Ultrasonic role to activate persulfate/chlorite with foamed zero-valent-iron: Sonochemical applications and induced mechanisms

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A B S T R A C T

The novel system, consisting of composite oxidants (persulfate/chlorite, $\text{S}_2\text{O}_8^{2-}$/$\text{ClO}_2^-$) and stationary phase activator (zero-valent-iron foam, Fe$^{0}$) driven by ultrasonic (US) field, was applied to treat the triphenylmethane derivative effectively even at low temperature ($\approx 289$ K). By comparisons of sub-systems, the US roles to $\text{SO}_4^{2-}$, $\text{ClO}_2^-$, and Fe$^{0}$ were serially analyzed. US made the reaction order of multi-component system tend to within 1 (leading to de-order reaction), and widened pH activating range of the Fe$^{0}$, by sonicate-polishing during the process of $\text{ClO}_2^-$ co-activating $\text{S}_2\text{O}_8^{2-}$. US and Fe$^{0}$ were affected by fluid eddy on activating $\text{SO}_4^{2-}$/$\text{ClO}_2^-$. The Fe$^{0}$ had slight effect on the temperature of US bubble-water interface but the addition of $\text{ClO}_2^-$ lowered it. The partitioning capacity of the above US active zone increased during the reaction. US and $\text{ClO}_2^-$ could enrich the kinds of degradation intermediates. The contributions of free radicals ($\text{ClO}_2^-$, $\text{SO}_4^{2-}$, and hydroxyl radicals (OH)) and non-free radicals ($\text{ClO}_2^-$ and O = Fe$^{IV}$/IV from ionic Fe under ~O-O~ of $\text{S}_2\text{O}_8^{2-}$) and cyclic adjustment reaction of $\text{ClO}_2^-$ processes by sonochemical induction were equally important by corresponding detection means. Especially, real-time and online high-resolution mass spectrum by self-developing further confirmed the chain transfers of different free radicals due to US role. The findings expanded the application of sono-persulfate-based systems and improved understanding on activation mechanism.

1. Introduction

A series of trace triphenylmethane derivatives detected in aquatic environment with low concentration (<$\mu$M level) as emerging contaminants have drawn the attention [1], therein no lack of triphenylmethane crystal-violet (tpm$\text{CV}$). Besides as the dye, the tpm$\text{CV}$ (Fig. S1 a), could be used not only in clinical treatment, but also as antimicrobial and antiparasitic agents in aquaculture to treat and prevent fungal and protozoal infections [2]. However, the United States, the European Union, China, and others have not approved the use of tpm$\text{CV}$ in aquaculture due to it with the possible carcinogen, mutagen and teratogen effects [1–3]. Even so, the use of the prohibited and persistent tpm$\text{CV}$ could be common occurrence, leading to its frequent detection in aquatic environment. Specially, the bio-concentration of organisms made tpm$\text{CV}$ convert into leuco crystal-violet (ltpm$\text{CV}$, Fig. S1 b) (more toxic and more difficult to be metabolized) [1,3], which might be seen as the persistent pollutants.

$H_2O \overset{(1)}{\rightarrow} \cdot OH + \cdot H$ (1)

The alternative US-based advanced oxidation processes (AOPs), as the promising and friendly treatment technologies with physicochemical processes of cavitation (gas-phase reaction zone effective temperature, $\approx 5200$ K, and high pressure, in the range of hundreds of bars), pyrolysis (breaking chemical bonds, and yielding hydroxyl radicals (Eq. (1)) [4]), supercritical water oxidation (depth and temperature of the liquid-phase reaction zone, $\approx 0.2 \mu$m and $\approx 1900$ K, respectively), and violent turbulence [5,6]; meanwhile, especially as the sono-catalysis technologies to activate oxidizing agents to produce active species to form combined system [5–7], have attracted particular concern for environmental remediation. Herein, as a kind of oxidizing agent, persulfate (involving peroxymonosulfate (H$\text{SO}_5^-$, PMS) or peroxydisulfate (S$\text{O}_6^{2-}$, PDS)) with direct oxidizing or producing $\text{SO}_4^{2-}$ ($E^\circ$ ($\text{SO}_4^{2-}$/$\text{SO}_2^{2-}$) = 2.60 – 3.10 $V_{\text{NHE}}$) by activation to improve the oxidizing capacity [8] via physicochemical means (e.g. alkali, Eq. (2); heat, Eq. (3) [9]; photo-; electro-; microwave; and US, Eq. (4)), metal-free catalysis

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metal-based materials (e.g. zero-valence metal, Eq. (5)) [11], and other methods (e.g. ozone, superoxide, and plasma), could be used to treat environmental contaminants as well.

\[
2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{O}_2 + 3\text{H}_2\text{O} + 4\text{H}^+ \\
S_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} \quad k = 1.0 \times 10^{-3} \text{s}^{-1} \quad (298 \text{ K}) \quad \text{or} \quad 5.7 \times 10^{-5} \text{s}^{-1} \quad (343 \text{ K})
\]

Therefore, further works for sono-persulfate based AOPs were worth exploring to extend acoustic catalysis and persulfate activation bilaterally, seemingly to become prospective treatment methods for the elimination of refractory organic contaminants above.

At present, the zero-valent-iron (ZVI, Fe\(_0\))-based materials in dispersive media by modified techniques (pre-magnetized [12], sulfidated [13], loaded/embedded [14], micro/nano [15]) or in stationary phase ZVI (e.g. foam-ZVI (Fe\(_0\)) consisting of three-dimensional porous form (Fig. S1c) with properties [16,17] of permeability, controlled pore size, foveolate structure, shape stability, and machinability) as the activated intermediary to connect the US and persulfate, have obtained great attention. Herein, the Fe\(_0\) for oxidant activation was rarely reported, however, functional materials based on Fe\(_0\) have drawn important attention, such as, electrode materials for hydrogen evolution reaction or oxygen evolution reaction (electrocatalytic water splitting) [17], which also had greater potential for environmental remediation. However, the surface passivation of ZVI has been a fatal problem affecting its activation to persulfate. Nevertheless, it’s just that introducing US could polish the above ZVI in activation process, and ease the burden of passivation to provide the fresh ZVI.

In addition, in order to promote corrosion of ZVI and regulate the activation cycle (e.g. ionic Fe cycle) under the action of US, the chlorite (ClO\(_2^-\), Cl(III)) could be introduced into the aforementioned process and combined with persulfate to form composite oxidants. Commonly, ClO\(_2^-\) with a higher quantum yield at 254 nm, 1.0–1.53 mol-Einstein\(^{-1}\) [18,19], comparing with H\(_2\)O\(_2\) (0.5 mol-Einstein\(^{-1}\)) and persulfate (0.7 mol-Einstein\(^{-1}\)) [20], could be activated by physical fields including UV-light stimuli [18], (Eq. (6)), heat [21], and US, or chemical agents including acid (Eq. (7)) and PDS [22] to produce chlorine dioxide (ClO\(_2\)).

\[
3\text{ClO}_2^- + \text{H}_2\text{O} \xrightarrow{254 \text{ nm}} 2\text{ClO}_2 + \text{Cl}^- + 2\text{OH}^- + 0.5\text{O}_2 \\
5\text{ClO}_2^- + 4\text{H}^+ + \text{Cl}^- + 4\text{ClO}_2 + 2\text{H}_2\text{O}
\]

The ensuing surface passivation of ZVI (Cl role) may impede its further activation, however, introducing US, as a “bridge”, could not only activate composite oxidants, persulfate/chlorite (O\(_{SC}\)), to generate SO\(_4^{2-}\) and ClO\(_2^-\) by co-catalysis (Eq. (8)) [23], but also polish the Fe\(_0\) to avoid aforementioned Fe\(_0\) passivation and to activate O\(_{SC}\) deeply (Eqs. (9)-(13)).

\[
S_2\text{O}_8^{2-} + \text{ClO}_2^- \quad \rightarrow \quad \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{ClO}_2^- \\
\text{Fe}^{II} + S_2\text{O}_8^{2-} \rightarrow \text{Fe}^{III} + 2\text{SO}_4^{2-} \\
\text{Fe}^{II} + \text{SO}_4^{2-} \rightarrow \text{Fe}^{III} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \\
\text{Fe}^{II} + \text{ClO}_2^- \rightarrow \text{Fe}^{III} + \text{ClO}_2^- \\
4\text{Fe}^{II} + \text{ClO}_2^- + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{III} + \text{Cl}^- + 4\text{OH}^- \\
2\text{Fe}^{III} + \text{polishedFe}^{II} \rightarrow 3\text{Fe}^{III}
\]

In this study, the novel treatment systems, namely, the combined system (US/Fe\(_0\)-O\(_{SC}\)) based on co-catalysis involving acoustic catalysis and multiple activation of composite oxidants, and sub-systems, were established. The commonly apparent effects of US may have been mentioned, however, because of that US has always been seemed as just an assistant method in environmental remediation, the researches on its applied potential (e.g. couple function as a “bridge” of systems above by series connection) and feasible mechanism of US role (e.g. US role to transformations of generated active species) may be neglected.

This study was therefore designed to (1) evaluate applications of the combined- and sub- systems based on US from comparisons of performances, affecting parameters, and pollutant degradation paths; (2) reveal the detailed sonochemical roles in apparent remediation by comparisons of coupling systems; and (3) explore the roles of US-induction in remediation mechanism by comparisons of free radicals and non-free radicals processes.

2. Experiment

2.1. Operating

The operating processes including chemicals, self-developed US/catalytic/activated reactors (UCARs), etc. were presented in Section S1.

2.2. Analytical methods

The intermediates of tpm\(_{CV}\) and methyl phenyl sulfoxide (PMSO) were detected by gas chromatograph-mass spectrometer (GC/MS, Trace 1300 ISQ-Quad, Thermo Fisher). The temperature programming (GC/MS) was: column temperature 323 K, hold time 3 min; 10 K-min\(^{-1}\) up to 573 K, hold time 10 min. Before the above analysis, 50 mL subsample at a certain treating time (5, 15, 25, 35, and 45 min) was extracted with 15 mL dichloromethane, respectively. Afterward, the extracted solution by mixing was dehydrated by anhydrous sodium sulfate and concentrated to 2 mL. The ClO\(_2^-\) and tpm\(_{CV}\) concentration were detected by UV–vis spectrum (TU-1810S, PGENERAL, China) at 360 nm [19] and 584 nm, respectively. The concentrations of “Fe” were determined by phenanthroline spectrophotometry at 510 nm (HJ/T 345–2007). The accurate acoustic-intensity entering the system was measured by the calorimetry method [24], presenting in Section S2 (Eq. S1). The compositions and micrographs of the Fe\(_0\), before and after treatment, were detected and examined by X-ray diffraction (XRD, HAOYUAN Instrument, DX-2700), and scanning electron microscopy (SEM, Zeiss, Germany), respectively. Before XRD and SEM, the Fe\(_0\) samples taken out from reaction solution needed dehydration immediately by adding into absolute ethyl alcohol, then drying out with filter papers, finally vacuum drying. The anions of S\(_2\text{O}_8^{2-}\)/ClO\(_2^-\) were detected by ion chromatography (IC, ThermoScientific, Aqion).

2.3. Spin trapping and EPR measurements

The US filed was applied in solution consisting of NaClO\(_2\) (1–20 mM) and \(\text{K}_2\text{S}_2\text{O}_8\) (ClO\(_2^-\) : S\(_2\text{O}_8^{2-}\) = 1:5 in molar ratio) to conduct sono-chemical experiments, then Fe\(_0\) was added as needed. DMPO with equal proportion of O\(_{SC}\) was utilized to trap the generated active species above. In addition, dimethyl sulfoxide (DMSO, as needed) was added into water to form mixture for comparison.

The electron paramagnetic resonance (EPR) spectra were obtained by a Bruker A200 spectrometer. General instrument settings were as follows unless otherwise noted: center field 3490 G, modulation frequency 100 KHz, modulation amplitude 1 G, receiver gain 1.42 \times 10^4, time constant 20.5 ms, conversion time 40 ms, sweep time 41 s, frequency 9.82 GHz, and power 19.47 mW. The hyperfine splitting constants were measured by using Bruker Win-EPR SimFonia (Version 1.2).
2.4. Real-time and online continuous detection

In Scheme 1, the real-time and online continuous (ROC) detections of reaction mixtures were realized with a self-developed pneumatic nebulization (PN)-droplet spray ionization (DSI) (electrospray ionization (ESI) with CH₃OH as an assist as required) coupled to LTQ and LTQ-Orbitrap high resolution mass spectrum (HRMS) (Thermo Scientific) in positive or negative mode with a resolution of 60,000. Online MS/MS analysis of the captured intermediates could be performed during the reaction process. Data were acquired in full scan in the m/z range 50–300 and in MS/MS with a collision-induced dissociation energy of 25. The instrument was calibrated routinely with the provided calibration solution by Thermo Scientific to ensure mass accuracy within ± 3 ppm.

The self-developed PN-DSI as Scheme 1 shown: the sealed glass device (7 mL) was equipped with mixture (5 mL) of S₂O₈²⁻ at 5 × 10⁻⁶ M, ClO₂⁻ at 1 × 10⁻⁶ M, and DMPO at 1 × 10⁻⁴ M under US generator; then the liquid along the capillary tube entered into the site of triple valve by N₂ inflating; and the charged samples from the above liquid, suffering the action of PN (its description in Section S3) by another N₂ flow, were transmitted into HRMS.

2.5. Simulation on US reactor

The Acoustic-Piezoelectric Interaction of COMSOL Multiphysics, including pressure acoustics Eq. (14), was applied to simulate heterogeneous reaction process and visualize the action of US-field in the solution (ESI) with CH₃OH as an assist as required) coupled to LTQ and LTQ-Orbitrap high resolution mass spectrum (HRMS) (Thermo Scientific) in positive or negative mode with a resolution of 60,000. Online MS/MS analysis of the captured intermediates could be performed during the reaction process. Data were acquired in full scan in the m/z range 50–300 and in MS/MS with a collision-induced dissociation energy of 25. The instrument was calibrated routinely with the provided calibration solution by Thermo Scientific to ensure mass accuracy within ± 3 ppm.

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3. Results and discussion

3.1. Comparisons of US-based systems

At low temperature (≈ initial 289 K), low pollutant concentration (10⁻⁶ M, μM level), and near-neutral pH (without adjustment), the novel US/Fe⁰/Ο₆C system presented good performance on removing tpM CV (details in Section S4, Eqs. S26-S28). By fitting concentration functions of the systems mentioned above, the optimal fitting orders (non-integer, R²Adj > 0.999, Fig. 1e) of O₆C, Fe⁰/Ο₆C, US-O₆C, and US/Fe⁰/Ο₆C systems were 1.35, 1.10, 0.90, and 0.75, respectively.

In order to further measure the synergistic effect among the above-mentioned systems (Fig. 1e) conveniently, the S and fᵢ (details in Section S6, Eqs. S29-S33) were calculated to evaluate interactions of each O₆C-based system with pseudo-first-order kinetics (R²Adj > 0.990) as below (kobs values (10⁻², min⁻¹) of O₆C, Fe⁰/Ο₆C, US-O₆C, and US/Fe⁰/Ο₆C: 46.82, 51.56, 57.22, and 85.64, respectively).

\[ S = \frac{k_{\text{obs}}}{\sum k_{\text{obs}}} \]

\[ f_i = \frac{k_{\text{obs}}}{k_{\text{obs}} - 1} \]

where S is the synergistic effect of the multicomponent system, fᵢ is the action of single i system, and kobs represents pseudo-first-order kinetic constant unless otherwise indicated.

The S was 1.83 (>1), and the f₁US and f₁eff in US/Fe⁰/Ο₆C (1.66, 1.50) were > those in US-O₆C (1.22, 1.10), which indicated that: i) US/Fe⁰/Ο₆C had well synergistic effect; ii) The action of US was slightly better than that of Fe⁰/Ο₆C, iii) Compared with dual systems, both action of US and Fe⁰/Ο₆C enlarged in ternary systems (further confirming their synergistic effect).

In addition, the adding of US (or ClO₂⁻) may enrich the varieties and amounts of active substances in the reaction system, which greatly weakened the influence of pollutant concentration, leading to de-order reaction, but Fe⁰/Ο₆C alone seemed to play not obvious role on the above.

3.2. Effects of factors

3.2.1. Effect of pH with/without US

The pH values greatly affected the systems of Fe⁰/Ο₆C, Fe⁰/Ο₆C, US-O₆C, and US/Fe⁰/Ο₆C (Fig. 2a) conveniently, the S and fᵢ (details in Section S6, Eqs. S29-S33) were calculated to evaluate interactions of each O₆C-based system with pseudo-first-order kinetics (R²Adj > 0.990) as below (kobs values (10⁻², min⁻¹) of O₆C, Fe⁰/Ο₆C, US-O₆C, and US/Fe⁰/Ο₆C: 46.82, 51.56, 57.22, and 85.64, respectively).

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Fe$_{0.5}$O$_{2c}$ seemed to be accelerated, but it would decelerate. The greater the alkaline, the more obvious the above-mentioned phenomenon, which could be ascribed to ClO$_2^-$ (alkali activation to form ClO$^*$ being different from acidic reaction to generate ClO$_2$ [20,22]. The S$_2$O$_8^{2-}$ was dominant, thus the alkali role to ClO$_2^-$ could not sustain over the whole reaction process. Due to US polishing (comparing the Fig. 3) and ClO$_2^-$ co-catalysis, the systems actually kept certain ability of treatment, and the passivation of Fe$_{0.5}$ obtained remission.

### 3.2.2. Effect of fluid eddy with/without US

The fluid eddy was realized by mechanical mixing. The liquid height [4] was determined based on the wavelength ($\lambda$) of the applied frequency ($f$), namely, $\lambda = c_s/f$ where $c_s$ was obtained as 1469.60 m s$^{-1}$ with the modified temperature equation (Eq. S34). The site of mechanical mixing was placed at 1/2 (distance from bottom) [5]. In order to describe the inherent attribute of fluid by the action of mechanical mixing, herein, the angular momentum (L), moment of inertia (I), and rotational kinetic energy ($E_{rot}$) were introduced to describe the role of fluid eddy with following Eqs. S35-S37 (Section S7).

By comparison of Fe$_{0.5}$O$_{2c}$ and US/Fe$_{0.5}$O$_{2c}$ systems in Fig. 2b, the fluid eddy both affected the removal of tpm$_{CV}$ varying in three stages (increased $\rightarrow$ decreased $\rightarrow$ restrained), which was partly consistent with the study of [5]. The difference was that the introduction of O$_{2c}$ (especially, ClO$_2^-$) and Fe$_{0.5}$ led to the appearance of restrained stage. Enlarging the fluid eddy made S$_2$O$_8^{2-}$ and ClO$_2^-$ react preferentially to consume themselves by Eq. (17) (sonic catalysis weakening) and accelerate Fe$_{0.5}$ surface oxidation (O$_{2c}$ and O$_2$) and even passivation.

\begin{equation}
S_2O_8^{2-} + 2ClO_2^- \rightarrow 2SO_4^{2-} + 2ClO_2
\end{equation}

(17)

Due to the action of US, the peak-shift (a right-ward shift) occurred in terms of variation of $k_{obs}$. The enhancement in the sonochemical oxidation was attributed mainly to the direct disturbance of the ultrasound transmission and the resulting change in the cavitation-active zone.

### 3.2.3. Effect of initial temperature with US

The temperature affected the performance of US/Fe$_{0.5}$O$_{2c}$ on removing tpm$_{CV}$ ($k_{obs}$ $10^{-3}$ min$^{-1}$) increasing from 85.64 to 309.47 when T increasing from 289 K to 318 K in Fig. 2c). The reaction thermodynamics of tpm$_{CV}$ removal was described by Eyring equation (Eqs. (18) and (19)) and Arrhenius equation (Eq. (20)) to obtain the experimentally derived free energy of activation ($\Delta G^*$), fitted enthalpy ($\Delta H^*$), entropy ($\Delta S^*$) of activation, and activation energy ($E_a$), respectively.

\begin{equation}
k_{obs} = \frac{k_0T}{h}e^{-(\Delta G^*/RT)}
\end{equation}

(18)

\begin{equation}
\Delta G^* = \Delta H^* - T \times \Delta S^*
\end{equation}

(19)

\begin{equation}
k_{obs} = Ae^{-(E_a/RT)}
\end{equation}

(20)

where R is the gas constant (8.314 J·mol$^{-1}$·K$^{-1}$); $k_0$ is the Boltzmann constant (1.38 $\times$ 10$^{-23}$ J·K$^{-1}$); h is the Planck’s constant (6.626 $\times$ 10$^{-34}$ J·s).
J-s); and the above equations were extended in Section S8 (Eqs. S38 and S39).

As shown in Fig. 2c, the liner relation in \( \ln(k_{\text{obs}}/T) \) vs. \( 1/T \) (\( R^2_{\text{Adj}} = 0.984 \)) and \( \ln(k_{\text{obs}}) \) vs. \( 1/T \) (\( R^2_{\text{Adj}} = 0.985 \)). Therefore, the \( \Delta H/\Delta S, E_a, \) and \( A \) were calculated as 31.117 kJ \( \cdot \) mol\(^{-1} \), 156.956 J \( \cdot \) mol\(^{-1} \) \( \cdot \) K\(^{-1} \), and 33.227 kJ \( \cdot \) mol\(^{-1} \), respectively. Therefore, for US/Fe\(_0\)-O\(_{SC}\) system, the relationships (\( \Delta G/\Delta S \) vs. \( T \) and \( k_{\text{obs}} \) vs. \( T \)) were expressed as \( \Delta G/\Delta S = 31.117 + 0.157 T \) (kJ \( \cdot \) mol\(^{-1} \)) and \( k_{\text{obs}} = 9.186 \times 10^4 \exp(-33.227 \times 10^3/RT) \) (min\(^{-1} \)).

3.2.4. Effect of US intensity and frequency

The effects of ultrasonic intensity and frequency (Fig. 2d) were discussed in Section S9.

3.3. Comparative analysis of degradation intermediates with/without US

In terms of US/Fe\(_0\)-O\(_{SC}\), mono-(S1-S13), di-(D1-D9), and tri-(T1-T4) phenyllic compounds (Table S1) were detected. Comparing with double-systems Fe\(_0\)-O\(_{SC}\) and US-O\(_{SC}\), the US/Fe\(_0\)-O\(_{SC}\) seemed to make the intermediates more diversified (Fig. S3) [25], especially, to produce more Cl-adducts (because of ClO\(_2^-\)) [22] and mono-benzene compounds (Fig. 4a) [26]. The detailed analysis was shown in Section S10.

3.4. Assessing US bubble/water interface

The \( k_{\text{obs}} \) could be measured at the macro-level based on the total UCAR solution. However, in order to obtain concrete rate constants for catalyactivation according to effectively reactive volume (\( k_{\text{intr}} \) at bubble–liquid interface zone of cavitation nucleus where the reaction sites for catalysis and activation of US (or Fe\(_0\)) to O\(_{SC}\) (or PDS) mainly located), the mass balance expression, as Wei et al. [27] mentioned, could be used to make a conversion from \( k_{\text{obs}} \) to \( k_{\text{int}} \):

\[
k_{\text{int}} = \frac{V_{\text{total}}}{V_{\text{int}}} \times k_{\text{obs}}
\]

where \( k_{\text{int}} \) was the rate constant at the phase interface, \( V_{\text{total}} \) was the volume of wastewater in treatment, and \( V_{\text{int}} \) was the volume of interfacial shell surrounding cavitation bubbles. Here, assuming the interface thickness was 10% of the radius of the cavitating bubble, an empirical value of \( V_{\text{total}}/V_{\text{int}} \) was obtained from the calculation of [27].

The effective mean temperature of the interfacial region was estimated by \( k_{\text{int}} \) and Arrhenius equation. The Arrhenius parameters (\( \ln A = 36.6 \) and \( E_a = 134 \) kJ\( \cdot \)mol\(^{-1} \)) were referred to the study of thermal dissociation of PS [27,28]. Therefore, at optimal degradation order, the corresponding temperatures of US/Fe\(_0\)-O\(_{SC}\), US-O\(_{SC}\), US/Fe\(_0\)-PDS, and US-PDS were calculated to be 531 K, 535 K, 737 K, and 744 K, respectively, which illustrated that i) Fe\(_0\) had slight effect on the interface temperature; ii) ClO\(_2^-\) lowered the interface temperature. Although the interfacial zone would have a steep temperature gradient between the hot cavitation bubble and the ambient temperature of the bulk solution [27], the calculated temperatures above could be considered as the mean effective temperatures of the interfacial region for O\(_{SC}\) (or PDS)
dissociation (activated by Fe$^0$ under the US role), but $\delta < 1900$ K found in the liquid region surrounding the collapsing cavitation bubbles in alkane solvents at 5 Torr vapor pressure under argon [29,30]. As Misik et al. [31] described, the contaminants with different structures may also influence the interface temperature at sonochemical regions.

In addition, the calculated Ea of US/Fe$^0$-O$_{SC}$ was 33.227 kJ mol$^{-1}$ > 10–13 kJ mol$^{-1}$, indicating that degradation process was dominated by an intrinsic chemical reaction rather than a diffusion process. According to study of Cui et al. [32], the modified Freundlich Isotherm (Eq. (22)) could be applied to describe the relationship between the amounts of molecules partitioning (adsorption) at the interface of cavitation bubble and the initial concentration at equilibrium in US-based systems.

$$\log(n) = \frac{1}{k_f} \log\left(c_{tpm_{CV}}\right) + \log(K_f)$$

where $r_0$ (µM min$^{-1}$) was the decomposed rate of tpm$_{CV}$ (Eq. S40), $k_f$ was called as the reactivity constant, and $K_f$ was the adsorption capacity. According to the calculating of $r_0$, the Section S11 was presented as the general form.

Therefore, according to US/Fe$^0$-O$_{SC}$, the log($r_0$) vs. log($c_{tpm_{CV}}$) had a good linear relation ($R^2_{Adj} = 0.996$, Fig. 5a), and the $k_f$, $k_{o,b}$, indicating the adsorption intensity, was 0.823, while the $K_f$, $b$, as [32] described, represented the capacity of tpm$_{CV}$ molecules adsorbing or partitioning to the reactive zone (gas–liquid interface) and was 0.0442. Similarly, the $k_{o,b}$ was 0.728, while the $K_{o,b}$ was 0.0659 ($R^2_{Adj} = 0.987$). By comparison, the adsorption or partitioning capacity of tpm$_{CV}$ to the reactive zone was increased as the degradation progressed.

### 3.5. Discussion of degradation mechanism induced by US

#### 3.5.1. Contribution of main active species with/without US

The reaction rate of tert butyl alcohol (TBA) vs. *OH (3.8–7.6 × 10$^8$ M$^{-1}$ s$^{-1}$) was much higher than that of TBA vs. SO$_4^{\cdot}$ (4.0–9.1 × 10$^5$ M$^{-1}$ s$^{-1}$) [33], while the reaction rate of methyl alcohol (MA) vs. *OH (9.7 × 10$^8$ M$^{-1}$ s$^{-1}$) was close to that of MA vs. SO$_4^{\cdot}$ (2.5 × 10$^7$ M$^{-1}$ s$^{-1}$) [34]. The results of inhibition reactions of different systems with different scavengers were shown in Fig. 5b and Fig. S4. According to Eq. (23), the relative degrees of dependence in 0 OH or SO$_4^{\cdot}$- could be obtained.

$$\delta_i = \frac{\Delta k_{obs}}{k_{obs}(max)}$$

where $\delta_i$ represented the shielding effects of different systems with different scavengers, $\Delta k_{obs}$, $i$ represented the difference values of different scavengers, and $k_{obs}(max)$ represented the difference values of different scavengers, and $i$ represented MA or TBA.

By comparison of $\delta$ (MA 6 M, TBA 1 M, relatively enough):

- i) $\delta_{MA}$(Fe$^0$-O$_{SC}$) (0.692) > $\delta_{MA}$(O$_{SC}$) (0.691); both generated *OH and SO$_4^{\cdot}$ of O$_{SC}$ and Fe$^0$-O$_{SC}$ could be controlled by 6 M MA.
- ii) $\delta_{TBA}$(Fe$^0$-O$_{SC}$) (0.283) < $\delta_{TBA}$(O$_{SC}$) (0.528) but $k_{obs}$(Fe$^0$-O$_{SC}$) > $k_{obs}$(O$_{SC}$); some other active species (maybe Fe$^{IV}$) existed.
- iii) $\delta_{MA}$(US-O$_{SC}$) (0.805) > $\delta_{MA}$(O$_{SC}$) and $\delta_{TBA}$(US-O$_{SC}$) (0.594) > $\delta_{TBA}$(O$_{SC}$); the introduction of US could promote the system to generate...
more both of ‘OH and SO₄²⁻‘.

\( \delta_{\text{MA}}(\text{US/Fe}^0\text{-O}_\text{SC}) (0.515) < \delta_{\text{MA}}(\text{all the others}) \) but \( \delta_{\text{MA}}(\text{US/Fe}^0\text{-O}_\text{SC}) (0.643) > \delta_{\text{MA}}(\text{all the others}) \): the ‘OH and SO₄²⁻‘ were also the main active species of systems, but the introduction of US tended to promote the active species to transform to more ‘OH.

### 3.5.2. Variation of common Fe and detection of ClO₂ with/without US

The variations of the dissolved Fe (Fe⁰ and Fe⁷), suspending Fe & dissolved Fe, and Fe weight loss (suspending Fe, dissolved Fe, and sedimentary Fe) in US/Fe⁰-O₃Sc were shown at Fig. 5c. The dissolved Fe seemed to exist a dynamic (fluctuant) equilibrium, indicating a ferrickinetics utilization process. By comparisons of Fe⁰ morphology changes among Fe⁰-O₃Sc and US/Fe⁰-O₃Sc (SEM, Fig. 3), and Fe⁰-PDS and US/...
Fe\textsuperscript{0}•-PDS (previous study), US also had the polishing role in US/Fe\textsuperscript{0}•-O\textsubscript{SC}, but more serious Fe-corrosion in O\textsubscript{SC} indicated that ferrikinetics may be not sourced from Fe-self circulation (different from PDS), which is mainly attributed to the ClO\textsubscript{2}– role. ClO\textsubscript{2}/generated-ClO\textsubscript{2} took part in the reaction of Fe, enriching the transformation ways, due to US polishing role, to not only ease Fe\textsuperscript{0}• surface passivation but also accelerate Fe\textsuperscript{0}• surface corrosion (Fig. 3b). But interestingly, without US polishing, the Fe corrosion and formation process of Fe\textsubscript{x}O\textsubscript{y} on Fe\textsuperscript{0}• surface could be observed under enhanced role of O\textsubscript{SC} (Fig. 3a smooth → Fig. 3c rough → Fig. 3d "flower"-like). Meanwhile, the relative intensities of characteristic peaks (three) of Fe\textsuperscript{0}• were also changed under O\textsubscript{SC}.

In addition, the ClO\textsubscript{2} was detected by UV–Vis spectrum (ClO\textsubscript{2} different from other chlorines in water, existing absorption peak around 360 nm) [20,21]. From Fig. 5d, the produced ClO\textsubscript{2} presented throughout the reaction process (gradually increasing) on US-O\textsubscript{SC} by the reaction of Eq. (17). In addition, the anions of S\textsubscript{2}O\textsubscript{8}\textsuperscript{2–}/ClO\textsubscript{2} after reaction consisted of ClO\textsubscript{2}–, Cl\textsuperscript{–}, SO\textsubscript{4}\textsuperscript{2–}, and a few ClO\textsubscript{3}– (Fig. S5) by IC detection.

3.5.3. ROC-HRMS and EPR detection with/without US

3.5.3.1. ROC-HRMS detection. The spin trapping of DMPO•–SO\textsubscript{4}– was the predominant O-centered adduct for SO\textsubscript{4}•–, and the adduct could be protonated and decomposed over time to DMPO–OH [35].

According to US-O\textsubscript{SC} system (at negative mode), the peak at m/z 209 was detected by LTQ and LTQ-Orbitrap, respectively. The MS/MS results of m/z 209 in US-O\textsubscript{SC} system was totally different to those in background, and the peak (m/z 209) in background was weak and sporadic but in US-O\textsubscript{SC} system was stable by parallel experiments, thus indicating that the above peak in background belonged to signal noise but in US-O\textsubscript{SC} system was a new peak. By MS/MS results, the peak at m/z 209 was much close to DMPO•–SO\textsubscript{4}– (Interestingly, the peak at m/z 209 being observed in both positive and negative modes with similar but different MS/MS results). Especially, the fragment “m/z 97” failing to capture MS/MS/MS result) in m/z 209 in negative mode implied an unstable whole structure just like “-OSO\textsubscript{3}(H)” [36–38]. In addition, the unstable peaks at m/z 209(+1, +2) with Δ m/z (peaks at m/z 209(+1, +2) and 112(+1)) around 97(-1, +1), would appear alternately in positive mode (inferring as Scheme 2b).

PN-HRMS analysis also confirmed the presence of a peak at m/z 130 (only in positive modes) by MS/MS results, which could be explained with DMPO•–OH after abstraction of H from another molecule in the sample mixture (observed mass was shifted at + 1 Da relative to the mass of DMPO•–OH [39]) (inferring as Scheme 2a). Previous studies associated m/z 130 with an adduct between the DMPO and -OH [40–42] (Δ m/z 18 between m/z 130 and 112 representing de –OH and -H),

![Figure 5](https://via.placeholder.com/150)

**Fig. 5.** (a) Freundlich degradation isotherms of tpmCV in Fe\textsuperscript{0}•-O\textsubscript{SC} solution media under US irradiation (f 28 kHz, I 30 W⋅L\textsuperscript{-1}), (b) inhibition of different systems via screening agents (6 M MA and 1 M TBA), (c) variation of various Fe concentrations in US/Fe\textsuperscript{0}•-O\textsubscript{SC}, and (d) ClO\textsubscript{2} detection of US-O\textsubscript{SC} by UV–vis spectrum (T 303 K).
which was also observed in EPR in our experiments. As continuous reaction and detection, the peak at \( m/z \) 209 gradually weakened even disappeared, but the peak at \( m/z \) 130 enhanced (compared with Fig. 6b & 6d, the peak could be clearly captured in LTQ-Orbitrap over time). Meanwhile, the ESI with the adding MA (compared with Fig. 6c & 6d) attempted to enhance the effect of peaks appearance.

Scheme 2. Transformations of DMPO-R, -R$^\bullet$ \([35,40–42]\).

Fig. 6. ROC detection by MS or MS/MS (molar ratio \( \text{SO}_4^{2–} / \text{ClO}_2^- \) 5:1, pH without adjustment): (a) \( \text{O}_5\text{SC} \), positive mode, LTQ; (b) US-\( \text{O}_5\text{SC} \), positive mode, LTQ & LTQ-Orbitrap (long-time); (c) US-\( \text{O}_5\text{SC} \), negative mode, LTQ & LTQ-Orbitrap; and (d) US-\( \text{O}_5\text{SC} \), positive mode, LTQ & LTQ-Orbitrap (note: i. operating parameters in Section 2.4; ii. MS/MS results in embedded figure; iii. here presenting comprehensive MS results of continuous period not representing one time point, and continuous period ranging from 3 to 15 min).
but resulted in that peaks at m/z 130 and 209 were weaken, and other peaks remained unchanged or indeed enhanced. Herein, two points (mutual supporting) could be further obtained: i) MA indeed could quench both of SO$_4^{\bullet-}$ and OH$^-$; and ii) peaks at m/z 130 and 209 most likely corresponded to DMPO$^-$OH and DMPO$^-$SO$_4^{\bullet-}$, respectively.

According to OSC system [Fig. 6a], however, the peak (m/z 209) was clearly detected but the peak (m/z 130) was hardly detected, suggesting that the main free radicals of OSC were SO$_4^{\bullet-}$. Actually, because of the Scheme 3 [35], the difficulty of free radical identification was increased [43]. However, by PN-HRMS with ROC detecting, the detection (consumption) was along with the reaction (from "without US originally" to "after introducing US") to gain the variations of peaks at m/z 130 and 209 in real time, illustrating that i) OH$^-$ mainly originated from reaction of US-OSC, not Scheme 3; ii) after introducing US, the type of dominant free radicals tended to be ‘OH in the system and the transformation may be mainly initiated from SO$_4^{\bullet-}$ (being consistent with Section 3.5.1-iii); and iii) the PN-HRMS with ROC detecting (with comparing traditional detecting means, liquid chromatograph/mass spectrometer (LC/MS) or EPR with intermittent sample testing one by one) at a certain degree could avoid the potential misjudgement due to Scheme 3.

But most importantly, the ROC-HRMS seems to prove the radical chain reaction (chain transfer SO$_4^{\bullet-}$ to ‘OH) directly in the reaction process.

3.5.3.2. EPR signals. The EPR signals of different systems (ClO$_2^{\bullet-}$, US-ClO$_2$, OSC with different molar ratio, US/PDS, US-OSC, Fe$^{\text{III}}$/PDS, Fe$^{\text{III}}$/O$_3$, US/Fe$^{\text{II}}$/PDS, US/Fe$^{\text{II}}$/O$_3$) were detected to conduct comparative analyses. Commonly, introducing US would not change the peak shapes of EPR signals (e.g. ClO$_2^{\bullet-}$ vs. US-ClO$_2$, OSC vs. US-OSC, Fe$^{\text{III}}$/O$_3$ vs. US/Fe$^{\text{II}}$/O$_3$, etc.). Differently, single PDS with USO would still have the signals, which was consistent with study of Zamora and Villalena [35], possibly due to -O$^\bullet$(H) and -OH.

The DMPO-X$_7$ ($\bullet$) signal with a single nitrogen ($\alpha^N = 16.50$ G (16.30–16.60), a triplet 1:1:1 [44]) may contribute from the oxidation of DMPO itself, but according to study of Kondo et al. [45], peaks labeled \( \wedge \) may be due to DMPO$^-$H adducts showing a primary triplet ($\alpha^N = 16.50$ G) further split by two secondary hydrogens ($\alpha^H$ = 22.40 G). From Fig. 7a, no ‘OH signal was observed in ClO$_2$ and US-ClO$_2$, however, besides DMPO-X$_7$ signal, the remaining signal DMPO-X$_8$ ($\bullet$) seemed to be closed to ClO$^\bullet$ signal [46] and ClO$^\bullet$-Cl$^\bullet$ signal [47]; in addition, according to description of Ozawa et al. [48], combining with the DMPO-X$_7$ and DMPO-X$_8$, it may contribute from oxidation of spintraps by ClO$_2^\bullet$; while according to the study of Nishikawa et al. [49], ClO$_2$ ($\alpha^N = 2$, 3) radicals led to the above phenomenon. Due to the Cl(III) in ClO$_2$, an intermediate valence [50], it could be explained as ClO$_4$ ($\alpha = 0$–3) radicals contributed to the above-mentioned results.

In terms of OSC and US-OSC, DMPO-X$_7$ signal was almost disappeared, the DMPO$^-$SO$_4^{\bullet-}$ (\( \bigcirc \)) signal ($\alpha^N = 13.78$ G, $\alpha^H = 9.97$ G, $\Delta H_{1/2} = 1.47$ G, $\alpha^H_{1/2} = 0.98$ G (O-centered adducts) and DMPO$^-$OH (\( \bigcirc \)) signal ($\alpha^N = 14.91$ G, a quartet 1:2:2:1) were clearly observed. Specially, in terms of relative peak intensity in same spectrum, the relative DMPO$^-$SO$_4^{\bullet-}$ signals in OSC (S$_4$O$_6^{2-}$/ClO$_2$: 5:1) or after introducing US were more highlighted than that of OSC (1:1) or single PDS, which illustrated co-activation between ClO$_2$ and PDS.

In terms of Fe$^{\text{III}}$/O$_3$ and US/Fe$^{\text{III}}$/O$_3$, the DMPO$^-$SO$_4^{\bullet-}$ and DMPO$^-$OH signals could be still detected but the DMPO-X$_7$ signal was enhanced obviously, which indicated that the introduction of Fe$^{\text{III}}$/O$_3$ accelerated reaction, meanwhile may produce other strongly oxidizing substance besides radicals to result in oxidation of DMPO.

In addition, DMSO as the probe was added the above systems to detect free radicals indirectly [51] due to the reaction of Scheme 4. As the addition of DMSO (Fig. 7b), unfortunately, the CH$_3$OH signal could not be detected; instead, the quartet signal DMPO-X$_7$ (+ & *, near to 1:1:1:1, $\Delta H_{1/2} = a^H = 14.50$ G) appeared (Fig. 7b & 7c). The phenomenon was also observed by Zalibera et al. [52] (the mixtures (DMSO/H$_2$O) with the lower dielectric permittivity significantly influenced the hyperfine coupling constants and the observed signals largely deviated from typical DMPO$^-$OH adduct in aqueous media); but it seemed to be consisted with the study of Jiang et al. [53] (contributing from SO$_4^{\bullet-}$ [54] which had been explained by Ranguevola et al. [55]). And according to study of Zamora and Villalena [35], the above quartet signal may source from SO$_4^{\bullet-}$ (S-centered adducts) and ‘OH with different proportions. In addition, the DMPO$^-$SO$_4^{\bullet-}$ signal was disappeared, which may result from the competition reaction of DMSO vs. SO$_4^{\bullet-}$ [56].

For comparison, the EPR of Fe$^{\text{II}}$/PDS and US/Fe$^{\text{II}}$/PDS was operated (Fig. 7c). The detected signal of Fe$^{\text{II}}$/PDS was matched to the study of Zhu et al. [57] (adopting Fe-base activation), belonging to “DMPOX”, but it seemed to be more closed to composite of DMPO-X$_7$ and DMPO-X$_8$. However, after introducing US, the signals were complex because of the appearance of DMPO-X$_4$ (+, ?). Meanwhile, the introducing of Fe$^{\text{II}}$ would force and make the EPR signals right-shift and complex (Fe$^{\text{III}}$/O$_3$ vs. US/Fe$^{\text{III}}$/O$_3$, Fe$^{\text{II}}$/PDS vs. US/Fe$^{\text{II}}$/PDS).

3.5.4. Exploration of US role to O = Fe$^{\text{IV}}$/V

Catalytic iron center formed a highly oxidizing irox-iron species Fe$^{\text{IV}}$/V (namely, O = Fe$^{\text{IV}}$ and Fe$^{\text{V}}$) [65] which had the reaction with the sulfoxide in Scheme 5 to generate the corresponding sulfone by oxygen atom transfer step [61,62]. Formally, O = Fe$^{\text{V}}$ was best described as an oxo-(Fe(IV)-porphyrin radical cation, namely, O = Fe$^{\text{V}}$(Por)$^+$ (O = Fe$^{\text{IV}}$) [65,66]. The PMSO was used as chemical probe in this study, and the methyl phenyl sulfone (PMSO$_2$) with m/z of 156, 141, 125, etc. in Table 1 was detected by GC/MS (Fig. 4b), which could demonstrate that the existence of Fe$^{\text{IV}}$/V in Fe$^{\text{IV}}$/O$_3$ (tq 9.34 min) and US/Fe$^{\text{IV}}$/O$_3$ (tq 9.32 min) systems with larger proportion. Meanwhile, it was also corresponding to the aforementioned OH$^-$ of Fe$^{\text{IV}}$/O$_3$ (namely, TBA could not effectively inhibit the reduction). In terms of Fe$^{\text{IV}}$/O$_3$ (US/Fe$^{\text{IV}}$/O$_3$), the formation of Fe$^{\text{IV}}$/V as shown in Scheme 6, on the one hand, sourced from conversion reaction between “O-O-$^-$” from (PDS and Fe$^{\text{II}}$/H$_2$O$_2$ (from Fe$^{\text{II}}$) [63,64,66,67]; on the other hand, contributed from adjustment reaction between ClO$_2^\bullet$ and Fe$^{\text{II}}$/III [68], which were operated through a Fe$^{\text{II}}$/Fe$^{\text{IV}}$ cycle [65,66,68]. The kinds and relative peak intensities of the intermediates (especially, PMSO$_2$ in US/Fe$^{\text{IV}}$/O$_3$ were greater than those in Fe$^{\text{IV}}$/O$_3$, implying that US could facilitate the transformation reaction.

In addition, the detailed information of other formed intermediates P1-P4 was shown in Table 1. PMSO (sulfoxide) would undergo the reaction of “Pummerer rearrangement” to transfer to Ph-thiol (unstable in oxidation system), then further turn into Ph-S-Ph (P2) and Ph-S-S-Ph (P3), meanwhile, P2 would be oxidized into P4 (the detailed process could be seen in Fig. 4e) [69]. In addition, PMSO under the role of ClO$_4$ would turn into P1 via substitution.

In terms of Fe$^{\text{III}}$/O$_3$ and US/Fe$^{\text{III}}$/O$_3$, the DMPO$^-$SO$_4^{\bullet-}$ and DMPO$^-$OH signals could be still detected but the DMPO-X$_7$ signal was enhanced obviously, which indicated that the introduction of Fe$^{\text{III}}$/ accelerated reaction, meanwhile may produce other strongly oxidizing substance besides radicals to result in oxidation of DMPO.

By detected results and literatures, the possible mechanism of degradation process in terms of US/Fe$^{\text{III}}$/O$_3$ was inferred and proposed as follows: at neutral pH, Fe$^{\text{IV}}$ would be as the important intermediate in Fenton like reaction [71], but Fe$^{\text{IV}}$ would reduce the contribution in ZVI/PDS as result of the decrease of available Fe$^{\text{III}}$ [72]. However, US/Fe$^{\text{II}}$/O$_3$ at near-neutral pH still kept well activity, therefore, the introduction of ClO$_2^\bullet$ not only cooperated with PDS to generate co-activation
process (SO$_4^{\cdot-}$ and ClO$_2^-$) but also promoted the production and circulation of Fe$^{IV}$ in presence of Fe$^{0}$ (with the cycle of Fe$^{II}$, Fe$^{III}$, O = Fe$^{IV}$, and O = Fe$^{IV}$). Meanwhile, US could play another role on the circulation by polishing the surface of Fe$^{0}$ to provide the fresh ZVI source. Importantly, US would also promote
and calculation of US cavitation model involving bubble–liquid dy-
mamics should be further enhanced.

In this study, the EPR was applied to detect the radicals species of
different systems for comparison. The ROC-MS (substitution of EPR) was
a preliminary attempt to track the radicals transformation. The US
apparent roles to removal reaction were expounded (e.g. de-order re-
action, widening the applied range of pH and fluid eddy). The inherent
roles of US were stated as follows:

i) US could induce ClO₂ to co-activate PDS, low the bubble-water
interface temperature, and promote the production and circulation of
Fe³⁺/Fe⁰; ii) US could enrich the kinds of contaminant intermediates,
polish the surface the Fe⁰ to avoid surface passivation to provide fresh
Fe source, promote the production and transformation of O₂ = Fe⁰/III, and
push free radical chain transfer from SO₄²⁻ to OH⁻.

In addition, the US/Fe³⁺/O₃ may reveal other roles: relatively
economical treating cost and potential (ClO₂) disinfection.

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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Appendix A. Supplementary data

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