation of iopamidol [54]. Thus, it was speculated that free radicals such as $SO_5^{\bullet-}$ and $SO_3^{\bullet-}$ were also involved in the degradation of organic matter during the sulfite oxidation process in preserved fruits wastewater. Nevertheless, the free radicals generated in this process might tend to preferentially oxidize sulfite, resulting in only a small fraction of organic matter being degraded in preserved fruits wastewater.

3.4.2. Chemical precipitation by calcium oxide

After Fe(III)-catalyzed oxidation, the wastewater pH decreased to 2–3, which was not suitable for direct biological treatment, so it was necessary to implement neutralization and precipitation in order to eliminate iron ions as well as sulfate.

In this process, calcium oxide (CaO) was selected as an alkaline pH regulator and coagulant aid, because it is cheap and can form calcium sulfate precipitate [55]. When the wastewater pH is adjusted to neutral or alkaline, the catalyst Fe(III) ion acts as a coagulant and is converted to $Fe(OH)_3$ flocs. With the aid of CaO, some organic and inorganic pollutants would be settled down [54,56]. Hence, this step can achieve neutralization and precipitation at the same time.

According to the preliminary experiment, the dosage of CaO for neutralization and precipitation was determined as 1 g/L (Fig. S5). After the treatment with CaO, it was observed that sediment was produced and the supernatant was clarified (Fig. S6). Due to chemical precipitation, COD further decreased from 6,570 to 5,615 mg/L, while total Fe decreased from 287.9 to 26.6 mg/L (Table 1). This iron concentration would not be harmful to the biological treatment system [57]. In addition, the sulfite was further oxidized, rendering it undetectable (Table 1). It was reported that the solubility of calcium sulfate was 2.1 g/L, and increased to 3.5 g/L when 6.9 g/L Cl^- is present [58]. In this study, the high concentration of Cl^- in preserved fruits wastewater enhanced the solubility of calcium sulfate, leading to 1,900 mg/L sulfate remaining in the wastewater (Table 1).

3.4.3. Feasibility analysis of the pretreatment of Fe(III)-catalyzed oxidation and calcium oxide precipitation

The integration of Fe(III)-catalyzed oxidation with CaO precipitation is a simple and cost-effective pretreatment process for preserved fruits wastewater. In the whole pretreatment process, the sulfite was completely removed, ensuring pH stability in subsequent biological treatments. COD of preserved fruits wastewater was reduced by 32.2%, and 92.4% of Fe(III) added as a catalyst was removed by precipitation (Table 1). More importantly, the BOD_5/COD increased to 0.96 (Table 1), indicating that the pre-treated preserved fruits wastewater had very excellent biodegradability, which was suitable for direct aerobic biological treatments. From the aspect of economic applicability, the chemicals cost of the Fenton oxidation followed by the flocculation–sedimentation process was 8.42 RMB/(ton wastewater), while the chemicals cost of Fe(III)-catalyzed oxidation coupled with CaO precipitation was 1.99 RMB/(ton wastewater), which was 76% lower than the former method in terms of chemicals cost (Table 3). Therefore, this novel pretreatment exhibits an extremely competitive advantage over the traditional pretreatment process of preserved fruits wastewater (Fenton oxidation with flocculation–sedimentation).

4. Conclusions

In this work, Fe(III) ion was screened out as the most effective catalyst for sulfite oxidation in preserved fruits wastewater. The optimal operating condition was 0.10 L/min of aeration and 5 mmol/L of Fe(III) dosage with unadjusted pH_0, under which 80.1% of sulfite and 20.7% of COD were removed. The sulfite could not be completely removed in Fe(III)-catalyzed oxidation reaction, which was attributed to the presence of organic matters in preserved fruits wastewater. Despite this, when the initial concentration of sulfite ranged between 10–50 mmol/L, this catalytic oxidation technology displayed good sulfite oxidation performance (residual sulfite kept below 270 mg/L). Fe(III)-catalyzed sulfite oxidation reaction in the preserved fruits wastewater was deduced as the combination of complexation and free radical reaction. In addition, free radicals may also contribute to the degradation of organic matters, leading to partial removal of COD during sulfite oxidation. After the pretreatment of Fe(III)-catalyzed oxidation followed by CaO precipitation, the sulfite and COD were removed by 100% and 32.2%, respectively, and total iron ions were reduced to 26.6 mg/L, while the biodegradability was improved by 21.5%, which were favorable for subsequent aerobic biological treatment. As a consequence, Fe(III)-catalyzed oxidation integrated with CaO precipitation can be used as a promising pretreatment process before the biotreatment of preserved fruits wastewater to remove sulfite as well as reduce the organic load.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

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Supporting information

Table S1
Purity of chemical reagents

Reagents	Molecular formula	Purity
DTNB(5,5′-Dithiobis-(2-nitrobenzoic acid))	$C_{14}H_8N_2O_8S_2$	98.0%
Ethanol	C_2H_5OH	99.7%
Sodium sulfite	Na_2SO_3	98.0%
Sodium sulfate	Na_2SO_4	99.0%
Disodium hydrogen phosphate	Na_2HPO_4	99.0%
Potassium dihydrogen phosphate	KH_2PO_4	99.5%
Calcium oxide	CaO	98.0%

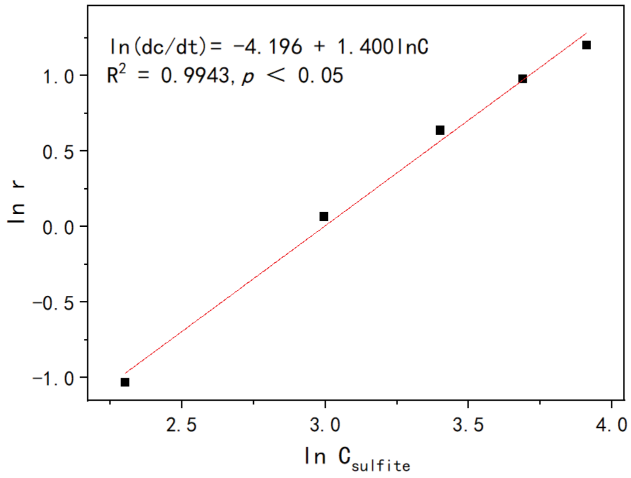

Fig. S1. Linear fitting was performed for ln*r* and $\ln_{C_{sulfite}}$.

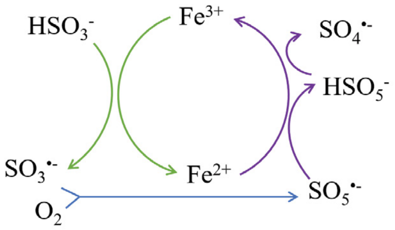

Fig. S2. Radical mechanism of Fe(III)-catalyzed sulfite oxidation.

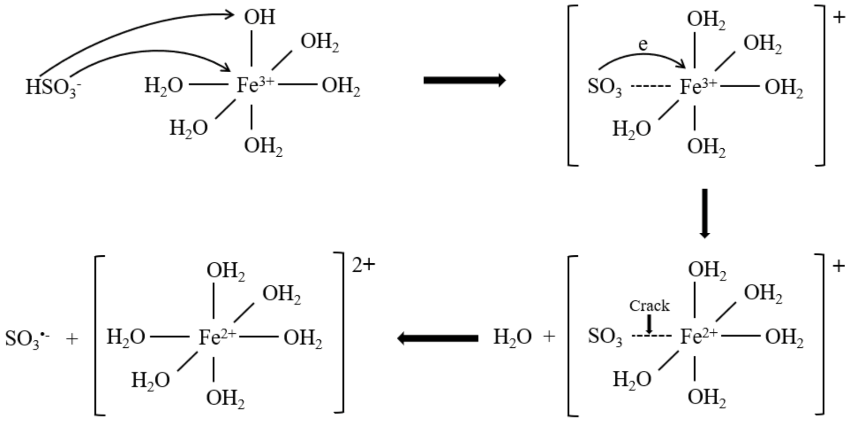

Fig. S3. Bimolecular nucleophilic substitution of HSO_3^- and Fe^{3+}, modified from Lai et al. [37].

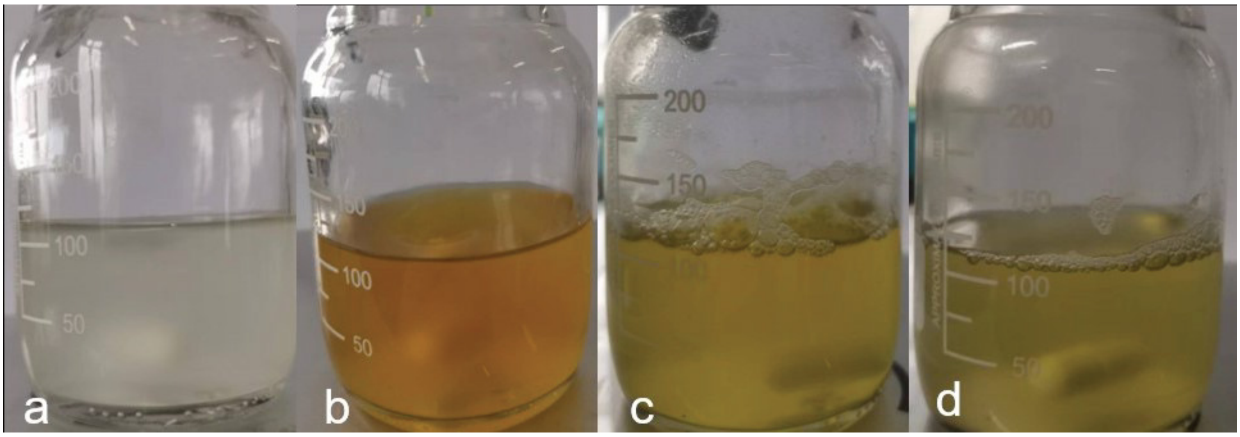

Fig. S4. Color changes during oxidation in raw wastewater (a) and after adding 5 mmol/L Fe(III) ion, (b) 0 min, (c) 30 min and (d) 120 min.

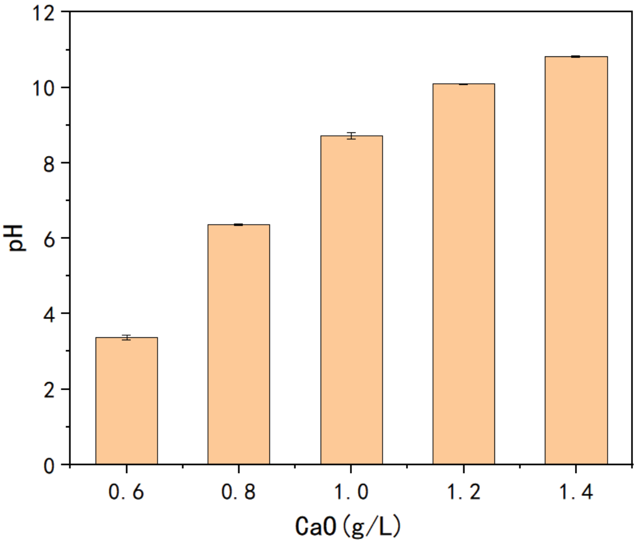

Fig. S5. Effect of calcium oxide (CaO) dosage on pH value.

Fig. S6. Observation of sediment after CaO treatment.