Original Research

Iron species activating chlorite: Neglected selective oxidation for water treatment

Qihui Xu a, Zhipeng Li b, Feng Liu b, Hong You a, b, *, Binghan Xie a, b, **

a State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, Harbin, 150090, China
b School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai, 264209, China

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A B S T R A C T

Chlorite (ClO2) is the by-product of the water treatment process carried out using chlorine dioxide (ClO2) as an effective disinfectant and oxidant; however, the reactivation of ClO2 has commonly been overlooked. Herein, it was unprecedentedly found that ClO2 could be activated by iron species (Fe0, FeII, FeIII, or FeIII), which contributed to the synchronous removal of ClO2 and selective oxidative treatment of organic contaminants. However, the above-mentioned activation process presented intensive H+ dependent reactivity. The introduction of FeII significantly shortened the autocatalysis process via the accumulation of Cl− or ClO− during the protonation of ClO2 driven by ultrasonic field. Furthermore, it was found that the interdependent high-valent-Fe-oxo and ClO2, after identification, were the dominant active species for accelerating the oxidation process. Accordingly, the unified mechanisms based on coordination catalysis ([FeⅢ(H2O)6(ClO2)x]n−P) were putative, and this process was thus used to account for the pollutant removal by the FeII-activated protonated ClO2. This study pioneers the activation of ClO2 for water treatment and provides a novel strategy for “waste treating waste”. Derivatively, this activation process further provides the preparation methods for sulfones and ClO2, including the oriented oxidation of sulfoxides to sulfones and the production of ClO2 for on-site use.

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1. Introduction

Chlorite (ClO2), as a redox agent with wide application prospects, can be used not only as an alkaline Cl oxidant with a high oxidation capacity [1] but also as a source of chlorine dioxide (ClO2) via electron loss [2] (e.g., ultraviolet (UV) activation [3]). As a selective oxidant, the produced ClO2 could be considered a stable radical species which is significantly reactive toward phenolic, aniline, olefin, and amine moieties through electron-transfer reactions [4]. Moreover, ClO2 was used as a strong disinfectant in water treatment plants, which acted as an alternative to chlorine [5,6]. It was also found that ClO2 was the most efficient disinfectant in killing bacteria and, in particular, successful in deactivating viruses over a wide pH range [7]. However, ClO2 has been seen as the by-product of ClO2 treatment, and the Environmental Protection Agency has recently labeled ClO2 as a major water contaminant. ClO2 could result in suspected health risks such as childhood anemia [2]. According to “Standards for drinking water quality, GB5749-2022” in China, the limited concentration of ClO2 after ClO2 disinfection was reported to be 0.7 mg L−1 [8]. Therefore, a method to remediate ClO2 is of great practical interest from an environmental standpoint [2].

Currently, the catalysts, including various chlorite-dismutases (e.g., FeIII-Clds) [9–12] or non-heme metalloporphyrins/metal complexes (e.g., MnIII-Pors) [13–18], are also utilized to catalyze ClO2 detoxification, which results in the formation of harmless chloride (Cl−) and dioxygen (O2) [9–15] or ClO2 [16–18]. Moreover, the corresponding trivalent metal (MIII) gets transformed into high-valent metal (HVM), O=−MIV, or O=−MIII+[9–18].

Recently, in advanced oxidation processes (AOPs), the formation and role of aqueous FeIV-oxo complex (FeIV(O2)3+) have also attracted significant research attention in ferrous ion (Fe2+)-initiated AOPs by employing the oxidants including ozone, hydrogen peroxide, persulfates, peracetic acid (PAA), etc. [19]. Compared to the long-
recognized free radicals, FeIVO²⁺ has been shown to remove various pollutants (e.g., phosphate, amoxicillin, and sulfamethoxazole) [19,20]. Moreover, Fe²⁺O²⁻ could react with organic compounds through various pathways (hydrogen-atom, hydride, oxygen-atom, and electron transfer, as well as electrophilic addition) at moderate reaction rates [19]. Fe⁴⁺O²⁻ could also present selective reactivity toward inorganic ions prevailing in natural water [19]. This hints at the potential application prospects of high-valent iron in environmental treatment due to the production of the above-mentioned HVM in the catalysis of ClO₂:

\[ 4\text{Fe}^{3+} + \text{ClO}_2 + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3(s) + \text{Cl}^- + 8\text{H}^+ \quad (1) \]

In terms of the reactions between ionic iron and ClO₂, Fe⁴⁺ was commonly adopted to reduce ClO₂ to form the by-product Cl⁻ (95%) [21], in particular, under the alkaline condition for efficient ClO₂ removal (as shown in equation (1)) [21,22]. However, a few studies indicated that the different phenomenon with a certain ClO₂ uptake might provide a novel insight into the coordination mechanism in the contributions of the dominant active species for pollutant removal, based on the treatment of organic pollutants with by-product ClO₂.

2.2. Instrumentation

The liquid phase reactions were driven by ultrasound (US) in a self-prepared bath-ultrasonic generator (28 kHz, 30 W L⁻¹) coupled with a cylindrical acrylic reactor, as reported in our previous study [28]. The tpmCV solution (12 mg L⁻¹) was prepared and placed in the above-mentioned reactor. Briefly, certain amounts of H₂SO₄, NaClO₂, and Fe⁰ were added successively, and then the ultrasonic reactor was turned on to conduct the batch reaction. At the fixed reaction time, the tpmCV concentration was determined at λmax = 584 nm by UV-visible (vis) spectroscopy. The initial pH of solutions was adjusted by NaOH (1 M) and H₂SO₄ (1 M), and no attempt was made to maintain a constant pH during the process. UV-vis spectra were recorded using a scanning spectrophotometer (Pgeneral TU-1810S). The converted products of PMSO were detected by gas chromatograph-mass spectrometry (GC/MS, Trace 1300 ISQ-QD, Thermo Fisher). Before the GC/MS analysis, a sub-sample (15 mL) at a certain treating time (5, 15, and 25 min) was extracted with dichloromethane (10 mL), respectively. Next, the extracted solution was dehydrated with anhydrous sodium sulfate and concentrated to 2 mL. Before and after treatment, the micrographs of the Fe⁰ were examined by scanning electron microscopy (SEM, Zeiss, Germany), respectively. Before the SEM test, the Fe⁰ samples taken out from the reaction solution immediately required dehydration by adding absolute ethyl alcohol, then the samples were dried with filter papers and finally vacuum-dried.

3. Results and discussion

3.1. Fe⁰ activation for chloride

3.1.1. Coupling effect

As shown in Fig. 1a, activators including Fe⁰, Fe²⁺, and Fe⁴⁺ were utilized to catalyze the decomposition of ClO₂ for removing tpmCV at acidic pH under the ultrasonic field. The tpmCV, as the emerging contaminant, has been widely used in medical, veterinary, and aquaculture applications. However, the “Lancet Oncology” reported that tpmCV has been restricted in veterinary or cosmetic applications [29]. The system exhibited a coupling effect; namely, removal effect in the following: Fe⁴⁺ > Fe³⁺ > Fe⁰ > no activator. The apparent second-order kinetics constants of the H⁺–US/Cl/Fe⁴⁺ and H⁺–US/Cl/Fe³⁺ systems were 0.043 μM⁻¹ min⁻¹ (Radj = 0.996) and 0.115 μM⁻¹ min⁻¹ (Radj = 0.995), respectively. When the H⁺–US/Cl/Fe⁰ system was utilized, Fe⁰, in the presence of H⁺, could be converted to Fe³⁺, and Fe³⁺ could be further oxidized into Fe⁴⁺ via equations (3) and (4) [27,30]. Next, Fe⁴⁺ could catalyze ClO₂ to produce reactive species for decomposing ClO₂ and tpmCV. For the H⁺–US/Cl system, ClO₂ could react with H⁺ to generate ClO₂ via equation (5) [31], and then protonated ClO₂ formed HClO₂, which was subjected to sonolysis to produce ClO₂. In terms of the H⁺–US/Cl and H⁺–US/Cl/Fe³⁺ systems, both the removal processes exhibited an early stage of “build-up”. Based on the dynamics fitting, the piecewise kinetics of the above-mentioned systems (Fig. 1b) proved this point.
5Fe²⁺ + ClO₂ + 4H⁺ → Cl⁻ + 5Fe³⁺ + 2H₂O (3)

4Fe²⁺ + HClO₂ + 3H⁺ → Cl⁻ + 4Fe³⁺ + 2H₂O (4)

5ClO₂ + 4H⁺ → Cl⁻ + 4ClO₂ + 2H₂O (5)

3.1.2. Piecewise kinetics: transition state

Owing to the removal reaction presenting an “S”-process, namely, existing transition state, traditional one-step dynamics with integer order failed to meet the requirement of exploring such piecewise oxidation stages. Fortunately, equation (6) is universal, that is

\[
\frac{d[tpmCV]}{dt} = f' (\frac{c[tpmCV]}{C_0})
\]

Multiple inflection points (IPs) directly obtained from the process of “dc/dt vs. t” further indicated the existence of the piecewise kinetics processes for both H⁺-US/Cl and H⁺-US/Cl/Fe⁰ systems (Fig. 1c). After logarithmic transformation, the apparent-kinetics-orders (non-integer) of the H⁺-US/Cl and H⁺-US/Cl/Fe⁰ systems were 0.90 and 1.56, respectively.

Moreover, in view of excess active oxidizing species (3 mM ClO₂⁻ >> 30 μM tpmCV), equation (7) could be obtained.

\[
f' (\frac{c[tpmCV]}{C_0}) = -kC[tpmCV]^n
\]

Then, by feasible approximation, the piecewise kinetics processes were more obvious when 1 and 1.5 orders were utilized to fit kinetics curves of the H⁺-US/Cl and H⁺-US/Cl/Fe⁰ systems, respectively (Fig. 1b).

According to the H⁺-US/Cl system, two IPs at 12.5 and 22.5 min indicated the existence of three piecewise removal processes. Moreover, processes occurring in the time range of 0–12.5 min and 12.5–22.5 min with slow reaction rates indicated the potential autocatalytic feasibility, and the reaction at 22.5–37.5 min showed pseudo-1-order kinetics constant with a value of 0.113 min⁻¹. After introducing Fe⁰ the time of the stage of “build-up”, namely, IP was shortened to 7 min, and 7–25 min exhibited pseudo-1.5-order kinetics constant with a value of 0.056 μM⁻⁰.⁵ min⁻¹, which indicated that non-single oxidizing-species contributed to the pollutant removal. As a result, it is speculated that multiple oxidizing species may compete for the oxidation process.

3.1.3. Surface action by US

As shown in Fig. 2, SEM images showed more features with a relatively large size (20 μm), such as the honeycomb frame and the oxidation regions. With the prolongation of reaction time, the erosion and oxidation on the surface of Fe⁰-foam became more significant. Even so, most regions on surface of Fe⁰-foam still consisted of exposed fresh Fe⁰ sources due to the “polishing” role from ultrasonic via surface heat transfer, mechanical friction, and cavitation impact [28]. Owing to the synergistic effect between H⁺-assisted corrosion and ultrasonic-assisted polishing, the catalytic reaction of ClO₂⁻ could be sustained.

3.1.4. Modeling

Complex reactions tended to multistage processes during the heterogeneous system (i.e., the abovementioned system) at a certain treating time. It may be unsuitable to describe reaction processes under overall evaluation only with a single quasi-dynamic equation. Here, a novel indicator was used to evaluate the removal effect in a heterogeneous system. In particular, at a certain time, the degraded momentum, namely, the concentration movement of removing contaminant μ (M min⁻¹), could be defined to determine the overall trends of the removal [32].

\[
\mu = \frac{t_e - c(t)}{c_0 - t_0} \times \frac{c_0 - c_f}{t_e - t_0}
\]

where \( \frac{c_f}{c_0} \) was the concentration gradient of contaminant (\( c_f/c_0 \in [0,1] \)), \( t_0 \) and \( t_e \), represented the start and end times of the reaction. Theoretically, the value \( \mu_{\text{max}} \) equals the value \( t_e \), namely, \( c_f/c_0 \) reached 0 at \( t_0 \).
3.2. Influencing factors

3.2.1. pH

As shown in Fig. 3a, the removal reaction could be improved by introducing H⁺ into the H⁺-US/Cl/Fe⁰ system (φ increased from 0.856 to 1.331). H⁺ could cause the conversion of Fe⁰ to ionic Fe for activation. However, once the system presented a neutral or basic state, it became fatal to Fe⁰-activation. The abovementioned system was close to only US/Cl or OH⁻-US/Cl, leading to a very limited oxidation effect. However, it seemed that the removal effect under alkaline conditions (φ = 0.090) was slightly better than under neutral conditions (φ = 0.909). The sonolysis of ClO₂ was ever investigated to obtain that the removal reaction at 8 M/C₂ and 6 M/C₂ were 0.827 and 0.831, respectively. Therefore, low-dosage ClO₂ (0.1 mM) showed a slight effect on improving tpmCV (φ = 0.908), which indicated that the reaction was not interfered with by the ions themselves except the hydrolysis.

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \quad \text{⇌} \quad \text{H}^+ + \text{HCO}_3^- \\
\text{pK}_a & \quad \text{of} \quad \text{H}_2\text{CO}_3 & \quad = 6.38
\end{align*}
\]

3.2.2. ClO₂ dosage

The solution produces OH⁻ due to the hydrolysis of ClO₂ [33]. More ClO₂ dosage leads to the generation of more OH⁻, which can increase the consumption of H⁺. As a result, the amount of H⁺ actually acting on Fe³⁺ and ClO₂ decreases. However, more reactant ClO₂ could bring more effective collisions and improved utilization efficiency of other reactants (e.g., H⁺). The removal reaction in system H⁺-US/Cl/Fe⁰ maintained a balance (Fig. 3b) (φ around 0.959–1.008).

3.2.3. Anions

The anions, including SO₄²⁻ (φ = 0.981) and Cl⁻ (φ = 1.002) (3 mM), would not interfere with the solution-phase oxidation; however, ClO₃⁻ (1 mM) exhibited significant influence on the removal of tpmCV (Fig. 3c) in the H⁺-US/Cl/Fe⁰ system (φ = 0.140). The main reason for the phenomenon was that the formation of OH⁻ via hydrolysis of CO₂⁻ (equation (11)) resulted in competitive consumption of H⁺ [34]. Furthermore, OH⁻ led to the formation of the colloidal or precipitated Fe(OH)₃, which adversely affected the activation of ClO₂ with Fe⁰. Therefore, low-dosage ClO₂ (0.1 mM) showed a slight influence on removing tpmCV (φ = 0.837), which indicated that the reaction was not interfered with by the ions themselves except the hydrolysis.

\[
\text{Fe}^{IV} \text{O}^{2+} + \text{DMSO} \rightarrow \text{DMSO}_2 + \text{Fe}^{2+} \\
\text{H}_2\text{CO}_3 \quad \text{⇌} \quad \text{H}^+ + \text{HCO}_3^- \quad \text{⇌} \quad 2\text{H}^+ + \text{CO}_2^- 
\]

3.3. Inhibition

The reaction rate of MA vs. •OH was 9.7 × 10⁸ M⁻¹ s⁻¹; therefore, MA could be used as a scavenger for •OH [35]. However, when MA (1 M) was added to the solution, the removal trend seemed to remain constant (φ = 0.982) (Fig. 4a). Therefore, the •OH (at least in the liquid phase) showed little contribution to the removal of tpmCV, illustrating that ultrasonic provided other roles rather than •OH role in the catalytic system.

Notably, DMSO has recently been used to identify oxygen atom transfer reactions, such as reaction with Fe⁴⁺[36]. However, DMSO could also react with •OH to generate methyl radical (•CH₃) (equation (13)) [37].

\[
\text{Fe}^{IV} \text{O}^{2+} + \text{DMSO} \rightarrow \text{DMSO}_2 + \text{Fe}^{2+} \\
•\text{OH} + \text{DMSO} \rightarrow •\text{CH}_3 + \text{CH}_3\text{SO}_2\text{H}
\]

The screening test of MA ruled out the role of •OH; thus, the decrease in the removal of tpmCV after adding DMSO should be attributed to the active species causing an oxygen atom ([O]) transfer step. Moreover, it was demonstrated that DMSO could be an excellent masking agent for aqueous chlorine (e.g., Cl₂ or ClO⁻ (HClO)), without affecting ClO₂, ClO₂, and ClO⁻ by the co-existence of excess DMSO [30,38,39].

PBQ could be used to scavenge superoxide radical (O₂⁻) with a reaction rate at 8 × 10⁸ M⁻¹ s⁻¹ [40], but the result indicated the
absence of $O_2^-$ and the addition of PBQ also promoted the removal of tpMCV ($\phi = 1.159$) (Fig. 4a). The PBQ acted as an important redox reagent. Its applications range from organic synthesis to mediation of electron transfer in biochemical systems and solar cells [41]. On the one hand, the PBQ-based derivatives with electron-withdrawing substituents were employed as electron acceptors, and the quinones could serve as catalysts to shuttle electrons; thus, both facilitated the degradation of the starting aromatic compound [42]. On the other hand, the mixing of solutions of halide anions (I⁻, Br⁻, or Cl⁻) with PBQ acceptors resulted in the instantaneous formation of anion–π complexes [41]. This pointed out the charge-transfer character of these associates (equation (14)) [41].

$$\text{BO} + \text{X}^- \rightarrow \text{BO}^{*+} + \text{X}^+ \quad (14)$$

### 3.4. Competition and coordination

Oxalic acid and EDTA, as the chelating agents for metal ions, bonded with Fe³⁺, which impeded Fe²⁺-induced activation of ClO₂ (Fig. 4). Oxalic acid could react with Fe³⁺ to form some complexes, i.e., $[\text{Fe}^{\text{III}}(\text{O}_2\text{H})_6]^{2-}$ and $[\text{Fe}^{\text{II}}(\text{O}_2\text{H})_6]^{2-}$ [43], leading to the competing reaction ($\phi = 0.756$). In particular, EDTA could combine with $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{2+/3+}$ to form the coordination complex. For instance, $[\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{2-}$ was the seven-coordinated species with a monocapped trigonal-prismatic geometry [44]. On acidification, EDTA chelate could be protonated to form a monoprotonated species $[\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{-}$ with pentagonal–bipyramidal geometry [44]. The autodissociation of $[\text{Fe}^{\text{II}}(\text{EDTA})]$: the $[\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{-}$ (20-electron) could start the reaction with $O_2$ to form $\text{H}_2\text{O}_2$, and the reaction was controlled by electron transfer and the associated reorganization barrier. The reactions were presented as equations (15)–(20) [44]. Thus, with the increase in the EDTA dosage, the autodissociation effect surpassed the metal chelation effect, resulting in promoting the removal ($\phi$ increased from 0.291 to 0.666). Furthermore, more EDTA resulted in the decrease of the pH of the solution, which was also beneficial for the removal (Fig. 4b).

$$\text{Fe}^{2+} + \text{EDTA} \rightarrow [\text{Fe}^{\text{II}}(\text{EDTA})]^{2-} + \text{H}_2\text{O} \rightarrow [\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{2-} \quad (15)$$

$$[\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{2-} + \text{H}^+ \rightarrow [\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{-} \quad (16)$$

$$[\text{Fe}^{\text{II}}(\text{EDTA})\text{H}_2\text{O}]^{-} + \text{O}_2 \rightarrow [\text{Fe}^{\text{II}}(\text{EDTA})\text{O}_2]^{-} + \text{H}_2\text{O} \quad (17)$$

$$[\text{Fe}^{\text{II}}(\text{EDTA})\text{O}_2]^{-} \rightarrow [\text{Fe}^{\text{III}}(\text{EDTA})\text{O}_2]^{-} \quad (18)$$

$$[\text{Fe}^{\text{II}}(\text{EDTA})\text{O}_2]^{-} + \text{Fe}^{\text{II}}(\text{EDTA})\text{O}_2]^{-} \rightarrow [\text{Fe}^{\text{III}}(\text{EDTA})\text{O}_2]^{-} \quad (19)$$

$$[\text{EDTA}]^{2-} + [\text{Fe}^{\text{III}}(\text{O}_2^2)\text{Fe}^{\text{III}}(\text{EDTA})]^{-} \rightarrow [\text{Fe}^{\text{III}}(\text{O}_2^2)\text{Fe}^{\text{III}}(\text{EDTA})]^{-} + \text{H}_2\text{O} \quad (20)$$

When NaN₃ was used (Fig. 4b), the study reported that without spin trap agent N-tert-butyl-α-phenylnitrone, the reaction of ClO₂ with azide (N₃⁻) was strongly inhibited by ClO₂ due to rapid back-electron transfer. This led to additional mechanistic pathways, complex kinetics, and the formation of an unusual set of products, including N₃⁻, N₂O₅, NO₃, Cl⁻, and ClO₂ as represented in equations (21)–(26) [45]. Furthermore, in the presence of an iron(III)-azide system, the complex formation reaction occurred via the conjugate acid/conjugate base pathway (equation (27)) [46].
oxidation processes, part of the sulfones was generated [49]. Therefore, by elimination process, the ClO\(^-\) was also likely to cause the generation of PMSO\(_2\). As a result, this might be a good explanation for why a small amount of PMSO\(_2\) (retention time (t\(_R\)) = 9.27 min, m/z of 156, 141, 125, 94, and 77) was detected by GC/MS (Fig. 6), and the remaining most PMSO (t\(_R\) = 8.43 min, m/z of 140, 125, 97, and 77) was present in the H\(^+\)-US/Cl system. Then the introduction of Fe\(^0\) led to the production of PMSO\(_2\) in large quantities (Fig. 6), which should be attributed to HVI-oxo species due to the (relatively stable) imperceptible change in ClO\(^-\)/C\(_0\)). Moreover, this process clearly brought forward that the H\(^+\)-US/Cl/Fe\(^0\) system provided an effective preparation method for directional oxidation from PMSO to PMSO\(_2\).

3.5.2. Transformation

Consequently, the results further indicated that produced HVI-oxo species and ClO\(_2\) exhibited a certain transforming relationship. Previously, Fabian and Gordon proposed the formation of FeClO\(_2^+\) (Fe\(^{3+}\) + ClO\(_2\)) intermediates, but they did not deny the existence of Fe\(^{4+}\) [24–26]. According to FeClO\(_2^+\), Wang et al. proposed the combination of “Fe\(^{3+}\) + ClO\(_2\)”, which involved the reduction of ClO\(_2\) to ClO\(_2\) by aqueous Fe\(^{3+}\). This proceeded by both outer-sphere (86%) and inner-sphere (14%) electron-transfer pathways [27]. Moreover, the traditional mainstream views of the catalysis of ClO\(_2\) by metalloporphyrin or Clds were as follows (considering Fe-Pors as an example, Scheme 1), heterolytic (Route 1, to obtain Compound I [Por\(^{1+}\)···Fe\(^{IV}\)=O] and hypochlorite (HOCl\(^-\)/OCl\(^-\)) and homolytic (Route 2, to obtain chlorine monoxide (ClO\(_\bullet\)) and Compound II [Por\(^{1+}\)···Fe\(^{IV}\)=O]) cleavage of ClO\(_2\) [10,11].

Recently, a study used the natural substrate, ClO\(_2\), and the model substrate, PAA, under x-Cld role to reveal the formation of distinct intermediates; i.e., the transient triplet-state biradical species distinct from Compound I and Compound II [11]. Moreover, the studies also offered convenient routes to produce ClO\(_2\) in water by catalyzing ClO\(_2\) via non-heme Fe\(^{III}\)- or Mn\(^{IV}\)-complexes. The processes underwent the proton-coupled electron transfer (Mn\(^{IV}\)) [2] or initiated the formation of high-valent Fe and Mn\(^{IV}\)-OH intermediates with oxidant PAA (Mn\(^{III}\)) [18].

However, combined with the identifications in this study and based on the analogy of ClO\(_2\) catalysis of Mn\(^{IV}\)-complexes [2], a possible Fe\(^0\) catalytic mechanism for ClO\(_2\) to form interdependent high-valent-Fe-oxo and ClO\(_2\) was proposed under protonation (Scheme 2). The proposed Fe\(^0\) catalytic mechanism also involved Fe\(^{II}\) and Fe\(^{III}\) activation processes. Relying on the role of H\(^+\), the surface corrosion of Fe\(^0\) to form ionic Fe led to interfacial catalysis, and then the ultrasonic field provided the driving force for the mass transfer to undergo diffuse catalysis (a transition process from interfacial catalysis to liquid phase (bulk phase) catalysis). Furthermore, the ultrasonic cavitation could provide the activation of HClO\(_2\) to produce ClO\(_2\), and polish the surface of Fe\(^0\) to continuously expose fresh Fe\(^0\) sources (Fig. 2, Scheme 2). The ions release of Fe\(^0\) led to subsequent chain transfer processes of [Fe\(^{II}\)(H\(_2\)O)\(_6\)]\(^{3+}\) [51] and [HO\(^-\)-Fe\(^{III}\)-(H\(_2\)O)\(_2\)]\(^{3+}\), which sourced from the hydrolysis of [Fe\(^{III}\)(H\(_2\)O)\(_5\)]\(^{3+}\) [52,53]. Direct addition of Fe\(^{III}\) and Fe\(^{III}\) afforded the pseudo-second-order kinetics dependence, while Fe\(^0\) expressed the pseudo-1.5-order kinetics dependence after the ion accumulation stage (0–7 min, Fig. 1b), which indicated that the ion leaching of Fe\(^0\) affected reaction equilibrium. The as-formed HVI-oxo species, O=Fe\(^{IV}\) or O=Fe\(^{IV}\)[\(^+\)], corresponding to the catalytic transfer station: one pathway generated ClO\(_2\), which involved protonation of the oxo ligand on Fe\(^{IV}\) and thus accounted for the observed pH dependence (pH with great effect) for ClO\(_2\) production (Fig. 5c) [2]. Other pathways led to the formation of ClO\(_3\) and Fe\(^{III}\), which rapidly reacted with ClO\(_2\) to form [HO–Fe\(^{III}\)]\(^{2+}\), thus re-entering the catalytic cycle [2] (macroscopically being consistent with the process: Fe\(^{II}\)+ ClO\(_2\)  →  FeClO\(_2^+\)  →  Fe\(^{III}\)+ + ClO\(_2\) [24–26]).

The dominant species, [HO–Fe\(^{III}\)]\(^{2+}\), reacted with ClO\(_2\) in the presence of protons via homolytic Cl\(^-\)/O bond cleavage to form ClO\(_2\) and regenerate the O=Fe\(^{IV}\) species or via heterolytic Cl\(^-\)/O bond cleavage to form ClO\(^-\) and regenerate the O=Fe\(^{IV}\)[\(^+\)] species [2,10]. The generated ClO\(_2\) or ClO\(_2\) with strong reactivity entered reaction toward the low-valence Cl\(^-\). Furthermore, the previous research also reported and supported that the [Fe\(^{II}\)(H\(_2\)O)\(_6\)]\(^{3+}\) under HClO\(_2\) could allow the production of O=Fe\(^{IV}\) [54].
protonation.

Q. Xu, Z. Li, F. Liu et al. Environmental Science and Ecotechnology 14 (2023) 100225

ClO₂ throughout the liquid phase to increase the chance of collision process of ClO₂. Kieffer and Gordon reported that Cl⁻ pollutant removal underwent autocatalysis due to the formation of HClO₂ [31]. Cl⁻ intermediate, HOCl, led to the unique redox reaction [55]. Olagunju et al. reported that ClO₂ production after the induction period was considered that the autocatalysis concerning HCl⁻ from equation(5) to equation(28) [31]. Furthermore, Horvath et al. study also supported the abovementioned result. The accumulation of intermediates, Cl⁻ could alter the reaction process by using the HCl⁻US/CI system (Fig. 1a). Attention: in general, purity of commercial sodium chloride is around 80%, which is accompanied by part of chloride ions; therefore, the commodity might have itself contributed to autocatalysis.

4ClO₂ + 2H⁺ → ClO₃⁻ + Cl⁻ + 2ClO₂ + H₂O (28)

However, in terms of the H⁺-US/Cl⁻/Fe⁺ system, the coordination catalysis, i.e., effective contact catalysis/activation, could be proposed based on the abovementioned analyses presented in sections 3.5.1 and 3.5.2. The as-formed coordination center [Fe³⁺(H₂O)₆]³⁺ could be obtained by complexation of reactive intermediates such as ClO₂ (ClO₂⁻) or ClO₂⁻ by substituting H₂O, and its valence state could also be affected to form the possible [Fe³⁺(H₂O)₆(ClO₂⁻)]³⁺ complex, briefly, Fe³⁺ClO₂⁻ species. This process could be analogous to hemoglobin carrying oxygen, which could act as one transmission type. The [Fe³⁺(H₂O)₆]³⁺ could carry ClO₂ throughout the liquid phase to increase the chance of collision or contact among the molecules, particularly when driven by the US. Owing to the abovementioned coordination, the solute contaminant macromolecules were caught by the water molecules with intermolecular forces (similarly, pollutant molecules were trapped by the friction) to form localized/limited catalysis or activation, namely, [Fe³⁺(H₂O)₆(ClO₂⁻)]³⁺-Ptpm complexes, which easily led to the outer-sphere and inner-sphere electron transfers. Furthermore, the processes of free radical and non-free radical oxidation and active species for removing contaminants could all be produced. The above-mentioned catalytic processes were generally selective for contaminant structures.

4. Conclusions

(1) The system, namely, FeCl₂ activating protonated ClO₂, could be utilized to synchronously remove inorganic ions (ClO₂⁻) and organic pollutants (tpm-derivatives) by interdependent high-valent-Fe-oxo and ClO₂. However, the redox system presented selective oxidation rather than non-selective oxidation for contaminants removal.

(2) Differences were observed between metal porphyrin/complexes and ion catalysis. FeCl₂-induced activation of protonated ClO₂ seemed to approach Mn-porphyrin/complexes/activation of ClO₂; both processes produced ClO₂. In contrast, Fe-Cld/porphyrin catalysis more tended to catalyze ClO₂ to produce Cl⁻ and O₂.

(3) Interestingly, this study further provided the preparation methods of two products, i.e., ClO₂ and sulfones. The FeCl₂-activated ClO₂ could correspond to a method of oriented oxidation of sulfoxides to sulfones and environmentally allow for ClO₂ preparation for the on-site use (e.g., disinfection or sterilization) and further ClO₂ production.

(4) Owing to the micro/small dosage of activators used in this study, the autocatalytic process became explicit. In general, the studies were based on a high dosage of activators or homogeneous activation except for the autocatalysis caused by the pollutant structures (e.g., hydroquinone or benzoquinone), which shortened the autocatalytic accumulation processes. However, it has also made a preliminary exploration for the controlled release-catalysis of ionic Fe with small/micro dosages.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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