



Short Communication

Rapid removal of organic pollutants by activation sulfite with ferrate

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HIGHLIGHTS

- PPCPs, dyes and phenol were almost decomposed in 30 s in sulfite/Fe^{VI} process.
- Oxygen increases sulfite/Fe^{VI} performance slightly.
- Sulfite/Fe^{VI} is a chain reaction involving SO₃^{•-}, SO₅^{•-}, SO₄^{•-} and ·OH.
- Sulfite/Fe^{VI} process is efficient under neutral and alkaline conditions.

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ABSTRACT

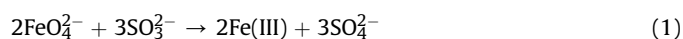
With the addition of sulfite, almost complete removal of seven out of eight tested contaminants, i.e. benzotriazole, phenol, ciprofloxacin, methyl blue, rhodamine B, methyl orange and sulfamethoxazole, was observed in 30 s except for sulfamethoxazole at pH 9.0, while Fe(VI) alone only resulted in less than 6% removal. In this study, the mechanism of sulfite/Fe(VI) process was explored for the first time. Firstly, sulfite attacks Fe(VI) via a 1-e⁻ transfer forming the primary sulfite radical (SO₃^{•-}), then SO₃^{•-} reacts rapidly with oxygen in a diffusion controlled rate to form a much more reactive peroxy radical SO₅^{•-}, which further reacts with HSO₃⁻ and produces SO₄^{•-}. All the signals of sulfite, sulfate and hydroxyl radicals were observed in the electron spin resonance (ESR) analysis. The DMPO and alcohol quenching experiments confirmed that sulfite/Fe(VI) process involves radicals as the plausible reactive species for decomposition of organic pollutants, and SO₄^{•-}/·OH instead of SO₃^{•-}/SO₅^{•-} are the major reactive oxygen species. Since oxygen participates in the formation of the secondary radicals, i.e. SO₅^{•-}, SO₄^{•-} and ·OH, the sulfite/Fe(VI) process open to air displayed better performance than that purged with nitrogen. Compared with previous sulfite/Cr(VI) and sulfite/Mn(VII) processes, which are only effective under acidic conditions, sulfite/Fe(VI) process provides an alternative under neutral and alkaline conditions. The extraordinarily fast oxidation of pollutants in sulfite/Fe(VI) process suggests that activation of sulfite by Fe(VI) might lead to a new class of advanced oxidation processes (AOPs) in water treatment.

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1. Introduction

Sulfites are often used as a food or wine preservative or enhancer in order to prevent microbial spoilage in industry. An advanced reduction process (ARP) that combines sulfite with UV light was developed to destroy various organics in water treatment. The one-electron oxidation of sulfite or bisulfite ions, either chemically or photolytically, generally produces sulfite radical. Ferrate (FeO₄²⁻, Fe(VI)) is being explored as an efficient agent for abatement of pollutants in water (Sharma et al., 2015). Over the pH

range from 5.0 to 11.0, the oxidative capability of Fe(VI) is comparable to that of permanganate, but much lower than ozone (Jiang et al., 2012) and other radicals produced in advanced oxidation processes (AOPs), i.e. ·OH and SO₄^{•-}. In our recent study, we surprisingly discovered that adding sulfite into Fe(VI) solution resulted in greatly accelerated oxidation rates of organic contaminants. To our knowledge, the exact mechanism between sulfite and Fe(VI) is not being covered yet, not to mention the synergistic effect of sulfite and Fe(VI) in organic pollutants removal. Johnson and Bernard (1992) proved that the reaction stoichiometry for sulfite to ferrate was 3:2. Thus this supports the overall reaction (Eq. (1))



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They also observed the second-order rate constants depends on the sulfite and hydrogen ion concentrations as below (Eq. (2)):

$$-\frac{d[\text{Fe(VI)}]}{dt} = (1.8 \pm 0.2) \times 10^{12} \text{ M}^{-2} \text{ s}^{-1} [\text{Fe(VI)}] [\text{SO}_3^{2-}] [\text{H}^+] \quad (2)$$

The reaction between sulfite and Fe(VI) was very fast and could reach completion within 30–50 s (Johnson and Read, 1996). Thus this may lead us to think why the organic pollutants can be effectively decomposed in such a short time. Given the absence of information on this topic, we initiated an investigation of sulfite/Fe(VI) process in aqueous. We selected serials of popular organics (PPCPs, phenol and dyes) as model compounds and reported herein the significant effect of Fe(VI) on sulfite and the detailed mechanism.

2. Material and methods

See Text S1 in Supporting Information.

3. Results and discussion

As shown in Fig. 1, almost complete disappearance of seven out of eight test contaminants was observed in 30 s except for sulfamethoxazole at pH 9.0. Fe(VI) alone only resulted in less than 6% removal for all tested organics, and there was no detectable reaction between organics with sulfite alone (not shown). It should be noted that since the addition of sulfite, the reaction reaches a completion in 30 s at pH range of 6.0–12.0 with the fading of Fe(VI) and the stable residual concentration of pollutants. Even though sulfite/Fe(VI) is powerful for organic pollutants decomposition, less than 8% mineralization for all target organics was achieved (as DOC) in 30 s, indicating the logistics for achieving sustained and complete contaminant oxidation during water treatment should be addressed in future work (Fig. S1).

A variety of reactive intermediate species, responsible for the rapid oxidation of pollutants, might be formed in sulfite/Fe(VI) process. We proposed two possible pathways for sulfite/Fe(VI) based on the literature review (Sharma, 2013): (i) 1-e⁻ transfer of Fe(VI)/Fe(V) and Fe(V)/Fe(IV) with the formation of sulfite radical

(SO₃⁻) from sulfite, then radicals or Fe(V)/Fe(IV) react with organics to form oxidized organics; (ii) oxygen-atom transfer to produce Fe(IV) and an oxygen atom added to sulfite resulting in SO₄²⁻ formation. Thus the lower states Fe(IV, V) and/or newly formed radicals are the major plausible reactive species. It is well known that Fe(IV, V) species are about 2–4 orders of magnitude more reactive than Fe(VI) (Sharma et al., 2008), thus causing the enhanced degradation of organics. According to Manoli et al. (2017), the oxygen has no effect on the Fe(VI) oxidation process involving Fe(IV, V) as intermediates, unless there are some organic ligands to stabilize Fe(IV, V). In sulfite/Fe(VI) process, no organic ligand was added, but approximately 10% higher sulfamethoxazole degradation was achieved from pH 6.0–12.0 in the system open to the air when comparing with that purged with nitrogen (Fig. 2). Then the mechanism with Fe(IV, V) as the major plausible reactive species might be excluded from our system, which leads us to guess that the newly SO₃⁻ radicals may have significant contribution to sulfite/Fe(VI) process. According to Huie and Neta (1984), SO₃⁻ can act as both a mild oxidant and a strong reductant. Phenols, amines, hydroquinone and ascorbic acid reacts with SO₃⁻ with moderate reaction rates of 10⁴–10⁸ M⁻¹ s⁻¹ (Neta and Huie, 1985), while for most of organic pollutants studied in this study, the reaction rates were not reported yet. Considering that the concentration of Fe(VI) is ten-fold higher than that of organic pollutants, SO₃⁻ is more likely to attack Fe(VI) than the organic pollutants. While in the presence of oxygen, SO₃⁻ reacts rapidly with oxygen in a diffusion controlled rate (1.5 × 10⁹ M⁻¹ s⁻¹) to form a much more reactive peroxy radical SO₅⁻ (Neta and Huie, 1985), which further reacts with HSO₃⁻ and produces SO₄²⁻ (Jiang et al., 2015; Xu et al., 2016; Yu et al., 2016; Kuo et al., 2006). Thus considerable amount of SO₃⁻ would be transformed to secondary radicals in the presence of dissolved oxygen, rather than reacting with Fe(VI) and organic pollutants directly. This suggests the reaction with the involvement of SO₃⁻ may be an oxygen consumption process. Oxygen is one of the major end products during the self-decay or decomposition of Fe(VI) with the ratio of oxygen to decomposed Fe(VI) in the range of 0.8–0.85 in DI water (Kolar et al., 2016), which means one molar Fe(VI) would produce 0.8–0.85 M oxygen. Thus in our study no matter the system was purged with nitrogen or open to the air, there was the newly formed oxygen from Fe(VI) in the reactors, while a higher oxygen concentration was achieved in the system open to air,

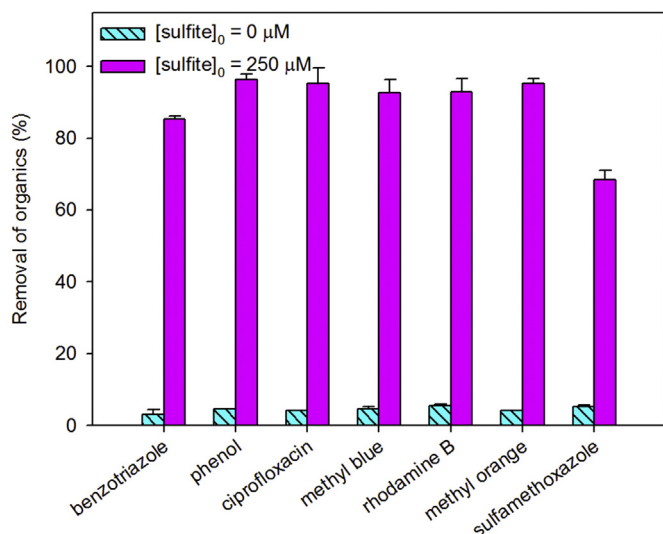


Fig. 1. Removal of benzotriazole, phenol, ciprofloxacin, methyl blue, rhodamine B, methyl orange and sulfamethoxazole in Fe(VI) alone and sulfite/Fe(VI) processes. Conditions: [Fe(VI)]₀ = 50 μM, [sulfite]₀ = 250 μM, [organic pollutant]₀ = 5 μM, pH = 9.0, reaction time 30 s.

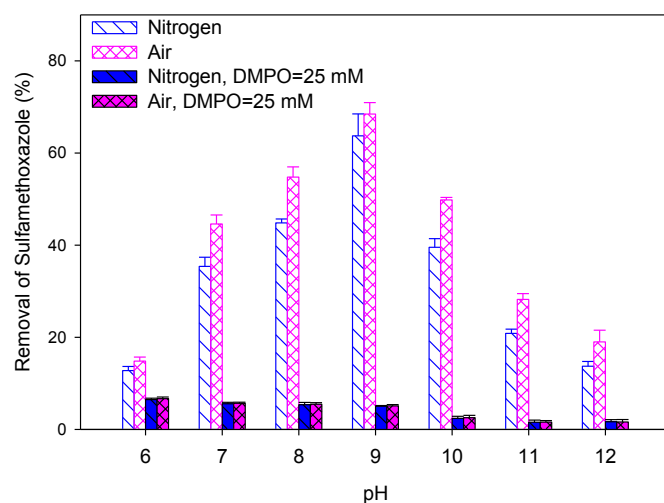


Fig. 2. Removal of sulfamethoxazole in sulfite/Fe(VI) process at pH 6.0–12.0 under nitrogen and air atmosphere with and without DMPO. Conditions: [Fe(VI)]₀ = 50 μM, [sulfite]₀ = 250 μM, [sulfamethoxazole]₀ = 5 μM, [DMPO] = 0 or 25 mM, reaction time 30 s.

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