

Enhanced effects of reducing agent on oxalate chelated Fe(II) catalyzed percarbonate system for benzene degradation

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ABSTRACT

The addition of hydroxylamine hydrochloride (HAH), ascorbic acid (ASC), sodium ascorbate (SAS) to the OA-Fe(II)/SPC system could promote the generation of HO[•] by accelerating Fe(II)/Fe(III) recycles and H₂O₂ decomposition. The enhancement of HAH on HO[•] generation surpasses ASC and SAS in the OA-Fe(II)/SPC system. The generation of O₂^{•-} was also enhanced by HAH, ASC and SAS, and more significant promotion of O₂^{•-} generation was observed with ASC and SAS addition. More effective benzene removal was achieved in an OA-Fe(II)/SPC system with suitable HAH, ASC and SAS addition, compared to the parent system. Excessive HAH, ASC or SAS had a negative effect on benzene removal. Results of scavenger tests showed that HO[•] is indeed the dominant free radical for benzene removal in every system, but the addition of HAH, ASC and SAS increased the contribution of O₂^{•-} to benzene degradation. HAH, ASC and SAS enhanced OA-Fe(II)/SPC systems could be well utilized to acidic and neutral conditions, while HCO₃⁻, high concentration of HA and alkaline conditions were not favorable to benzene removal. Moreover, the addition of HAH, ASC and SAS are conducive to benzene removal in actual groundwater, and HAH was the optimal reducing agent for the enhancement of the OA-Fe(II)/SPC system.

Key words: benzene degradation, groundwater remediation, percarbonate, reactive oxygen species, reducing agent

HIGHLIGHTS

- Benzene removal performance in an RA-OA-Fe(II)/SPC system was investigated.
- HAH is more conducive to HO[•] generation than ASC and SAS.
- Significant promoted generation of O₂^{•-} was observed with ASC and SAS addition.
- HAH, ASC and SAS weakened negative effects of the solution matrix on benzene removal.
- HAH, ASC and SAS are conducive to benzene removal in actual groundwater.

1. INTRODUCTION

Benzene, a toxic and hazardous compound of the BTEX family, has been listed as a USEPA priority pollutant and its maximum contaminant level was limited at 5 µg L⁻¹ under the Safe Drinking Water Act (ATSDR 2004; USEPA 2009). This noxious compound can frequently be detected in contaminated groundwater and soils, and behaves as a significant menace to human health owing to its neurological damage and high carcinogenicity (Fu *et al.* 2015). In recent years, many effective methods have been applied for remediation of benzene and other organic pollutants from groundwater and soil (Johnson 1998; Siegrist *et al.* 2011; Muhammad *et al.* 2014; Neriah & Paster 2016). *In situ* chemical oxidation (ISCO) has been regarded as one of prominent and well-known technologies for contaminated groundwater and soils remediation because of its high cleanup efficiency. Several oxidants, such as Fenton's reagent (Ojinnaka *et al.* 2012), persulfate (Petri 2010), peroxymonosulfate (Ahn *et al.* 2016), permanganate (Mahmoodlu *et al.* 2014), ozone (Hu & Xia 2017), and percarbonate (Fu *et al.* 2016; Zang *et al.* 2017) have been applied in the ISCO process. Sodium percarbonate (2Na₂CO₃·3H₂O₂, SPC) can be dissociated to H₂O₂ and Na₂CO₃ when dissolved in water, providing a Fenton-like reaction. Besides, numerous

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advantages of SPC compared to H_2O_2 , such as wider pH range applicability, effective contaminants degradation, and alkaline properties have attracted the attention of many researchers.

Effective benzene removal was achieved in the Fe(II)/SPC system; however, the rapid consumption of the soluble Fe ion was unfavorable to continuous degradation of benzene (Fu *et al.* 2015). Miao *et al.* and Fu *et al.* utilized chelating agents to keep the Fe ion in soluble form, thereby enhancing the degradation of organic contaminants (Fu *et al.* 2016; Miao *et al.* 2015a). Furthermore, it was reported that high reactivity of chelated-Fe(II) with SPC could improve the utilization of SPC, which eventually improved the contaminant's degradation (ElShafei *et al.* 2010). Fe(II) was also consumed rapidly within several minutes, and chelated-Fe(III) was the governing form of soluble Fe ion in the chelated-Fe(II)/SPC system (Fu *et al.* 2016; Zang *et al.* 2017). This impeded the further degradation of contaminants because of the low reactivity between chelated-Fe(III) and SPC. Thus, looking for reducing agents (RA) to enhanced Fe(II)/Fe(III) recycles is a favorable method for the promotion of contaminant degradation.

Zou *et al.* found hydroxylamine (HAH) could accelerate the recycling of Fe(III)/Fe(II) and then improve benzoic acid degradation in the Fe(II) catalyzed peroxymonosulfate system (Zou *et al.* 2013). Zhang *et al.* indicated that ascorbic acid (ASC) could not only enhance the reduction of Fe(III) to Fe(II) but also maintain the Fe ion in a soluble form (Zhang *et al.* 2017). This technique strengthened the generation of reactive oxygen species for further trichloroethylene removal in an Fe(III)-catalyzed calcium peroxide system. Fukuchi *et al.* reported that HAH, ASC, gallic acid, oxalic acid (OA), humic acid (HA), and p-hydroquinone could enhance the removal of 2,4,6-tribromophenol in a heterogeneous Fenton-like system catalyzed by iron-loaded natural zeolite (Fukuchi *et al.* 2014). The HAH had the most significant promoting effect of 2,4,6-tribromophenol removal among these several reducing agents. Enhanced effects of HAH, sodium ascorbate (SAS), sodium thiosulfate, ASC, and sodium sulfite (SS) on trichloroethylene removal were also observed in an Fe(II)-catalyzed per-sulfate system (Wu *et al.* 2015).

The above discussion concluded that reducing agents can be applied to alleviate the drawback of rapid Fe(II) consumption in a chelated-Fe(II)/SPC system, then improve the oxidation ability of the chelated-Fe(II)/SPC system for benzene removal. Therefore, we exploited the RA-OA-Fe(II)/SPC system to (i) investigate the effects of several reducing agents on the generation of free radicals by radical probe compounds and electron paramagnetic resonance (EPR) analysis, (ii) demonstrate the efficiency of benzene removal in RA-OA-Fe(II)/SPC systems, (iii) depict the contribution of free radicals to benzene removal by scavengers tests, (iv) valiate the effects of solution matrix on benzene removal and the applicability of RA-OA-Fe(II)/SPC systems for benzene removal in actual groundwater.

2. MATERIALS AND METHODS

2.1. Materials

Benzene (>99.7%), ferrous sulfate heptahydrate (99.0%), oxalic acid (>99.0%), sodium sulphate (99.0%), sodium bicarbonate (99.5%), l-ascorbic acid (>99.0%), sodium nitrate (99.0%), methanol (99.8%), sodium chloride (99.5%), carbon tetrachloride (99.5%), nitrobenzene (99.0%), sodium sulfite (>99.0%), chloroform (99.0%), methanol (99.8%), hydroxylamine hydrochloride (>98.5%), isopropyl alcohol (99.5%) and sodium ascorbate (>99.0%) were achieved from Aladdin (Shanghai, China). Sodium percarbonate (98%) and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Acros Organics (Shanghai, China) and Sigma (Shanghai, China), respectively. 1,10-phenanthroline monohydrate (98%), potassium biphthalate (99.0%) and humic acid (fulvic acid >90%) were achieved from Shanghai Jingchun Reagent Ltd Co. (Shanghai, China). H_2SO_4 (0.1 M) and NaOH (0.1 M) was applied to adjust initial solution pH. Ultrapure water was produced by a Milli-Q water process (Classic DI, ELGA, Marlow, U.K.). The actual groundwater was obtained from a 10 m deep well in Minhang, Shanghai, China. Its characteristics were as follows: pH: 7.5, total organic carbon: 11.5 mg/L, SO_4^{2-} , Cl^- , NO_3^- and HCO_3^- concentrations (mg/L): 90.7, 53.6, 6.7 and 101.4, Fe(II) and total Fe ion concentration (mg/L): 1.0 and 1.4.

2.2. Experimental procedures

The stock solutions were prepared by dissolving pure non-aqueous phase liquid benzene, CT and NB in Milli-Q water or actual groundwater for 1 h. Then desired concentrations of benzene, CT and NB of 1.0, 0.15 and 1 mM respectively were obtained by diluting certain volume stock solutions into a 250 mL cylindrical glass reactor with a magnetic stirrer. The temperature during the reaction process was controlled at 20 °C by the flow of temperature-controlled water in the reactor's jacket. The experimental setup is shown in Supplementary Material (Fig. S1). Benzene, CT and NB were conducted in blank tests without addition of other reagents to validate the effect of volatilization during degradation. Predetermined dosages of

reducing agents, Fe(II), OA, and other demanded chemicals were added into the reactor for 10 min mixing prior to addition of SPC to initiate the reaction. 2.5 mL samples were taken periodically from the reactor into a headspace vial with 1.0 mL methanol for benzene analysis by headspace-gas chromatography (HS-GC). Finally, 1.0 mL DMPO solution (8.84 mM), a radical trapping agent was mixed with periodical samples (0.5 mL) for 1 min and placed in a capillary tube to detect the intensity of free radicals in EPR analysis.

2.3. Analytical methods

One headspace-gas chromatograph (Agilent 6890N, Palo Alto, CA) equipped with an auto-sampler (COMBI-PLA, CTC, Switzerland), an HP-5 column (30-m length, 0.32-mm I.D., 0.25- μ m thickness) and a flame ionization detector (FID) were applied for benzene concentration analysis.

Headspace conditions include incubation temperature (50 °C), agitator speed (500 rpm), incubation time (5 min) and syringe temperature (60 °C). The GC oven temperature follows the process: an initial 40 °C was held for 2 min, increased to 80 °C at the rate of 30 °C/min, and held for 1 min. The temperatures of the injector and detector were fixed at 150 and 250 °C, respectively. N₂ is carrier gas with a flow rate of 3.0 mL/min. A 500 μ L sample from the upper space was injected with splitless ratio. The concentrations of CT and NB were analyzed by a gas chromatograph (Miao *et al.* 2015a, 2015b). The intensity of free radicals was detected by EPR, more details of EPR analytical conditions are shown in the Supplementary Material. Fe(II) and total soluble Fe ions were determined with the application of the 1,10-phenanthroline method (Tamura *et al.* 1974). H₂O₂ was measured with the TiCl₄ spectrophotometric method (Eisenberg 1943). The solution pH was measured by a pH meter (Mettler-Toledo DELTA 320, Greifensee, Switzerland).

3. RESULTS AND DISCUSSION

3.1. Effects of reducing agent on the production of free radicals

Based on our previous work, both HO \cdot and O₂ \cdot^- exists in the OA-Fe(II)/SPC system (Fu *et al.* 2016). To explore the effect of reducing agent (RA) on HO \cdot and O₂ \cdot^- generation in the OA-Fe(II)/SPC system, nitrobenzene (NB) and carbon tetrachloride (CT) were applied as oxidant and reductant probes, respectively (Buxton *et al.* 1988). Identical initial concentrations of RA, Fe(II), OA, and NB were set at 1 mM, and 2 mM of SPC and 0.05 mM of CT were applied in the probe test.

3.1.1. Effects of reducing agent on HO \cdot generation

Figure 1 shows very little loss of NB due to volatilization in the blank test. But a significant removal of NB was noticed, showing the presence of HO \cdot in the OA-Fe(II)/SPC system, which is consistent with our previous work (Fu *et al.* 2016).

Compared to 13.6% final NB removal in the simple OA-Fe(II)/SPC system, 70, 36, and 29% of final NB removal were achieved with the addition of HAH, ASC, and SAS to the OA-Fe(II)/SPC system, respectively. Furthermore, as shown in Figure 2, HO \cdot intensity at 2 min detected by EPR technique were stronger individually with SAS, ASC, HAH addition to

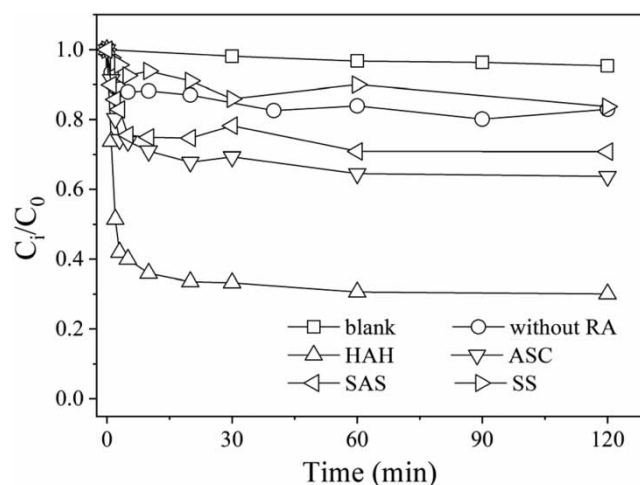


Figure 1 | Effect of reducing agents on NB degradation in OA-Fe(II)/SPC system ([NB]₀ = [RA]₀ = [OA]₀ = [Fe(II)]₀ = 1 mM, [SPC]₀ = 2 mM, T = 20 ± 0.5 °C).

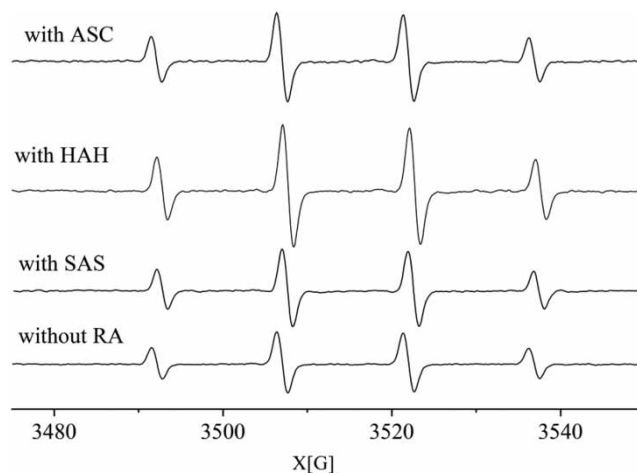


Figure 2 | The intensity of HO[•] in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC, SAS-OA-Fe(II)/SPC and OA-Fe(II)/SPC systems ([NB]₀ = [Fe(II)]₀ = [RA]₀ = [OA]₀ = 1 mM, [SPC]₀ = 2 mM, T = 20 ± 0.5 °C).

OA-Fe(II)/SPC system. These indicated that HAH, ASC and SAS could promote the production of HO[•], and HAH was the optimal reducing agent on HO[•] generation. However, a decrease of NB removal rate to 16.3% was observed with SS addition, indicating that SS was not conducive to HO[•] generation.

To investigate the mechanism of HAH, ASC, SAS and SS on the generation of HO[•] in the OA-Fe(II)/SPC system, concentration changes of total soluble Fe ions, Fe(II) and H₂O₂ were measured in each system, as shown in Tables 1 and 2. The

Table 1 | Total Fe ion and Fe(II) concentrations in various RA-OA-Fe(II)/SPC systems

Time (min)	Total Fe ion concentration (mM)					Fe(II) concentration (mM)				
	Without RA	HAH	ASC	SAS	SS	without RA	HAH	ASC	SAS	SS
0	0.991	0.992	1.012	0.996	1.01	0.994	0.972	0.997	1.011	0.988
2	0.900	0.923	0.926	0.909	0.418	0.167	0.252	0.224	0.177	0.092
5	0.869	0.911	0.871	0.884	0.423	0.147	0.204	0.138	0.136	0.044
10	0.856	0.921	0.903	0.829	0.383	0.103	0.217	0.146	0.143	0.053
30	0.807	0.901	0.876	0.853	0.410	0.065	0.184	0.158	0.137	0.058
60	0.872	0.948	0.930	0.905	0.327	0.072	0.227	0.145	0.138	0.035
120	0.830	0.970	0.924	0.875	0.302	0.059	0.300	0.209	0.135	0.040

^a [NB]₀ = [Fe(II)]₀ = [RA]₀ = [OA]₀ = 1 mM, [SPC]₀ = 2 mM, T = 20 ± 0.5 °C.

Table 2 | H₂O₂ concentration in various RA-OA-Fe(II)/SPC systems

Time (min)	Blank	Without RA	HAH	ASC	SAS	SS
0	0.009	0.019	0.019	0.021	0.017	0.005
1	2.767	2.329	1.247	1.008	0.404	2.168
2	2.959	2.306	1.497	1.192	0.857	2.002
5	2.933	2.262	0.762	0.888	0.777	2.071
8	2.932	2.205	0.360	0.788	0.642	2.051
10	2.945	2.104	0.378	0.797	0.607	1.972
30	2.922	1.821	0.198	0.413	0.274	1.854
60	2.805	1.694	0.114	0.255	0.153	1.858
120	2.638	1.600	0.064	0.174	0.130	1.732

^a [NB]₀ = [Fe(II)]₀ = [RA]₀ = [OA]₀ = 1 mM, [SPC]₀ = 2 mM, T = 20 ± 0.5 °C.

results elucidated that addition of HAH, ASC, and SAS to the OA-Fe(II)/SPC system, the total soluble Fe ion concentrations are higher than its concentration in the parent system, indicating that HAH, ASC and SAS is conducive to maintaining Fe in a soluble form. This improves the catalytic ability of the system, and enhances the generation of HO[•] to a certain extent. NB removal in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems within 2 min were 48.6%, 19.8% and 14.3%, respectively, higher than its removal (10.7%) in the OA-Fe(II)/SPC system, indicating more HO[•] generation within 2 min in RA-OA-Fe(II)/SPC systems. This is due to the higher Fe(II) concentration caused by RA within 2 min, which reacts with H₂O₂ rapidly in RA-OA-Fe(II)/SPC systems. The Fe(II) concentration in the HAH-OA-Fe(II)/SPC system decreases from 0.972 to 0.252 mM within 2 min, but is still higher than 0.167 mM in the OA-Fe(II)/SPC system. This resulted in the rapid consumption of H₂O₂, the concentration of which decreased to 1.497 mM from 2.959 mM, thereby producing more HO[•] in the HAH-OA-Fe(II)/SPC system (Table 2). It is noted that the remaining H₂O₂ were 1.497, 1.192, and 0.857 mM, showing 1.462, 1.767, and 2.102 mM H₂O₂ were consumed in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively. Compared to its corresponding NB degradation (48.6%, 19.8% and 14.3%), a higher consumption of H₂O₂ can be deduced in ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems than in HAH-OA-Fe(II)/SPC system.

The H₂O₂ concentration decreased from 2.306 to 1.60 mM (120 min). Meanwhile, the Fe(II) concentration in the OA-Fe(II)/SPC system decreased to 0.059 mM continuously, in comparison to a total soluble Fe ion concentration of 0.83 mM. This indicated that Fe(III) was the main form of soluble Fe ion at this stage, which can react with H₂O₂ slowly, leading to the higher generation of HO[•] after 2 minutes. Fe(II) concentration remained at a high level after 2 min in RA-OA-Fe(II)/SPC systems. Fe(II) concentrations at 120 min were 0.3, 0.209 and 0.135 mM with addition of HAH, ASC and SAS to the OA-Fe(II)/SPC system, respectively, significantly higher than that in the OA-Fe(II)/SPC system. This indicates that the addition of HAH, ASC and SAS, as strong reducing agents, accelerates Fe(II) regeneration from Fe(III), leading to the improvement of the catalytic ability of the system. The corresponding concentrations of H₂O₂ decreased to 0.064, 0.174, and 0.13 mM, respectively in all systems. This indicated that the enhanced regeneration of Fe(II) during this stage promotes the production of HO[•], which can be reflected by the continuous degradation of NB. It should be noted that the highest Fe(II) concentration and lowest concentration of remaining H₂O₂ were observed in HAH-OA-Fe(II)/SPC system. This validated the strongest reducing ability of HAH on Fe(II)/Fe(III) cycles, resulting in the optimal enhancement of HO[•] generation.

On the contrary, total soluble Fe ion concentration is significantly lower in SS-OA-Fe(II)/SPC system. This indicates that the addition of SS is not conducive to the presence of the soluble Fe ion. In addition, the lowest Fe(II) concentration and largest H₂O₂ remaining amount showed the weak reducibility of SS on Fe(II)/Fe(III) cycles that further affected HO[•] generation.

3.1.2. Effects of reducing agent on O₂⁻ generation

Figure 3 showed the degradation of CT, which is a probe compound of O₂⁻ in the RA-OA-Fe(II)/SPC and OA-Fe(II)/SPC systems. Compared to the negligible volatilization of CT in blank test, 14.6% CT removal indicates the presence of O₂⁻ in

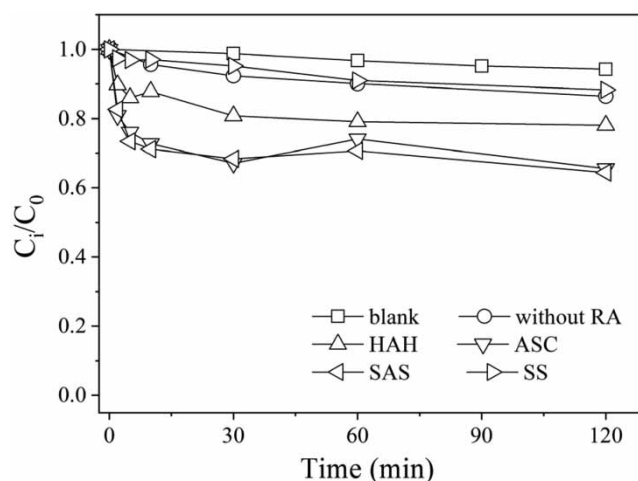


Figure 3 | Effect of reducing agents on CT degradation in OA-Fe(II)/SPC system ($[RA]_0 = [Fe(II)]_0 = [OA]_0 = 1$ mM, $[SPC]_0 = 2$ mM, $[CT]_0 = 0.05$ mM, $T = 20 \pm 0.5$ °C).

OA-Fe(II)/SPC system. CT removal rate reached 22, 34, and 36% in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively, much greater than in OA-Fe(II)/SPC system. This indicates the addition of HAH, ASC and SAS can enhance $O_2^{\cdot-}$ generation. The effect on CT removal was partly observed with the addition of SS to OA-Fe(II)/SPC system.

In ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC system, ASC and SAS can dissociate into ascorbate anion ($C_6H_7O_6^-$) when releasing one hydrogen ion and sodium ion, respectively. $C_6H_7O_6^-$ can react with HO^{\cdot} to yield oxidized dehydroascorbic acid radical ($C_6H_6O_6^{\cdot-}$) which could react with dissolved oxygen (O_2) to generate $O_2^{\cdot-}$ via one electron-transfer. In HAH-OA-Fe(II)/SPC system, NH_2OH may reduce Fe(III) to Fe(II) via one-electron transfer, leading to the generation of H_2NO^{\cdot} radical. H_2NO^{\cdot} radical can further deprotonate to $HNO^{\cdot-}$ radical ($pK_a = 12.6 \pm 0.3$). Then $O_2^{\cdot-}$ would also be generated via one electron-transfer between $HNO^{\cdot-}$ radical and O_2 at a rate constant of $2.2 \times 10^8 M^{-1}s^{-1}$. These may be the reason for the enhanced generation of $O_2^{\cdot-}$ in the RA-OA-Fe(II)/SPC systems (Lind & Merényi 2006; Lin & Liang 2013; Yang *et al.* 2015; Zhou *et al.* 2018).

In summary, the addition of HAH, ASC, and SAS can promote the generation of HO^{\cdot} and $O_2^{\cdot-}$. The enhanced effect of HAH on HO^{\cdot} generation is significantly better than that of ASC and SAS, compared to on $O_2^{\cdot-}$ generation.

3.2. Benzene degradation performance in RA-OA-Fe(II)/SPC systems

Benzene degradation in various RA-OA-Fe(II)/SPC and OA-Fe(II)/SPC systems with different RA dosages were conducted with benzene, OA, Fe(II) and SPC concentrations of 1, 1, 1 and 2 mM, respectively. The results are shown in Figure 4. The optimal enhanced effect of RA on benzene removal was observed with HAH, ASC and SAS addition at the concentration of 1 mM. Compared to the 48.9% benzene removal rate in the OA-Fe(II)/SPC system, the addition of HAH, ASC, and SAS increased the benzene removal rate to 87.0%, 84.5%, and 81.9%, respectively. This indicated HAH, ASC and SAS can significantly enhance the ability of OA-Fe(II)/SPC system for benzene removal, and the enhanced effect of HAH, ASC, and SAS increased individually. This is due to the enhanced generation of HO^{\cdot} and $O_2^{\cdot-}$ in RA-OA-Fe(II)/SPC systems, which was discussed in section 3.1. However, SS inhibited the degradation of benzene, which reduced benzene removal rate to 39.4% from 48.9%.

It can be noted that benzene removal was inhibited to a certain extent with the increase in concentration of HAH, ASC, and SAS to 8 mM. This indicated excessive HAH, ASC, and SAS had a negative effect on benzene degradation. This is due to the scavenging effect of higher RA dosages which can react with HO^{\cdot} at a high rate constant, leading to scavenge HO^{\cdot} . For example, HAH can react with HO^{\cdot} at a rate of $5.0 \times 10^8 M^{-1}s^{-1}$ when solution pH is 4, and large amount of Cl^- along with HAH addition can also consume HO^{\cdot} via a series of propagation reactions (Yu & Barker 2003; Chen *et al.* 2011). This leads to the decrease of benzene removal to 61.9% at HAH concentration of 8 mM. Compared with HAH, a high concentrations of ASC and SAS have a more significant inhibitory effect on benzene degradation. ASC and SAS can react with HO^{\cdot} at a rate of

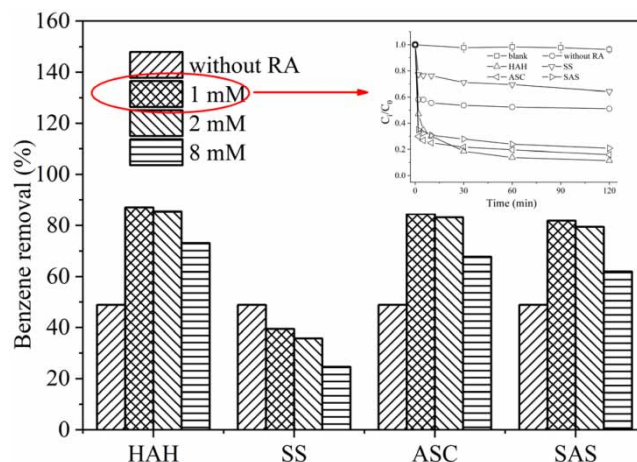


Figure 4 | Effect of reducing agent dosages on benzene degradation in various RA-OA-Fe(II)/SPC systems ($[Fe(II)]_0 = [OA]_0 = [Benzene]_0 = 1$ mM, $[SPC]_0 = 2$ mM, $T = 20 \pm 0.5$ °C). Inset figure: Benzene degradation performance in various RA-OA-Fe(II)/SPC systems with 1 mM reducing agents addition ($[RA]_0 = [Fe(II)]_0 = [OA]_0 = [Benzene]_0 = 1$ mM, $[SPC]_0 = 2$ mM, $T = 20 \pm 0.5$ °C).

$1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ and $1.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, respectively, which are significantly higher than the reaction rate between HAH and HO^\bullet . The reaction products are more likely to result in further consumption of HO^\bullet (Buxton *et al.* 1988). Besides, the increase of pH caused by high SAS concentration is also not conducive to the presence of the soluble Fe ion, weakening the catalytic ability of the system, and thus inhibiting benzene removal.

As shown in the inserted Figure of Figure 4, rapid benzene removal occurred in the first 2 min, and minor benzene removal was observed later in the OA-Fe(II)/SPC system. This is due to the rapid generation and consumption of HO^\bullet in the OA-Fe(II)/SPC system at the start. The continuous generation of HO^\bullet after 2 min in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems leads to the further degradation of benzene.

To clarify the role of HO^\bullet and O_2^- on benzene removal in RA-OA-Fe(II)/SPC systems at RA concentrations of 1 mM, scavenger tests were conducted in this study. 100 mM isopropanol (ISP) and 50 mM chloroform (CF) were employed as the scavengers of HO^\bullet and O_2^- , respectively. The contribution of HO^\bullet and O_2^- to benzene removal was analyzed by comparing the degradation of benzene in the system with or without scavengers. The results are shown in Figure 5. In OA-Fe(II)/SPC, HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, 42.4, 73.3, 69.3 and 72.7% decrease of benzene removal were observed with the addition of ISP. This indicated that HO^\bullet is indeed the dominant free radicals for benzene removal in every system. Even so, 6.5, 15.2, 14.6, and 6.5% of benzene were still degraded by OA-Fe(II)/SPC, HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively, showing that a non- HO^\bullet oxidation pathway may exist. The addition of CF to OA-Fe(II)/SPC, HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, benzene removal decreased to 3, 6.8, 6.7 and 5.2% respectively. This indicated that O_2^- participated in the benzene removal, and HAH, ASC, and SAS increased the contribution of O_2^- to benzene degradation.

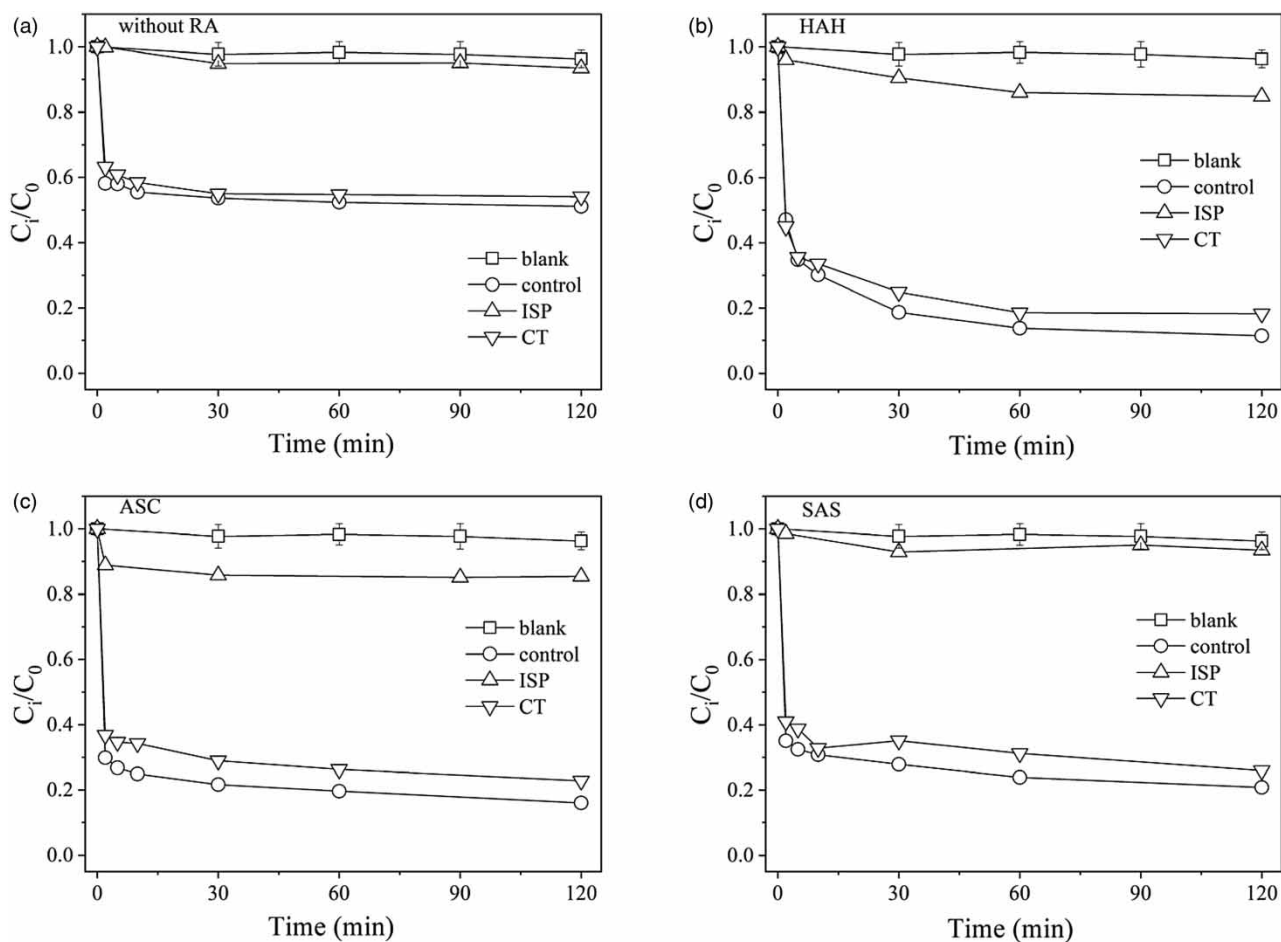


Figure 5 | Scavengers effect on benzene degradation in various RA-OA-Fe(II)/SPC systems: (a) without RA, (b) HAH, (c) ASC, (d) SAS ($[\text{RA}]_0 = [\text{Fe(II)}]_0 = [\text{OA}]_0 = [\text{Benzene}]_0 = 1 \text{ mM}$, $[\text{SPC}]_0 = 2 \text{ mM}$, $T = 20 \pm 0.5 \text{ }^\circ\text{C}$).

3.3. Effects of solution matrix on benzene removal in RA-OA-Fe(II)/SPC systems

In this section, the effects of solution matrix, including SO_4^{2-} , Cl^- , NO_3^- , HCO_3^- , initial solution pH and humic acid (HA) on benzene removal in RA-OA-Fe(II)/SPC systems were demonstrated thoroughly. The concentration of RA, benzene, OA, Fe(II), and SPC were fixed at 1, 1, 1, 1, and 2 mM, respectively. SO_4^{2-} , Cl^- and NO_3^- had negligible effects on benzene removal with the tested concentration ranges of 1–100 mM (data not shown). The effects of HCO_3^- , initial solution pH and HA on benzene removal are shown in Figure 6.

3.3.1. Effects of initial solution pH

Figure 6(a) shows the effect of various initial solution pH on benzene removal in RA-OA-Fe(II)/SPC systems to illustrate the applicable pH range of RA-OA-Fe(II)/SPC systems. Compared to the control test, which was not adjusted the initial solution pH, benzene removal slightly increased to 90.9% from 87.0% when adjusted the initial solution pH to 3 in the HAH-OA-

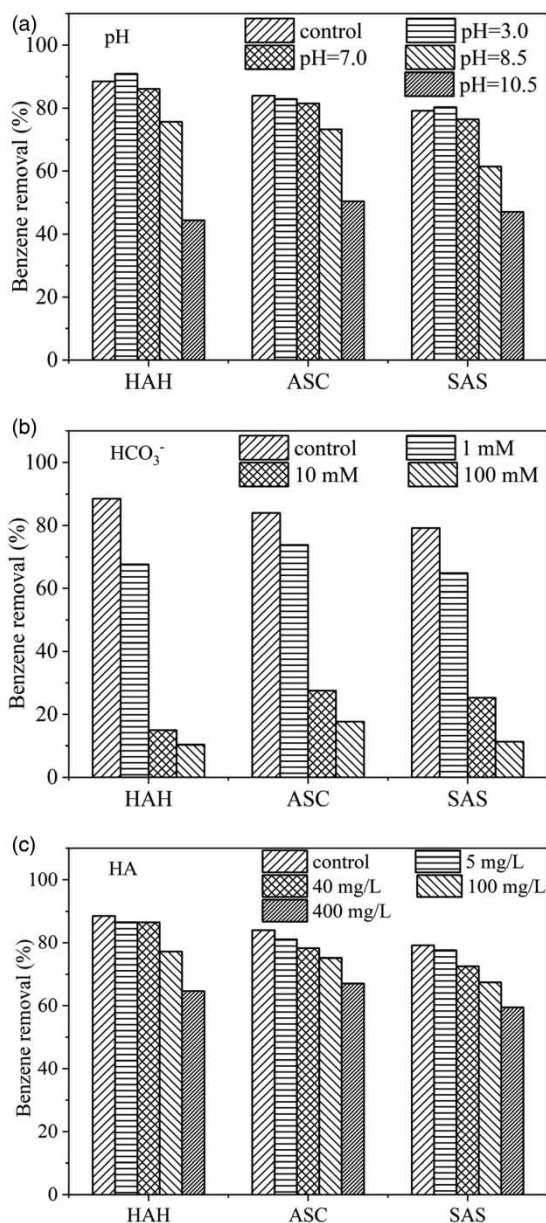


Figure 6 | Effect of solution matrix conditions on benzene removal in various RA-OA-Fe(II)/SPC systems ($[\text{RA}]_0 = [\text{Fe(II)}]_0 = [\text{OA}] = [\text{Benzene}]_0 = 1 \text{ mM}$, $[\text{SPC}]_0 = 2 \text{ mM}$, $T = 20 \pm 0.5 \text{ }^\circ\text{C}$).

Fe(II)/SPC system. In addition, benzene removal of 90.9% was achieved within 10 min when the initial solution pH is 3 (data not shown), much faster than 69.9% in the HAH-OA-Fe(II)/SPC system without adjusting the initial solution pH. This indicates acidic condition benefits to benzene removal in the HAH-OA-Fe(II)/SPC system. This may be due to the increase of catalyst concentration caused by acidic conditions, which can retard the precipitation of the Fe ion. Furthermore, when the pH is lower than 5.96, NH_3OH^+ is the main form of hydroxylamine, and the reaction rate between NH_3OH^+ and HO^\bullet is less than $5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. This can reduce the invalid consumption of HO^\bullet (Buxton *et al.* 1988; Zou *et al.* 2013).

Less than 2% inhibition of benzene removal was observed at pH = 7, indicated the applicability of HAH-OA-Fe(II)/SPC system at neutral conditions. However, benzene removal was inhibited when the initial solution pH was adjusted to 8.5 and 10.5, showing more significant effect at higher pH. Benzene removal decreased to 44.4% from 87.0% at pH = 10.5, leading to the inhibition rate of 49% $((87.0 - 44.4)/87.0)$. High solution pH can promote the precipitation of the Fe ion, reducing the catalytic ability of the system. The higher decomposition of H_2O_2 to H_2O and O_2 under high pH conditions can also lessen the generation of HO^\bullet . Besides, the major form of hydroxylamine under high pH conditions is NH_2OH , which can react with HO^\bullet faster, leading to more invalid consumption of HO^\bullet (Chen *et al.* 2011; Zou *et al.* 2013).

Slight effects of initial solution pH from 3.0 to 7.0 were observed in ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, indicating these two systems are suitable for acidic and near neutral conditions. But with the increase of pH to 10.5, benzene removal was inhibited significantly and its removal rate decreased to 83.9% and 79.2% from 50.5% and 47.1% in ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively. This indicated that high pH conditions also adversely affect benzene removal in ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems. Nevertheless, the inhibition rates are 40% $((84.5 - 50.5)/84.5)$ and 42.5% $((81.9 - 47.1)/81.9)$ in ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively, which are significantly lower than 49% in HAH-OA-Fe(II)/SPC system. It is speculated that ASC and SAS can not only reduce Fe(III) to Fe(II), but also act as a chelating agent to maintain Fe ion in a soluble form. This can weaken the effect of the initial pH on Fe ions, thereby lowering the negative effect of pH on benzene removal.

In summary, HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems can be well applied to acidic and neutral conditions for benzene removal, even though strong alkaline conditions can weaken their applicability to a certain extent.

3.3.2. Effects of HCO_3^-

It is reported that HCO_3^- is adverse to organic contaminants removal in multi-chemical oxidation systems because of the following reasons: (a) the increase of pH with HCO_3^- addition; (b) the formation of solid precipitates between soluble metal ions and HCO_3^- ; (c) scavenging effect on HO^\bullet (Liang *et al.* 2006; Gu *et al.* 2011; Fu *et al.* 2015). Therefore, effects of HCO_3^- on benzene removal were studied in RA-OA-Fe(II)/SPC systems at various concentration levels of 1.0, 10 and 100 mM.

As shown in Figure 6(b), 1 mM of HCO_3^- could inhibit the degradation of benzene in every RA-OA-Fe(II)/SPC system. The removal rate of benzene decreased from 87.0%, 84.5% and 81.9% to 67.7%, 73.9% and 64.8%, with the inhibition rate of 22.2%, 12.5% and 20.9% in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems, respectively. The increase in the concentration of HCO_3^- , a significant inhibition of benzene removal was observed in every RA-OA-Fe(II)/SPC systems. When the HCO_3^- concentration was increased to 100 mM, the benzene removal rate dropped to 10.6, 17.7 and 11.3%, and the inhibition rate reached to 87.8, 79.0 and 86.2%, respectively. This indicated HCO_3^- had an adverse effect on RA-OA-Fe(II)/SPC systems for benzene removal, and the adverse effect enhanced with the increasing concentration of HCO_3^- . It is noted that the inhibition rate of HCO_3^- decreased sequentially in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems with the same concentration of HCO_3^- , indicating that the ability of HAH, SAS and ASC to overcome the adverse effects of HCO_3^- increased in succession.

3.3.3. Effects of HA

Natural organic matters (NOM) exists ubiquitously in soil and groundwater, which can affect contaminants degradation. NOM was substituted by HA which is a main fraction of NOM in this study. Figure 6(c) shows the effects of HA with different concentrations (0–400 mg/L) on benzene removal in every RA-OA-Fe(II)/SPC system. Low concentrations of HA (0–40 mg/L) had a slight effect on benzene removal in every system, while high concentrations of HA (100 and 400 mg/L) inhibited benzene removal. When the concentration of HA is 400 mg/L, the benzene removal reduced to 64.6, 67.1, and 59.4% in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC, and SAS-OA-Fe(II)/SPC systems, respectively.

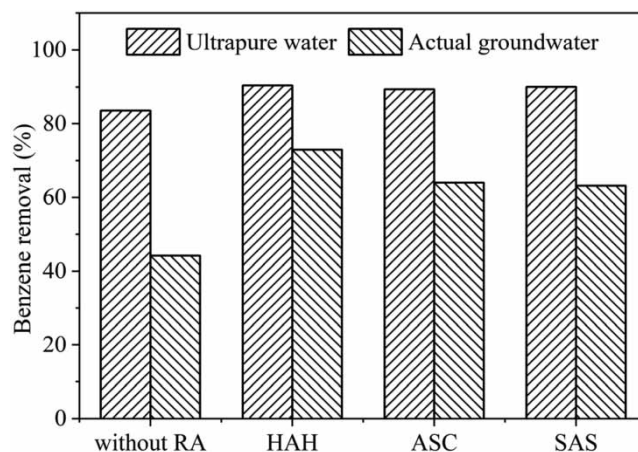


Figure 7 | Benzene degradation performance in actual groundwater by various RA-OA-Fe(II)/SPC systems ($[RA]_0 = [Benzene]_0 = 1$ mM, $[Fe(II)]_0 = [SPC]_0 = 2$ mM, $[OA]_0 = 4$ mM, $T = 20 \pm 0.5$ °C).

The inhibition of HA for benzene degradation in these systems could be explained from the following two aspects. In one hand, the presence of HA had a scavenging effect for HO^\bullet via Equation (1) and competed with benzene to consume HO^\bullet (Bogan & Trbovic 2003; Westerhoff *et al.* 2007; Khan *et al.* 2016). On the other hand, HA could react with dissolved Fe to generate a stable complex that furtherly inhibited the regeneration of Fe(II), thus decreasing the removal of benzene (Wang & Lemley 2004).



3.4. Benzene removal performance by RA-OA-Fe(II)/SPC systems in actual groundwater

The above results indicate that solution matrix has a significant effect on RA-OA-Fe(II)/SPC systems for benzene removal. In view of the complexity of actual groundwater, benzene degradation in actual groundwater by RA-OA-Fe(II)/SPC systems was investigated to evaluate the applicability of every system *in situ* remediation process. The concentrations of RA, benzene, Fe(II), SPC and OA were 1, 1, 2, 2, and 4 mM, respectively.

Figure 7 showed that benzene removal rate of OA-Fe(II)/SPC system in ultrapure water and actual groundwater were 83.6% and 44.2%, respectively. This indicates actual groundwater significantly affects benzene removal in the OA-Fe(II)/SPC system. Compared to 90.4, 89.4, and 90.0% benzene removal of HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC system in ultrapure water, benzene removal rate decreased to 73.0, 64.0, and 63.2% in actual groundwater, respectively. This indicated the actual groundwater had adverse effects on RA-OA-Fe(II)/SPC systems for benzene removal. However, benzene removal of every RA-OA-Fe(II)/SPC system is still higher than 44.2% in OA-Fe(II)/SPC system, indicating the addition of HAH, ASC and SAS benefits to benzene removal in actual groundwater. The highest benzene removal in HAH-OA-Fe(II)/SPC system showed HAH was the optimal reducing agents for the enhancement of OA-Fe(II)/SPC system.

4. CONCLUSIONS

In this study, the application of OA-Fe(II)/SPC systems enhanced by RA for benzene removal in groundwater was investigated. The addition of HAH, ASC and SAS could enhance the generation of HO^\bullet and $O_2^{\bullet-}$. The enhanced effect of HAH on HO^\bullet generation is superior to that of ASC and SAS, while ASC and SAS showed more significant promotion of $O_2^{\bullet-}$ generation than HAH. Benzene removal rate increased with suitable addition of HAH, ASC and SAS, while excessive addition of HAH, ASC and SAS was harmful to further improvement of benzene removal. SS was not conducive to HO^\bullet and $O_2^{\bullet-}$ generation leads to inhibition of benzene degradation. Scavenging studies showed that HO^\bullet were the principal radicals for benzene removal in HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems. Meanwhile, the addition of HAH, ASC and SAS increased the role of $O_2^{\bullet-}$ in benzene removal. The effects of SO_4^{2-} , NO_3^- , Cl^- and low concentration of HA on benzene removal were negligible. The effective benzene removal by HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and

SAS-OA-Fe(II)/SPC systems were observed in acidic and neutral conditions. On the other hand, the alkaline conditions and the presence of HCO_3^- and high concentration of HA were not beneficial to benzene removal in these systems. Furthermore, effective benzene removal by HAH-OA-Fe(II)/SPC, ASC-OA-Fe(II)/SPC and SAS-OA-Fe(II)/SPC systems was obtained in actual groundwater, indicating HAH, ASC and SAS enhanced OA-Fe(II)/SPC systems are applicable for benzene-contaminated groundwater remediation.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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