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New insight into the reactivity of Mn(III) in bisulfite/permanganate for organic compounds oxidation: The catalytic role of bisulfite and oxygen

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ABSTRACT

A recently discovered bisulfite(HSO_3^-)/permanganate(MnO_4^-) system was reported to produce highly reactive free Mn(III) that can oxidize organic compounds in milliseconds. However, this characteristic reactivity was not found in all other known reaction systems that can also produce free Mn(III). Why can Mn(III) in $NaHSO_3/KMnO_4$ be so active? Here, we found $NaHSO_3$ and O_2 acted as catalysts for the reaction between Mn(III) and organic compounds. Without O_2, 0% of organic compounds were oxidized in $NaHSO_3/KMnO_4$, indicating the absence of O_2 inactivated Mn(III) reactivity. When the reaction between $NaHSO_3$ and $KMnO_4$ was monitored in air, Mn(III) catalyzed rapid oxidation of $NaHSO_3$ by O_2. Then, the Mn(III) that could oxidize organic compounds was found to be the ones involved in the catalytic reaction between $NaHSO_3$ and O_2, thus the link between O_2 and Mn(III) reactivity was established. Finally, $NaHSO_3/O_2$ can be viewed as catalysts for the reaction between Mn(III) and organic compounds because 1) when Mn(III) was involved in oxidizing organic compounds, it stopped being the catalyst for the reaction between $NaHSO_3$ and O_2 so that they were consumed to a much smaller extent; and 2) without $NaHSO_3$ and O_2, Mn(III) lost its oxidation ability. To the best of our knowledge, this is the first report on “catalytic role exchange” where Mn(III) is the catalyst for $NaHSO_3/O_2$ reaction while $NaHSO_3/O_2$ are the catalysts for Mn(III)/organic compounds reaction. Understanding the critical role of oxygen in $NaHSO_3/KMnO_4$ will enable us to apply this technology more efficiently toward contaminant removal.

1. Introduction

Manganese(III) (Mn(III)) is viewed as a potentially strong oxidant due to its high reduction potential ($E^0 = 1.51V$) (Kostka et al., 1995), but it is very unstable in aqueous solution because of its fast disproportionation to Mn^{2+} and MnO_2 (Anderson and Kochi, 1970; Ladbury and Cullis, 1958). However, this disproportionation reaction can be effectively prevented by some ligands, e.g. pyrophosphate (PP), oxalate, citrate, and siderophores, through forming stable Mn(III)-ligand complexes (Anderson and Kochi, 1970; Chen et al., 2013; Duckworth and Sposito, 2005; Gao et al., 2018; Jiang et al., 2009, 2010; Klewicki and Morgan, 1998; Taube, 1947). These Mn(III)-ligand complexes are often directly used as oxidants for oxidation purposes, such as oxidative degradation of contaminants in wastewater (Gao et al., 2018; Jiang et al., 2009, 2010; Nowack and Stone, 2002). The preparation of Mn(III)-ligands is routinely through adding ligands prior to starting the reaction that can generate free Mn(III) (Davies, 1969; Jiang et al., 2010; Klewicki and Morgan, 1998). Examples of such reactions can be easily found in literature, including (1) oxidation of Mn^{2+}, such as $S_2O_8^{2-}/Mn^{2+}$, $Cr_2O_7^{2-}/Mn^{2+}$, and MnO_4^-/Mn^{2+} (Davies, 1969; Gupta and Ghosh, 1958; Jiang et al., 2010); and (2) reduction of MnO_4^- or MnO_2, e. g. oxalic acid/MnO_2, Mn^{2+}/MnO_4^- and H_2O_2/MnO_4^- (Chen et al., 2013; Davies, 1969; Jiang et al., 2010; Taube, 1947).

Recently, a newly discovered system HSO_3^-/MnO_4^- was also found to produce free Mn(III) (eq. (1)) (Gao et al., 2017; Hu et al., 2017; Sun et al. 2015, 2016), but it can oxidize organic compounds in milliseconds (eq. (2)). This millisecond reaction has triggered substantial interest in the advanced oxidation community because the system is very simple, practical, and fast. In addition to oxidizing organic compounds, some Mn(III) undergoes disproportionation to form Mn^{2+} and MnO_2 (eq. (3)). Moreover, $NaHSO_3$ can compete with organic compounds for Mn(III) (eq. (4)).

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$$2H^+ + 2HSO_3^- + MnO_4^- \rightarrow Mn(III) + 2H_2O + 2SO_4^{2-} \quad (1)$$

$$Mn(III) + \text{organic compound} \rightarrow \text{products} + Mn^{2+} \quad (2)$$

$$2Mn(III) + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \quad (3)$$

$$HSO_3^- + 2Mn(III) + H_2O \rightarrow 2Mn^{2+} + SO_4^{2-} + 3H^+ \quad (4)$$

These findings are inspiring in that there is no need to complex free Mn(III) with ligands as stable oxidants anymore because free Mn(III) itself can now oxidize organic compounds. However, if free Mn(III) itself is so active, (1) why has this high reactivity not been discovered for many decades, especially when reactions that can readily produce free Mn(III) are widely available, as mentioned above? (2) Why does Mn(III) have to be complexed with ligands rather than directly used as oxidants in previous systems? (3) Is this high reactivity of Mn(III) unique for $NaHSO_3/KMnO_4$? To address these questions, preliminary experiments were conducted to produce free Mn(III) based on two known reactions without adding ligands but in the presence of organic compounds. Table S1 in the supporting information (SI) indicated that, unlike the high reactivity of Mn(III) in $NaHSO_3/KMnO_4$, Mn(III) in oxalic acid/MnO_2 or $KMnO_4/Mn^{2+}$ could not oxidize organic compounds (phenol as a probe) in milliseconds. In fact, Chen et al. were only able to use the Mn(III) in oxalic acid/MnO_2 to catalyze carbadox *reduction* by oxalic acid (Mn(III) was also reported to catalyze atrazine de-alkylation) (Chen et al., 2013; Hu et al., 2017), while Jiang et al. had to complex the Mn(III) in $KMnO_4/Mn^{2+}$ with ligands to oxidize bisphenol A (Jiang et al., 2009, 2010). These results indicate that: (1) the high reactivity of Mn(III) in $NaHSO_3/KMnO_4$ is unique and not found in other systems, which makes it understandable why Mn(III) has been complexed with ligands as a routine way for further applications; and (2) the high reactivity of Mn(III) in $NaHSO_3/KMnO_4$ cannot be seen as a common property for Mn(III), and Mn(III) itself cannot be directly used as an oxidant due to its facile disproportionation. Meanwhile, these results raised a new question: why can Mn(III) in $NaHSO_3/KMnO_4$ be so active? This question is exactly what this study aims to address.

Here, we found the high reactivity of Mn(III) was due to the catalytic effect of $NaHSO_3$ and O_2. The importance of O_2 on the reactivity of Mn(III) was first investigated in an oxygen-free glove box. Then, the time courses of H^+ and dissolved oxygen (DO) during reaction were monitored to understand the reaction rates of $NaHSO_3$ and O_2. Next, MnO_2 formation in the presence of a large amount of $NaHSO_3$ was measured by UV-visible spectrometry (UV-vis) to confirm the catalytic role of Mn(III) in the reaction between $NaHSO_3$ and O_2. With phenol as the probe compound for Mn(III) oxidative reactivity, the relationship between the catalytic role of Mn(III) for $NaHSO_3/O_2$ reaction and the oxidant role of Mn(III) for organic compounds oxidation was also investigated. Finally, a new reaction mechanism was proposed for $NaHSO_3/KMnO_4$ and then verified by interpreting the effects of $NaHSO_3$:$KMnO_4$ ratio, DO concentration, $KMnO_4$ amount and phenol initial concentration. Results of this work will allow more cost-effective engineering systems to be designed to treat various contaminated water using this technology.

2. Materials and methods

2.1. Chemicals and materials

Potassium permanganate ($KMnO_4$, 99.2%, Fisher Chemical), sodium bisulfite ($NaHSO_3$, AR grade, Acros Organics), phenol (99%, Acros Organics), sodium pyrophosphate (99%+, Acros Organics), sodium hydroxide (NaOH, Fisher Scientific), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$) (99%+, Acros Organics), oxalic acid dehydrate (99.5%+, Acros Organics), hydroxylamine hydrochloride (99%+, Acros Organics), sulfuric acid (H_2SO_4, 95.7%+, Fisher Chemical) and caffeine (Sigmal-Aldrich) were purchased at the highest available purity and used as received. Deionized water (DI water, 18.2 MΩ cm) was obtained from a Millipore Milli-Q water purification system.

2.2. Oxidation experiments for organic compounds

The batch reactors were used rather than stop-flow reactors because we did not intend to monitor the reaction kinetics of organic compounds. The reaction kinetics of this system as well as the Mn(III) concentration measurements have been carefully investigated already (Sun et al., 2015). Hence, we focused on the oxidation efficiency of this system, that is, the overall conversion of organic compounds at the reaction time of up to ~10 seconds (because the reaction was reported to complete in milliseconds (Sun et al., 2015), and Fig. S1 shows that 10 seconds were enough for the reaction to finish). The batch reactors were open to air (referred to as "in air" hereafter) unless otherwise specified. For typical $NaHSO_3/KMnO_4$ systems, 20 μM phenol was first mixed with 250 μM $NaHSO_3$ solution using a magnetic stirrer, then 50 μM $KMnO_4$ was added into the above mixture (the total volume of solution was 50 ml). After reaction in 5–10 seconds, 500 μl samples were taken and immediately quenched by 10 μl of 1 M hydroxylamine hydrochloride to be analyzed by an Agilent 1260 High Performance Liquid Chromatography (HPLC) equipped with a diode array detector. Most experiments were conducted with phenol as the probe compound because it is known to be easily oxidizable. To test if the observed oxygen effect is not unique to phenol, caffeine, an organic compound that is known to be hardily oxidizable (Sun et al., 2015), was also examined in some experiments.

For the oxalic acid/MnO_2 system (Chen et al., 2013), 200 μM or 10 μM MnO_2 colloids were prepared by reacting $MnSO_4 \cdot H_2O$ with $KMnO_4$ at the 2.5:1 molar ratio for 2 h in solution. 40 μM phenol was first mixed with 10 mM or 250 μM oxalic acid and then the mixture was added into the above MnO_2 colloids. After all the MnO_2 was completely dissolved, 500 μl samples were taken and immediately quenched by 10 μl of 1 M hydroxylamine hydrochloride for HPLC analysis. For the $KMnO_4/Mn^{2+}$ system (Jiang et al., 2009, 2010), 40 μM phenol was first mixed with 300 μM Mn^{2+}, and 60 μM $KMnO_4$ was then added. After the color of $KMnO_4$ had disappeared, 500 μl samples were also taken and also immediately quenched by hydroxylamine hydrochloride. All oxidation experiments were conducted in duplicates.

For HPLC analysis, 20 μL samples were injected and separated by an Agilent Zorbax RX-C18 column (150 × 4.6 mm, particle size 5 μm) maintained at 40 °C with a flow rate of 1.0 ml/min. The mobile phase was composed of methanol and water (60:40, v/v). The wavelength for phenol and caffeine was set at 270 nm and 273 nm, respectively. The percentage of conversion of the organic compounds was calculated from the following equation:

$$\text{Conversion }(\%) = \frac{C0(\text{organics, initial}) - Ct(\text{organics, left})}{C0(\text{organics, initial})} \times 100\%$$

2.3. Effect of DO on Mn(III) reactivity

To ensure a strict oxygen-free environment, all anoxic experiments were conducted in a COY glove box (2–5% H_2 in N_2) equipped with Pd catalysts to ensure all O_2 to be reduced by H_2 to water.

Such an environment is referred to as "in nitrogen" hereafter. The same procedure as above in air was followed in the glove box. For the investigation of the effects of dissolved oxygen (DO) on phenol oxidation, 40 μM phenol was first mixed with 250 μM $NaHSO_3$. The solution was then bubbled with helium gas at different flow rates to achieve different DO contents. The DO contents were measured by an Accumet XL40 DO detector. After the DO meter reading became stable, 50 μM $KMnO_4$ was added. After seconds, samples were taken to be analyzed by HPLC.

2.4. Analysis of $NaHSO_3$, $[H^+]$ and DO contents

For the reaction of $NaHSO_3$ with either $KMnO_4$ or Mn^{2+} in the absence of phenol, in nitrogen or in air, 10 μM $KMnO_4$ or $MnSO_4$ was mixed with 250 μM $NaHSO_3$. After 1 min of reaction in air, samples were taken to be immediately analyzed by UV-vis. For the reaction in nitrogen, samples were taken and sealed with parafilm before removing from the glovebox, to protect them from oxidation by air, and then immediately analyzed by UV-vis. The details for $NaHSO_3$ detection by UV-vis are in SI Text S1.

In the reactions of $NaHSO_3$ with either $KMnO_4$ or Mn^{2+} (in air or in nitrogen), an OKATON pH 150 probe and/or an Accumet XL40 DO probe was first immersed into 250 μM $NaHSO_3$ solution. In the reactions of $NaHSO_3$ with MnO_2, MnO_2 colloids were first prepared as described in Section 2.2, and the solution pH was adjusted by NaOH addition to 4.77 to ensure the same initial pH as in 250 μM $NaHSO_3$. When the reaction proceeded in the presence of phenol, different amounts of phenol were first mixed with 250 μM $NaHSO_3$ and then the pH/DO probes were immersed into the solution. To minimize lag time in the measurements, all pH and DO measurements were conducted under constant stirring. After the pH/DO readings became stable in the initial solutions, 10 μM $KMnO_4$ or Mn^{2+} was added into the above solution and the pH/DO change was recorded with time. Additional details for pH and DO analysis are in Text S2. Because the reaction was very fast, a video camera was used to record the pH/DO changes and played at a slow motion afterward for the readings. To ensure the accuracy of the data, all experiments were conducted in duplicates. The H^+ and DO consumptions were calculated by the following equations:

$$[H^+]_{consumption} = [H^+]_{initial} - [H^+]_{left}$$

$$[DO]_{consumption} = [DO]_{initial} - [DO]_{left}$$

2.5. UV-vis analysis for MnO_2 formation

For MnO_2 formation, various amounts of organic compounds, $KMnO_4$ and $NaHSO_3$ were used depending on different purposes. Typically, 250 μM $NaHSO_3$ and 50 μM $KMnO_4$ reacted in the presence or absence of a certain amount of phenol. After 20 s, the solution was analyzed by UV-vis. The broad peak at 300–500 nm was attributed to the presence of MnO_2 colloids (Soldatova et al., 2017; Sun et al., 2015). Although the formed MnO_2 colloids were not soluble in water, they can form relative stable suspension due to their small initial sizes. Hence, MnO_2 formation could be analyzed by UV-vis giving a broad peak at 300–500 nm. The intensity of the MnO_2 peaks was used to qualitatively analyze MnO_2 colloid concentrations: the higher the intensity was, the higher the concentration of MnO_2.

3. Results and discussion

3.1. The O_2 effect on Mn(III) reactivity

To investigate the O_2 effect on the oxidation ability of the $NaHSO_3/KMnO_4$ system, a series of reactions were separately conducted in nitrogen and in air. Fig. 1A shows that in nitrogen, no organic compounds were oxidized at the time scale of seconds (0% conversion for all reactions) while in air 18%–85% of the organic compounds were converted under different conditions. These differences obviously resulted from the availability of O_2 as the absence of O_2 led to the inactivation of $NaHSO_3/KMnO_4$ toward organic compounds oxidation. Such inactivation was not specific to ratios of $NaHSO_3$:$KMnO_4$ (2:1 vs. 5:1), initial pH (pH_{in}) (4.77 vs. 3.5), or organic species (phenol vs. caffeine) and amounts (20 μM vs. 40 μM).

To exclude the potential interference of H_2 in glove box to the observed oxygen effects, two different levels of H_2 (2.5% and 1.0%) were first controlled in the glovebox, and the results in Table S2 indicate that the $NaHSO_3/KMnO_4$ system remained inactive in oxidizing phenol in both cases. Then, He and H_2 were used separately to bubble the solution to maintain the same DO content (1.85 mg/L). The results in Table S2 showed that the same amount of phenol was oxidized under both conditions, indicating the oxidation activity of $NaHSO_3/KMnO_4$ was not affected by the H_2 in the glove box.

To identify the reason for this inactivation, we first tested if Mn(III) can form in nitrogen because Mn(III) has been well demonstrated to be the origin of the oxidation ability of $NaHSO_3/KMnO_4$ (Sun et al., 2015). Two methods were used to detect Mn(III) based on the formation of MnO_2 and Mn(III)-PP complexes where the later one is a well-accepted method to detect Mn(III) (Sun et al., 2015). Because MnO_2 formation has been proven to be due to Mn(III) disproportionation, its presence can also be used as an indicator for Mn(III) formation (Sun et al. 2015, 2018). We conducted $NaHSO_3$:$KMnO_4$ (2:1 ratio) reaction in nitrogen, based on the stoichiometry in eq. (1), to observe if there was MnO_2 (without PP presence) or Mn(III)-PP complex (with PP presence) formed. It should be noted that we used 2:1 ratio of $NaHSO_3$:$KMnO_4$ rather than 5:1 because in nitrogen excess $NaHSO_3$ can further react with Mn(III)-PP to affect its detection. Fig. S3 clearly showed MnO_2 formation if PP was not present and Mn(III)-PP complex formation when PP was added, indicating that Mn(III) still formed in nitrogen and its formation was not affected by the absence of O_2. This finding thus excludes the possibility that the inactivity of $NaHSO_3/KMnO_4$ in nitrogen was due to the lack of Mn(III) formation. Meanwhile, this result also indicates that the formed Mn(III) in $KMnO_4/NaHSO_3$ did not oxidize the organic compounds in nitrogen (Fig. 1A), but disproportionated to MnO_2 and Mn^{2+} instead (Fig. S2). This inactivity of Mn(III) toward organic compounds in nitrogen is very similar to that in the $KMnO_4/Mn^{2+}$ system observed in the preliminary test (Table S1). However, the Mn(III) in $KMnO_4/Mn^{2+}$ was inactive in the presence of O_2, while for Mn(III) in $NaHSO_3/KMnO_4$, it became extremely reactive toward organic compounds in the presence of O_2 (Fig. 1A, in air). Hence, to unveil how O_2 drastically changed the behavior of Mn(III) in $NaHSO_3/KMnO_4$, it became critical to understand why Mn(III) in $NaHSO_3/KMnO_4$ can be so active.

Very recently, Sun et al. also noticed a similar promoting effect of O_2 when the removal efficiency of phenol increased with increasing DO from 1.0 to 8.0 mg/L (Sun et al., 2018). We also observed a similar trend (Fig. 1B). However, different from our

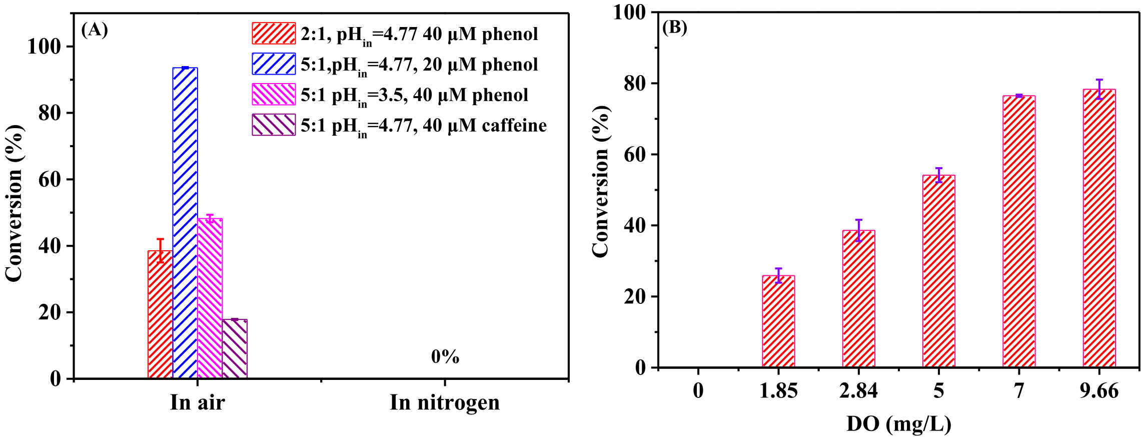


Fig. 1. (A) The O_2 effect on the oxidation of two representative organic compounds by Mn(III) generated in the reaction of 50 μM $KMnO_4$ with different amounts of $NaHSO_3$ under different conditions; (B) The effect of DO content on phenol conversion. Reaction conditions: 50 μM $KMnO_4$, 250 μM $NaHSO_3$, and 20 μM phenol. The samples were taken after reacting for about 10 seconds.

observation that there was 0% conversion in nitrogen, they observed minor oxidation of organic compounds with 0 mg/L DO. This difference should be due to the different methods used to control the O_2 contents. While they used a sealed reactor and flushed the reaction mixture with N_2 which may lead to a trace amount of DO remaining or leaking in solution, our reaction setup in a COY glove box ensured a strict oxygen-free environment. They explained this O_2 effect in that $NaHSO_3$ reacted with $KMnO_4$ to produce $SO_3^{\bullet-}$ radicals, which could compete with the organic compounds for Mn(III). With an increasing amount of DO, $SO_3^{\bullet-}$ radicals were increasingly consumed by DO, thus leading to more Mn(III) to react with the organic compounds (Sun et al., 2018). However, there was still Mn(III) formed in nitrogen, as showed above (Fig. S3). The above proposed mechanism cannot explain why this Mn(III) could not oxidize organic compounds (Fig. 1). Hence, the O_2 effect should be further investigated and reinterpreted.

3.2. The reaction between $NaHSO_3$ and O_2 as the bridge to link O_2 and Mn(III)

The key to understanding the O_2 effect on Mn(III) reactivity toward organic compounds would be to link the reactivity of Mn(III) to O_2. We started by investigating the reaction between $NaHSO_3$ and O_2 because this reaction can be easily catalyzed by metal ions, such as Fe^{2+}, Fe^{3+} and Mn^{2+} (Berglund and Elding, 1995; Berglund et al., 1993; Connick and Zhang, 1996; Zhang et al., 2018). Given the formation of Mn(III) ions during the reaction of $NaHSO_3/KMnO_4$, it is likely that Mn(III) also acted as a catalyst for the reaction between $NaHSO_3$ and O_2. Hence, we examined if the reaction between $NaHSO_3$ and O_2 can be affected when $NaHSO_3$ reacted with $KMnO_4$. The reaction between $NaHSO_3$ and O_2 is shown in eq. (5), based on which the production of H^+ and consumption of O_2 and HSO_3^- would indicate the reaction occurred.

$$2HSO_3^- + O_2 \rightarrow 2H^+ + 2SO_4^{2-} \tag{5}$$

Without adding $KMnO_4$, $NaHSO_3$ was relatively stable in air in 1 min because there was negligible production of H^+ and negligible consumption of O_2 and HSO_3^- even in the presence of 10 μM Mn^{2+} as the catalyst (Fig. 2). However, after adding 10 μM $KMnO_4$, the color of $KMnO_4$ disappeared immediately due to its reduction by $NaHSO_3$ (eq. (1)), followed by fast H^+ production and O_2 and HSO_3^- consumption in a short period (Fig. 2, H^+ formation as an indicator for $NaHSO_3$ consumption because it is from $NaHSO_3$ oxidation, as shown in eq. (5)). These results strongly indicate that eq. (5) proceeded at a fast rate. For comparison, if the reaction in eq. (5) did not occur, the reaction between $NaHSO_3$ and $KMnO_4$ would consume H^+ rather than produce H^+, as shown in eq. (6). Here, Mn^{2+} is the final product because $NaHSO_3$ (250 μM) was in large excess and could reduce all $KMnO_4$ (10 μM) to Mn^{3+} and finally to Mn^{2+} (additional evidence in SI Text S3).

$$5HSO_3^- + 2MnO_4^- + H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O \tag{6}$$

Also shown in Fig. 2A, H^+ concentration decreased when the same reaction was conducted in nitrogen, that is, the reaction in eq. (5) did not occur. Another evidence for the fast reaction in eq. (5) is the amount of $NaHSO_3$ consumed. Based on the stoichiometry in eq. (6), only 25 μM $NaHSO_3$ can be consumed by 10 μM $KMnO_4$ at most, as observed in nitrogen, while in air over 230 μM $NaHSO_3$ was consumed (Fig. 2C). The much larger amount of $NaHSO_3$ consumed can only be explained by the additional reaction with O_2. However, as mentioned above, the reaction between $NaHSO_3$ and O_2 could not proceed so fast even in the presence of Mn^{2+} as the catalyst. Thus, there must be new species acting as a much more efficient catalyst than Mn^{2+} for the reaction in eq. (5). Before concluding Mn(III) is the catalyst, however, we should first exclude all other possible species.

3.3. Mn(III) as the catalyst for the reaction between $NaHSO_3$ and O_2

The candidates for the catalyst for eq. (5) included Mn(III), Mn(IV)O_2, Mn(V), Mn(VI) and MnO_4^-. Upon mixing $NaHSO_3$ with $KMnO_4$ in air, H^+ started to form at ~130 ms (Fig. 2A inset). Note that although the pH reading had not stabilized within 130 ms, it had started to respond to the rapid change in solution pH in 130 ms so the H^+ release should have started before 130 ms. This was earlier than the reported time for MnO_2 appearance (~200 ms) (Sun et al., 2015), which implies that the catalytic effect already existed before MnO_2 formation. This result can exclude MnO_2 as the catalyst. Mn(V) and Mn(VI) species preferred to form in basic media (Ladbury and Cullis, 1958), while the initial solution was acidic ($pH_{in} = 4.77$) and H^+ continued to form through eq. (5), thus leading to a more acidic environment. Moreover, previous research did not observe their UV-vis absorbance at 660 and 610 nm (Hassan and Belal, 2002; Simandi et al., 1984), respectively, during the reaction between $NaHSO_3$ and $KMnO_4$ (Sun et al., 2015). Therefore,

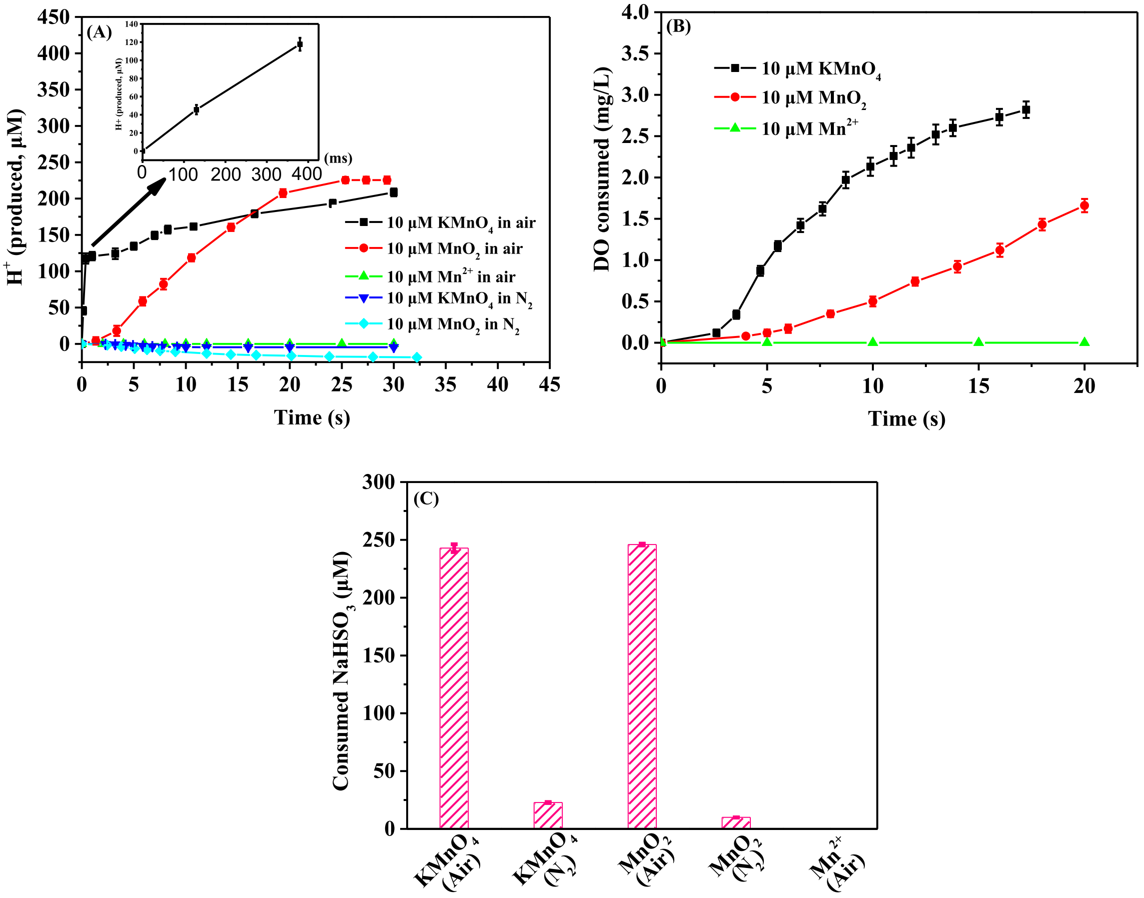


Fig. 2. Time course of (A) H^+ production (inset: H^+ time course in milliseconds) in N_2 or in air and (B) DO consumption in air when 250 μM $NaHSO_3$ reacted with 10 μM $KMnO_4$, MnO_2 or Mn^{2+}, and (C) $NaHSO_3$ consumption in 1 min under different conditions (250 μM $NaHSO_3$, 10 μM $KMnO_4$, MnO_2 or Mn^{2+}, in air or nitrogen). Note the use of slow pH/DO electrodes to monitor the rapid change had underestimated the actual values in (A) and (B).

Mn(V) and Mn(VI) species were also excluded as the catalyst.

To exclude MnO_4^- as the catalyst and to support the above conclusions that Mn(IV)O_2, Mn(V) and Mn(VI) were not the catalyst, the $MnO_2/NaHSO_3$ system was investigated because it also showed fast oxidation ability for organic compounds and Mn(III) was also believed to be responsible for this reactivity (Sun et al., 2015). The results are shown in Fig. 2. Similar to $NaHSO_3/KMnO_4$, the catalytic effect for eq. (5), i.e., generation of H^+ and consumption of $NaHSO_3$ and O_2, was also observed in $MnO_2/NaHSO_3$ but at slower rates. If MnO_2 were the catalyst, the reaction rates of H^+, $NaHSO_3$ and O_2 should be comparable or smaller in $NaHSO_3/KMnO_4$ than in $NaHSO_3/MnO_2$ because of the smaller amount of MnO_2 formed in the former. Therefore, MnO_2 can be indeed excluded as the catalyst. In addition, there is no MnO_4^-, Mn(VI) or Mn(V) in $MnO_2/NaHSO_3$, so they can be excluded as the catalyst as well. Because Mn^{2+} did not show any catalytic effect for eq. (5) within the time scale of seconds (Fig. 2), the only possible species left in $MnO_2/NaHSO_3$ is Mn(III). Moreover, we excluded the possibility of $KMnO_4$ and MnO_2 as the catalyst for HSO_3^-/O_2 reaction based on theoretical analysis (SI, Text S4).

The slower production rate of H^+ in $MnO_2/NaHSO_3$ was mainly attributed to the slower generation rate of Mn(III) in $MnO_2/NaHSO_3$ than in $KMnO_4/NaHSO_3$ (Sun et al., 2015). This was reflected in the slower oxidation of organic compounds by $MnO_2/NaHSO_3$ than by $KMnO_4/NaHSO_3$, although still significantly faster than many conventional oxidants (Sun et al., 2015). In other words, such differences in the catalytic reaction rates did not result from different catalytic species, but from the generation rates of the catalyst, i.e., Mn(III). Moreover, the catalytic role of Mn(III) can be well supported by previous research where even a trace amount of Mn(III) ($\leq 4 \times 10^{-8}$ M) could significantly catalyze HSO_3^-/O_2 reaction (Berglund et al., 1993; Connick and Zhang, 1996; Fronaeus et al., 1998). This was believed to be because Mn(III) participated in the rate-limiting chain initiation reaction (to form $SO_3^{\bullet -}$ radicals) so the radical chain reactions in HSO_3^-/O_2 are largely enhanced (Berglund et al., 1993).

Another evidence for the Mn(III) catalyst role in eq. (5) is the observed MnO_2 formation in the presence of a large excess of $NaHSO_3$. Based on eq. (6), when the ratio of $NaHSO_3$:$KMnO_4$ is greater than 2.5:1 where $NaHSO_3$ is in large excess, all $KMnO_4$ should be reduce to Mn^{2+} so no MnO_2 would form. Indeed, when 5:1 ratio of $NaHSO_3$ and $KMnO_4$ reacted in nitrogen, no MnO_2 formed (Fig. 3A). However, when the same reaction proceeded in air, MnO_2 formed even when there was only 20 μM $KMnO_4$ (versus 250 μM $NaHSO_3$) and the MnO_2 amount increased with $KMnO_4$ concentration (Fig. 3B). This can be well-explained by Mn(III) acting as a catalyst for eq. (5) (thus not consumed) so that $NaHSO_3$ was catalytically oxidized by O_2. Once all $NaHSO_3$ had been oxidized by O_2, the Mn(III) then disproportionated to Mn^{2+} and MnO_2. In other words, even though $NaHSO_3$ was used in large excess, as long as Mn(III) acted as a catalyst for eq. (5), MnO_2 would always form.

With the above evidence, we have established the catalytic role of Mn(III) for eq. (5) (Scheme 1 and eq. 7). For the trend in [H^+] change with time (Fig. 2A), it can be obviously divided into two

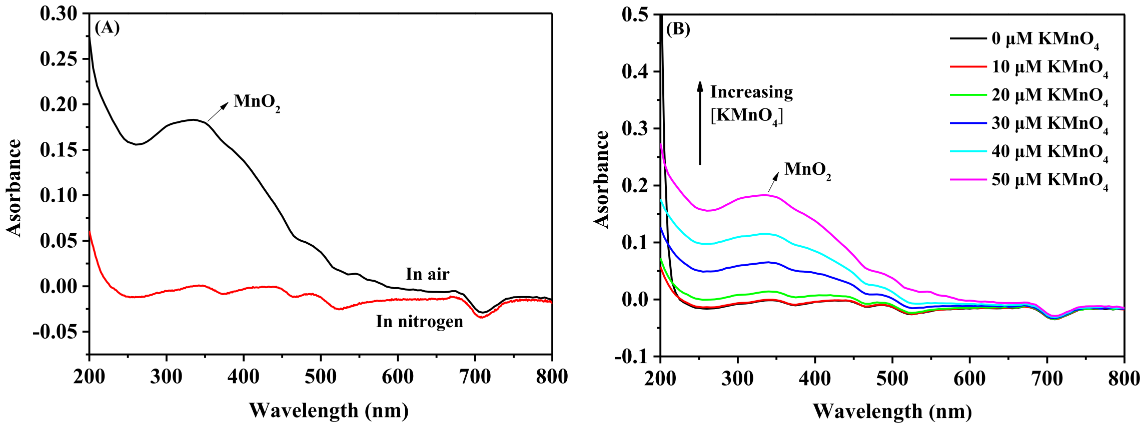
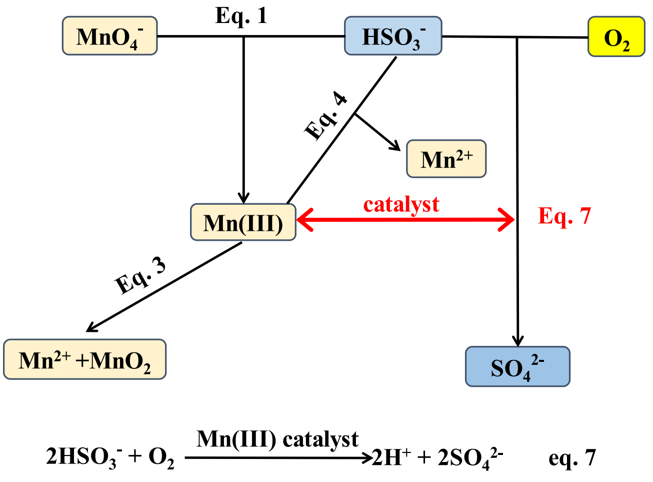


Fig. 3. (A) The MnO_2 formation in air or in nitrogen (conditions: 250 μM $NaHSO_3$, 50 μM $KMnO_4$, in air or nitrogen); (B) The effect of $KMnO_4$ initial concentration on MnO_2 formation in the absence of phenol (Conditions: 250 μM $NaHSO_3$ in air).



$$2HSO_3^- + O_2 \xrightarrow{\text{Mn(III) catalyst}} 2H^+ + 2SO_4^{2-} \qquad \text{eq. 7}$$

Scheme 1. The catalytic role of Mn(III) in the reaction between $NaHSO_3$ and O_2 (the double-headed red arrow represents that Mn(III) acts as a catalyst and hence will not be consumed in the reaction).

stages: the first stage shows a sharp increase (milliseconds, Fig. 2A inset) and the next shows a much slower increase. In previous research, MnO_2 appeared to form at about 200 ms due to Mn(III) disproportionation (Sun et al. 2015, 2018), indicating Mn(III) can only exist transiently in a short period. Hence, the sharp increase in $[H^+]$ in the initial reaction time was due to the fast oxidation of $NaHSO_3$ by O_2 with Mn(III) as the catalyst. Once Mn(III) started to disproportionate, the catalytic reaction between $NaHSO_3$ and O_2 became much slower, therefore, increase in $[H^+]$ became slower in the second stage.

3.4. *$NaHSO_3$ and O_2 as catalysts for the reaction between Mn(III) and phenol*

After the Mn(III) catalytic role for eq. 7 has been established (Scheme 1), we can see that when O_2 is not present, the reaction in eq. 7 cannot occur so Mn(III) cannot act as a catalyst; while with O_2 Mn(III) acts as a catalyst. This characteristic is very similar to the observed O_2-dependent oxidation ability of Mn(III) toward organic compounds, i.e., without O_2 Mn(III) lost its oxidation ability while with O_2 its oxidation ability resumed. Based on this, we proposed that only the Mn(III) with this catalytic role can exhibit oxidation activity toward organic compounds. To prove this hypothesis, we investigated the effect of phenol concentration on both the Mn(III) catalytic role and its oxidant role, and found Mn(III) that could oxidize organic compounds was indeed catalytically involved in eq. 7. As shown in Fig. S4, with an increase in phenol concentration, there was an increasing amount of phenol consumed. As a result of more Mn(III) reaction with phenol, less Mn(III) was available to catalyze eq. 7 so there is a decreasing amount of H^+ released (Fig. 4a). This H^+ change may also come from the reaction between Mn(III) and phenol, but because the amount of phenol consumed was small (<6 μM in Fig. S4), we believe the major source of H^+ is eq. 7. Moreover, the same decreasing trend was observed in DO consumption with increasing [phenol] (Fig. 4b), confirming eq. 7 was inhibited. These results strongly indicate that 1) the Mn(III) with the catalytic role for eq. 7 was the oxidant for phenol; and 2) Mn(III) was the catalyst for eq. 7 because the more it was consumed by phenol, the less the catalytic effect became.

Why can Mn(III) with this catalytic role oxidize organic compounds? To address this question, we have to first recognize that when Mn(III) is involved in eq. 7 as the catalyst, it obtained two characteristics: (1) it is protected from being reduced by $NaHSO_3$ because catalysts are not consumed in the same reaction; and (2) its disproportionation to Mn^{2+} and MnO_2 is somehow inhibited so it can react transiently in an unknown way (the specific catalytic process is yet unknown). It is likely that in the catalytic process, Mn(III) is stabilized by some sulfur-based species transiently, thus showing the millisecond oxidation ability toward organic compounds. This is very similar to the cases when Mn(III) was stabilized by ligands to oxidize organic compounds, as mentioned in Introduction (Anderson and Kochi, 1970; Gao et al., 2018; Jiang et al., 2009). Gao et al. also proved the feasibility of Mn(III) to form reactive complexes with reduced sulfur species (Gao et al., 2017). The specific Mn(III) species formed in the catalytic process, however, remains unknown and should be further investigated. For now, the attempts to identify such transient intermediates failed due to their highly unstable nature.

Based on these results, we can establish the relationship between Mn(III)'s catalytic role for eq. 7 and its oxidant role for organic compounds, as shown in Scheme 2A and eq. 8*. In short, the Mn(III) that can oxidize organic compounds is the one involved catalytically in eq. 7. On the other hand, Fig. 4 suggests that it is reasonable to see $NaHSO_3/O_2$ as a catalyst for the reaction between Mn(III) and organic compounds because (1) $NaHSO_3$ and O_2 were originally consumed in the Mn(III) catalyzed reaction in milliseconds (Fig. 2A inset), but they were decreasingly consumed once Mn(III) had reacted with phenol (Fig. 4); (2) without O_2 to oxidize

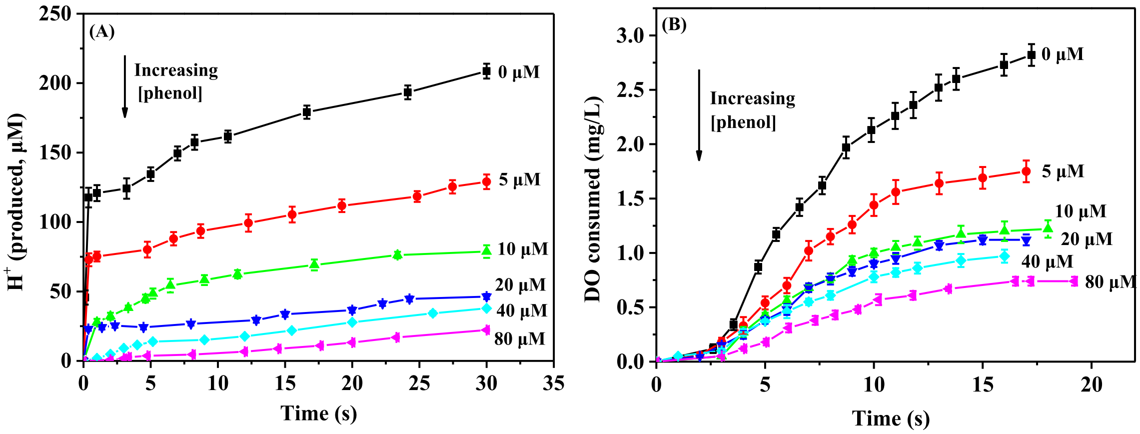
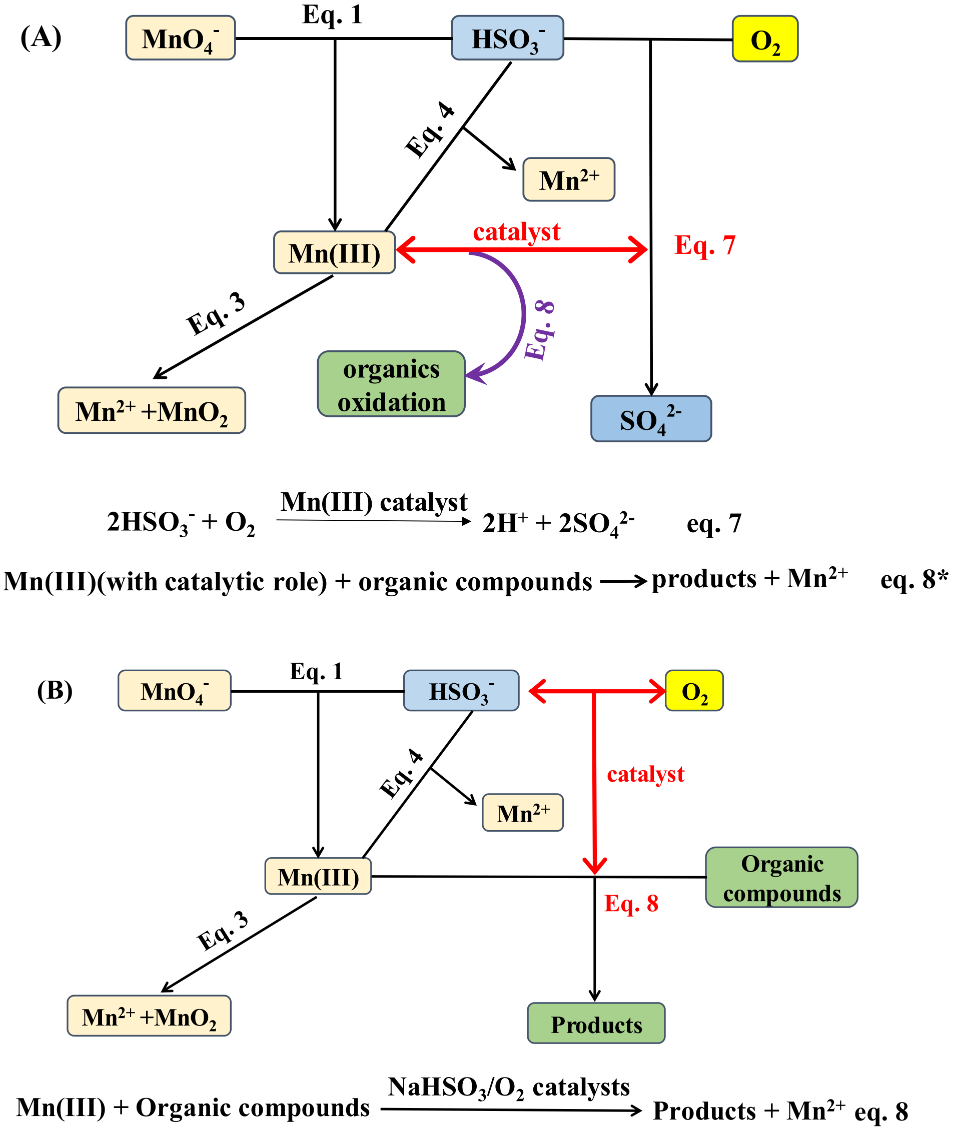


Fig. 4. The effect of phenol initial concentration on (A) $NaHSO_3$ consumption (as indicated by H^+ production based on eq. 7) and (B) DO consumption in 250 μM $NaHSO_3$ with 10 μM $KMnO_4$ in air.



$$2HSO_3^- + O_2 \xrightarrow{\text{Mn(III) catalyst}} 2H^+ + 2SO_4^{2-} \qquad \text{eq. 7}$$

$$\text{Mn(III)(with catalytic role)} + \text{organic compounds} \longrightarrow \text{products} + Mn^{2+} \qquad \text{eq. 8*}$$

$$\text{Mn(III)} + \text{Organic compounds} \xrightarrow{NaHSO_3/O_2\ \text{catalysts}} \text{Products} + Mn^{2+}\ \text{eq. 8}$$

Scheme 2. (A) The relationship between Mn(III) catalytic role for the reaction between $NaHSO_3$ and O_2 and its oxidant role for oxidation of organic compounds; (B) the new reaction mechanism for oxidation of organic compounds in $NaHSO_3/KMnO_4$.

$NaHSO_3$, Mn(III) could not oxidize phenol (Fig. 1A). These two features fit well to the catalyst definition as catalysts are not consumed in one reaction, but without them the reaction cannot proceed or proceeds very slowly. Based on the above results, a new reaction mechanism was proposed in Scheme 2B where $NaHSO_3$ and O_2 act as catalysts for the reaction between Mn(III) and organic compounds. When comparing Scheme 2A vs. 2B, one interesting phenomenon is that there exists a "catalytic role exchange" phenomenon between Mn(III) and $NaHSO_3/O_2$ where Mn(III) acted as the catalyst for eq. 7 in the absence of organic compounds while $NaHSO_3$ and O_2 acted as the catalyst for eq. 8 in the presence of organic compounds.

3.5. *Possible species that can complex with or activate Mn(III)*

Based on the new mechanism, Mn(III) is only involved catalytically in $NaHSO_3/O_2$ reaction, and it can oxidize organic compounds using $NaHSO_3/O_2$ as the catalyst. We also proposed that during the reaction of $NaHSO_3/O_2$, some species might form to have the ability to stabilize Mn(III) transiently. These species are most likely sulfur-based species in the reaction of $KMnO_4/NaHSO_3/O_2$. Sun et al. have investigated this reaction in detail and reported that $SO_3^{\bullet-}$ can directly form from HSO_3^- oxidation by MnO_4^- and then be further oxidized by O_2 to $SO_5^{\bullet-}$ (Sun et al., 2018). The obtained $SO_5^{\bullet-}$ can react with HSO_3^- to produce HSO_5^- and $SO_3^{\bullet-}$ while HSO_5^- can react with HSO_3^- to produce SO_4^{2-} and $SO_4^{\bullet-}$ (Das, 2001; Sun et al., 2015).

Based on recent research (Sun et al., 2018), the possible sulfur species include both stable ones: HSO_3^-, SO_4^{2-}, HSO_5^-, and unstable radicals: $SO_5^{\bullet-}$, $SO_4^{\bullet-}$ and $SO_3^{\bullet-}$. Because of the observed DO effect, the species that may complex/activate Mn(III) should be the ones that are generated when O_2 is involved. Thus, $SO_3^{\bullet-}$ can be first excluded because it can be directly produced by the reaction between HSO_3^- and $KMnO_4$, which is independent of O_2. SO_4^{2-} also can be excluded because in nitrogen SO_4^{2-} was also produced as the final oxidation product of HSO_3^-. The remaining possible species include $SO_5^{\bullet-}$, $SO_4^{\bullet-}$, HSO_3^- and HSO_5^-.

Although we had excluded the possibility of HSO_3^-/Mn(III) as the oxidant as proposed (Gao et al., 2017), it is still possible that the ternary system HSO_3^-/Mn(III)/O_2 acted as the oxidant. In the same way, the ternary system SO_4^{2-}/Mn(III)/O_2 may also be the reactive species. To check this possibility, we used $KMnO_4$ to react with Mn^{2+} to produce free Mn(III) in the presence of SO_4^{2-} in air. In this way, free Mn(III), SO_4^{2-} and O_2 co-existed to form a SO_4^{2-}/Mn(III)/O_2 ternary system. However, we did not observe any phenol oxidation in a short period (Table S2), thus excluding this possibility. The ternary $NaHSO_3$/Mn(III)/O_2 system, however, cannot be verified in the same way because HSO_3^- can react with $KMnO_4$. HSO_5^- is a strong oxidant and its oxidation of organic compounds can be catalyzed by metal ions (Anipsitakis et al., 2006); we did not test this possibility because the results would be unreliable. Also, it is difficult to verify the possibility of $SO_5^{\bullet-}$ and $SO_4^{\bullet-}$ due to their highly unstable nature.

For the potential contribution of these radicals to direct phenol oxidization, Sun et al. had excluded this possibility by using Mn^{2+} to catalyze the reaction of $NaHSO_3$ and O_2 in the presence of phenol (Sun et al., 2015). Because a significant amount of radicals was detected yet no phenol was degraded, the authors believed that the radicals in $NaHSO_3/O_2$ reaction had no direct contribution to phenol oxidation. Given the complexity of this system, further research is needed to elucidate the more detailed mechanism of the $MnO_4^-/HSO_3^-/O_2$ system.

3.6. *Validation of the new mechanism*

To validate a new mechanism, one needs to address all the well interpreted phenomena by previous mechanisms, but more importantly, to resolve the phenomena that cannot be reasonably interpreted by previous mechanisms. Here, the effects of four factors including $NaHSO_3$:$KMnO_4$ ratio, $KMnO_4$ amount, phenol concentration and DO level were investigated, as shown in Fig. 5. The phenomena that cannot be well explained by the previous mechanisms include the effects of $NaHSO_3$:$KMnO_4$ ratio and DO. For the ratio effect, the original mechanism (eqs. (1)–(4)) implied that the highest conversion of organic compounds should be at the 2:1 ratio of $NaHSO_3$:$KMnO_4$ (eq. (1)) because no $NaHSO_3$ would be left to compete with the organic compounds for Mn(III) (eq. (4)) (Sun et al., 2015). This is however not consistent with the experimental results where the highest phenol conversion was obtained at the ratio of 6.5:1 (Fig. 5A). Although an updated mechanism was recently proposed by Sun et al. based on the findings about the promoting effect of O_2, it still cannot effectively explain this ratio effect. Specifically, with an increasing ratio of $NaHSO_3$:$KMnO_4$, the mechanism would predict more $SO_3^{\bullet-}$ radicals produced. Because the radicals would compete with the organic compounds for Mn(III), it would decrease the oxidation efficiency, which is clearly contradictory to the experimental observations. To explain this ratio effect, Gao et al. proposed that Mn(III) needed extra HSO_3^- to form complexes as the oxidant (Gao et al., 2017), but this hypothesis cannot explain the oxygen effect (Fig. 1). Based on our new mechanism, $NaHSO_3$ is part of the catalysts for Mn(III)/organics oxidation. With its concentration increasing (ratio 2:1 to 6.5:1), phenol conversion should increase, as indeed observed (Fig. 5A). Further increase in $NaHSO_3$ concentration (6.5:1 to 16:1) would lead to Mn(III) loss by eq. (4), thus leading to decreased phenol conversion (85–40%) (Fig. 5A). Note that the decreased phenol conversion at higher ratios is not due to DO having been exhausted (Fig. S5). On the other hand, MnO_2 formation decreased gradually with increasing ratio (Fig. 5B) because additional Mn(III) had been consumed by reacting either with phenol at the ratio 2:1 to 6.5:1 or with $NaHSO_3$ at the ratio 6.5:1 to 16:1. At the higher ratios of 6.5:1 to 16:1, the Mn(III) was mainly reduced by excess $NaHSO_3$ because 1) the decreasing amounts of MnO_2 formed indicate less Mn(III) had disproportionated; and 2) the Mn(III) that did not disproportionate did not oxidize phenol either as shown by the decreased phenol conversion at higher ratios (Fig. 5A).

For the O_2 effects, the previous mechanisms proposed by both Sun et al. and Gao et al. cannot effectively explain them as discussed above. However, based on our mechanism, when O_2 was first introduced into the anoxic system, Mn(III) started to assume the catalytic role for eq. 7, thus phenol started to be oxidized (Fig. 1B). With increasing DO content (0–7 mg/L), the reaction in eq. 7 would proceed increasingly faster so that more Mn(III) was catalytically involved in eq. 7, leading to increased phenol conversion (Fig. 1B). From the catalyst point of view, because O_2 is part of the catalysts for the reaction between Mn(III) and organic compounds, it is anticipated and observed that the increased concentration of DO led to enhanced phenol conversion (Fig. 1B). Moreover, this enhancing effect of O_2 would eventually level off because the reaction rate is also limited by the fixed amount of $NaHSO_3$, as observed when DO concentration increased from 7.0 to 9.66 mg/L (Fig. 1B).

For the phenomena that had been well explained by the previous mechanisms, our proposed mechanism also can well explain them. First, for the effect of phenol concentration, an increasing amount of phenol was oxidized with increasing phenol initial concentration, while the amount of MnO_2 formed decreased (Fig. 5C and D). Increasing [phenol] would increase the reaction rate of eq. 8 so there was an increasing amount of phenol oxidized and, hence, more Mn(III) consumed. Also, the amount of MnO_2 formed gradually decreasing is expected based on less Mn(III) remain to

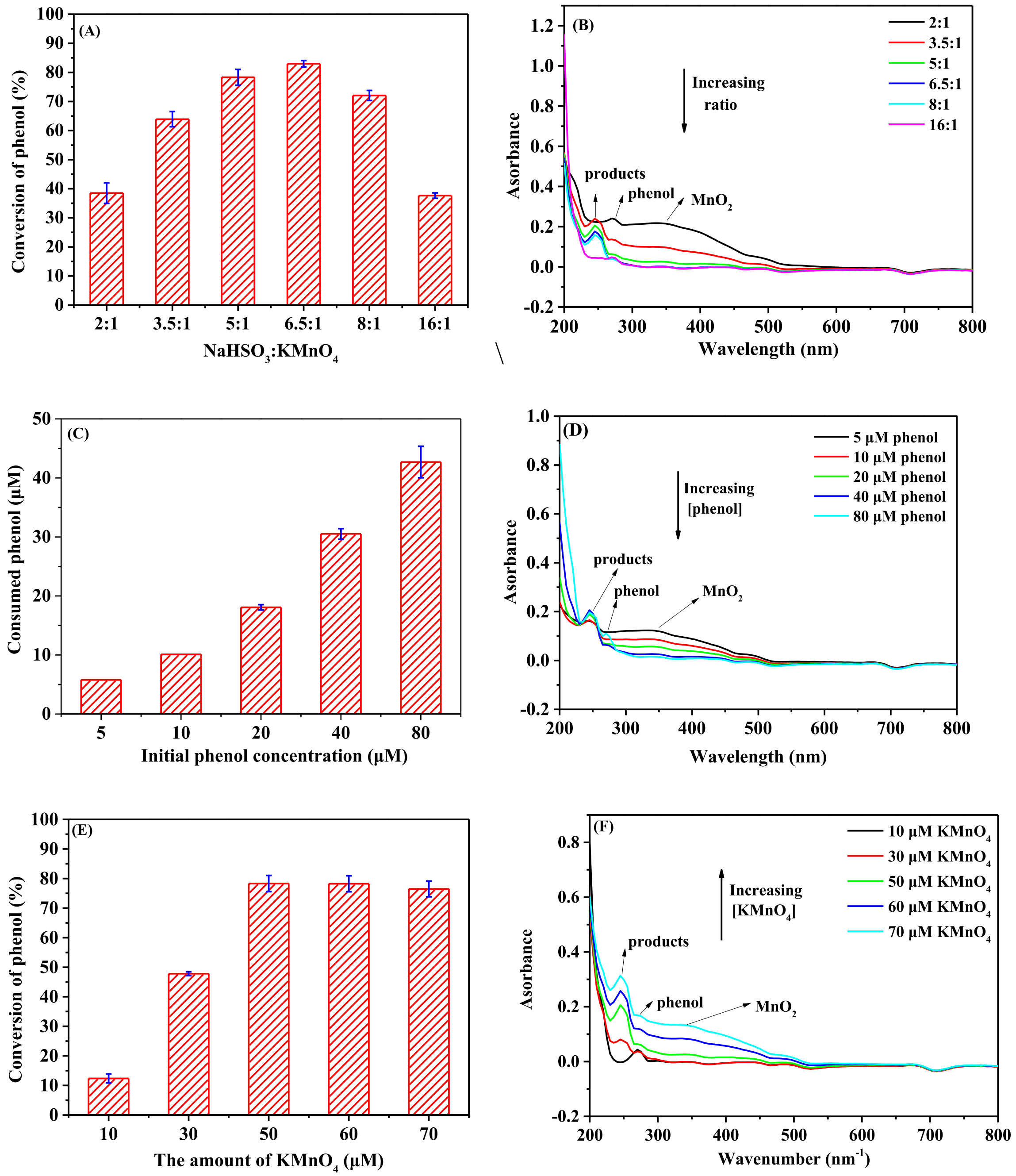


Fig. 5. The effects of various factors on phenol conversion and MnO_2 formation: (A) and (B) ratio of $NaHSO_3$ and $KMnO_4$ (50 μM $KMnO_4$, 40 μM phenol); (C) and (D) phenol concentration (250 μM $NaHSO_3$, 50 μM $KMnO_4$); (E) and (F) $KMnO_4$ amount (250 μM $NaHSO_3$, 40 μM phenol).

undergo disproportionation. Second, when $KMnO_4$ amount was increased, phenol conversion first increased due to the increasing amount of Mn(III) formed, but then leveled off because of the limited amount of $NaHSO_3$ available as the catalyst (Fig. 5E). The effect of $NaHSO_3$ availability is shown in Fig. 5A, where at 50 μM $KMnO_4$, increasing $NaHSO_3$ amount led to higher phenol conversion. The amount of MnO_2 formed also gradually increased with increasing [$KMnO_4$] (Fig. 5F) due to increasing amounts of Mn(III) formed. When comparing Fig. 5F to 3B, it is obvious that there was more MnO_2 formed in the absence of phenol. Therefore, the addition of phenol effectively suppressed MnO_2 formation because the MnO_2 precursor, i.e., Mn(III), had been consumed by phenol. This observation has also been reported previously (Sun et al., 2015).

4. Conclusions

In conclusion, this study revealed why Mn(III) in the $NaHSO_3$/$KMnO_4$ system was so active in oxidizing organic compounds. This is mainly because of Mn(III)'s catalytic role for the reaction between $NaHSO_3$ and O_2. In the catalytic cycle, Mn(III) became very reactive in oxidizing organic compounds in milliseconds and also disproportionated to Mn^{2+} and MnO_2. In the absence of O_2, however, Mn(III) lost this catalytic role due to the lack of the reaction between $NaHSO_3$ and O_2, thus Mn(III) only disproportionated. The facile disproportionation of Mn(III) is common for Mn(III) in other systems that can generate Mn(III) as an intermediate, while the millisecond oxidation of organic compound is unique for $NaHSO_3$/

$KMnO_4$. Hence, in most cases, the traditional way of using Mn(III), i.e., complexing with ligands, still holds. However, in $NaHSO_3$/$KMnO_4$, the specific process of how Mn(III) catalyzed the reaction between $NaHSO_3$ and O_2 and how such Mn(III) oxidized organic compounds still remain unknown, which warrant further research. This is also the first case about “catalytic role exchange” between Mn(III) (catalyst for the reaction between $NaHSO_3$ and O_2 in the absence of organic compounds) and $NaHSO_3$/O_2 (catalyst for the reaction between Mn(III) and organic compounds in the presence of organic compounds). Discovering the critical role of oxygen in $NaHSO_3$/$KMnO_4$ and having a correct understanding of the reaction mechanism will enable us to design more cost-effective systems based on this new, exciting technology for engineering applications such as water and wastewater treatment and site remediation.

Financial interests

The authors declare no competing financial interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2018.10.053.

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