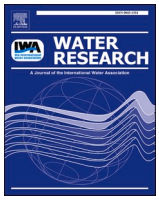
Water Research 258 (2024) 121760

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres



Small concentrations, big results: μM addition of photoactive iron oxides with PMS, PDS, or H_2O_2, leads to enhanced removal of viruses at near-neutral pH

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ARTICLE INFO

Keywords:
Iron oxides
Peroxydisulfate (PDS)
Peroxymonosulfate (PMS)
Near neutral pH
Virus inactivation

ABSTRACT

The photo-Fenton process is effective for pathogen removal, and its low-cost versions can be applied in resource-poor contexts. Herein, a photo-Fenton-like system was proposed using low concentrations of iron oxides (hematite and magnetite) and persulfates (peroxymonosulfate – PMS, and peroxydisulfate - PDS), which exhibited excellent inactivation performance towards MS2 bacteriophages. In the presence of bacteria, MS2 inactivation was inhibited in H_2O_2 and PDS systems but promoted in PMS-involved systems. The inactivation efficacy of all the proposed systems for mixed bacteria and viruses was greater than that of the sole bacteria, showing potential practical applications. The inactivation performance of humic acid-incorporated iron oxides mediating photo-Fenton-like processes was also studied; except for the PMS-involved system, the inactivation efficacy of the H_2O_2- and PDS-involved systems was inhibited, but the PDS-involved system was still acceptable (< 2 h). Reactive species exploration experiments indicated that ·OH was the main radical in the H_2O_2 and PDS systems, whereas $^1O_2$ played a key role in the PMS-involved system. In summary, hematite- and magnetite-mediated persulfate-assisted photo-Fenton-like systems at low concentrations can be used as alternatives to the photo-Fenton process for virus inactivation in sunny areas, providing more possibilities for point-of-use drinking water treatment in developing countries.

1. Introduction

Drinking water safety remains a problem worldwide, particularly in less developed countries. Pathogens in water can cause illnesses such as polio, cholera, hepatitis A, and diarrhea. It is estimated that each year, approximately 829,000 people die from diarrhea, which is caused by poor sanitation and consumption of substandard drinking water (McGuigan et al., 2012; Rodríguez-Chueca et al., 2019). Although conventional disinfection techniques, such as chlorination and ozonation, can effectively disinfect pathogens, the high operational costs (for these contexts) and toxic disinfection byproducts (DBPs) formed during the disinfection process must be considered (Meireles et al., 2016; López-Vinent et al., 2021). More importantly, in some remote rural areas of developing countries where there are no drinking water treatment facilities, cheap, effective, safe, easy-to-operate, and sustainable point-of-use water disinfection approaches should be developed.

Advanced oxidation processes (AOPs) can produce strongly reactive oxygen species and are considered potential alternatives to inactivate pathogens in water (Cibati et al., 2022; López-Vinent et al., 2021). Among various AOPs, the Fenton process is one of the most widely studied because of its strong oxidation ability and simple operation. In recent years, the photo-Fenton process has attracted considerable

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https://doi.org/10.1016/j.watres.2024.121760
Received 21 December 2023; Received in revised form 25 March 2024; Accepted 8 May 2024
Available online 9 May 2024

attention because of its excellent oxidation performance and the possibility of using solar energy as the driving force. Generally, photo-Fenton processes are used for the treatment of contaminants (Malato et al., 2009); however, there are considerably fewer studies on this process for pathogen inactivation.

Therefore, the use of iron (hydro)oxides with good chemical stability as iron sources to fuel the heterogeneous photo-Fenton process seems to be a feasible alternative, as previous studies have shown that iron-bearing minerals, such as hematite, magnetite, goethite, and ferrihydrite, can oxidize organic contaminants over a wide pH range when combined with H_2O_2 (Lin and Gurol, 1998; Pignatello et al., 2006). Nieto-Juarez et al. used four commercial iron (hydro)oxides to catalyze H_2O_2 peroxide bond breakage under solar light irradiation for MS2 bacteriophage inactivation, and found that the virus could be effectively inactivated by heterogeneous Fenton-like processes at neutral pH (Nieto-Juarez and Kohn, 2013). Similarly, in a previous study, under near-neutral pH conditions, iron-oxide-mediated heterogeneous photo-Fenton processes exhibited good performance for MS2 bacteriophage inactivation in wastewater, even with low amounts of iron oxides and H_2O_2 (Giannakis et al., 2017). These cases indicate that iron oxides are good alternatives to soluble iron, providing more possibilities for practical application of the photo-Fenton process.

Although the iron oxide-mediated photo-Fenton process can achieve interesting oxidation performance, it still has significant drawbacks. For instance, H_2O_2 decomposes easily and its liquid form leads to inconvenient transportation and storage owing to security concerns, which narrows the application scope of the technique. Hence, persulfates (peroxymonosulfate (PMS) and peroxydisulfate (PDS)) can be considered as alternative oxidants for the photo-Fenton-like process because they are solids at ambient temperatures and are more stable than H_2O_2. This is one of the main reasons why sulfate radical ($SO_4^{\bullet-}$)-based AOPs have recently attracted much attention. Besides, $SO_4^{\bullet-}$ has a higher redox potential ($SO_4^{\bullet-}$: $E^0 = 2.5–3.1$ V vs NHE, •OH: $E^0 = 1.9–2.7$ V vs NHE), a longer lifetime compared with •OH (30–40 μs), and generally, SR-AOPs are less affected by pH value (Nie et al., 2015; Berruti et al., 2023).

Several studies have reported that persulfate-based AOPs can effectively remove organic pollutants from water (Nie et al., 2015; Berruti et al., 2023). Therefore, this technique can be considered as an effective alternative to conventional disinfection approaches. Considering that various studies have used H_2O_2 to enhance photocatalysis, PMS and PDS are also good electron acceptors, aiding the separation of the photo-induced electron-hole pairs of the semiconductor to produce more reactive species for virus inactivation. However, virus inactivation using persulfate-based AOPs has not been extensively studied (Marjanovic et al., 2018). To the best of our knowledge, no study has investigated and compared virus inactivation by heterogeneous photo-Fenton processes using iron oxides in photo-Fenton-like processes with PMS and PDS as oxidants. The inactivation efficacy and mechanism of this technique remain unclear and require further in-depth investigation.

Therefore, this study aimed to study and compare the virus inactivation performance of iron oxides that mediate photo-Fenton-like processes using PMS and PDS as oxidants under near-neutral conditions. Hematite and magnetite, the two most common iron oxides found in natural environments, were selected as representatives of iron oxides and were synthesized using a simple method under laboratory conditions. The MS2 bacteriophage was chosen as the model virus because of its easy purification and rapid cultivation; however, it is not pathogenic to humans (Kuzmanovic et al., 2006) and has been frequently used as a model virus in many studies on microorganism inactivation, owing to its resistance to light-mediated disinfection. The inactivation performances of the different systems were assessed and compared to clarify the role of iron oxides, either as semiconductors or iron sources, in photo-Fenton-like processes. The influence of bacterial competition on inactivation performance was also assessed. In addition, it has been reported that the natural organic matter (NOM) is conducive to the complexation and solubilization of iron (Ruales-Lonfat et al., 2015), and the humic acid (HA, one of the most representative NOM) modified iron oxides has been studied in the heterogeneous photo-Fenton process for organic pollutant removal (Gonçalves et al., 2020), while its performance in heterogeneous photo-Fenton-like process for pathogens inactivation in water remains unclear, considering a series of advantages of NOM, this issue is worth exploring. Moreover, to better understand the mechanism of virus inactivation, the reactive species involved in each combined system were identified using quenching experiments and EPR tests. Finally, the underlying inactivation mechanism was proposed.

2. Materials and methods

2.1. Chemicals and reagents

Potassium peroxymonosulfate (Oxone™, Sigma-Aldrich, Switzerland), sodium persulfate (NaS_2O_8, Sigma-Aldrich, Switzerland), and hydrogen peroxide (H_2O_2, 30% w/v, Sigma-Aldrich, Switzerland) were used as the oxidants. Isopropanol (IPA, Merck, Spain), *tert*-butanol (TBA, Merck, Spain), deuterium oxide (D_2O, Merck, Spain), and superoxide dismutase (SOD, Merck, Spain) were used to identify reactive species. Hydrochloric acid (HCl, 36.5 %; Merck, Spain) and sodium hydroxide (NaOH, 98 %; Merck, Spain) were used to adjust the solution pH. All chemicals were reagent grade or above, and all solutions used in the experiments were prepared in purified water using a Millipore Elix 3 system equipped with a Progard filter (Millipore AG, Zug, Switzerland).

2.2. Preparation and characterization of iron oxides

The specific preparation and characterization methods of the iron oxides are presented in Text S1.

2.3. Microorganisms and quantification methods

The MS2 bacteriophage (DSMZ 13,767) and its *E. coli* host bacteria (DSMZ5695, antibiotic-resistant, 2 mg/L streptomycin) were obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ, Germany). Preparation of the MS2 bacteriophage, including propagation and purification, followed a procedure described elsewhere (Ortega-Gómez et al., 2015), and cultivation of the bacteria was based on a process similar to that used for *E. coli* K-12 (Giannakis et al., 2015).

The double agar layer method (DAL; EPA Method 1602, 2001) was employed to count the number of infective MS2 bacteriophages. Plates were incubated at 37 °C for 24 h, and the formed plaques were counted (PFU mL^{-1}) manually. The spread plate technique was used for bacterial enumeration, and the standard plate counting method was used to count the bacterial colonies after 24 h of incubation at 37 °C. The detection limit of these methods was 10 PFU mL^{-1}.

2.4. Inactivation experiments

The inactivation experiments were conducted in a 500 mL beaker with 150 mL of sterile carbonate buffer solution (CBS, 877 mg NaCl, and 8 mg $NaHCO_3$ dissolved in 1000 mL of water, pH = 8), 150 μL MS2 stock (10^9 PFU mL^{-1}) was added to the beaker, and the initial concentration of the virus suspension in the beaker was approximately 10^6 PFU mL^{-1}. Subsequently, 1 mg/L of iron oxides and 10 mg/L of oxidants from the freshly prepared stock solutions were successively added to the beaker under constant stirring.

The photocatalytic inactivation experiments were initiated by turning on the UVA light lamps. An array of TLD-type lamps (BLB, Philips) was employed as a UV light source (wavelength range: 320–400 nm, max emission at 365 nm, light irradiance at the sample: 9.55 ± 0.5 W/m^2), the emission spectrum of the UV light is displayed in Fig. S1. The reaction temperature did not exceed 35 °C. During the experiments, the samples were collected at predetermined times and immediately diluted with CBS. All experiments were performed in triplicate, and the

confidence level of the results was greater than 95 % (ANOVA analysis).

3. Results and discussion

3.1. Characterization of the iron oxides

The structure, morphology, and composition of the iron oxides were presented in Text S2 and Fig. S2.

3.2. MS2 inactivation performance in heterogeneous photo-Fenton(-like) processes

3.2.1. Hematite/Magnetite-driven H_2O_2-assisted processes

As shown in Fig. 1, within 120 min of reaction time, UVA alone led to approximately only 1.9-log U inactivation, which could be because the destruction of the virus genome by UVA impaired its infectivity to some extent (Wigginton et al., 2012). When the two iron oxides were exposed to light, the inactivation efficiency of the hematite-mediated system improved, achieving 2.8-logU inactivation, whereas the inactivation efficiency of the magnetite-mediated system was suppressed and only 1.2-log U inactivation was attained. The dark adsorption of viruses on hematite/magnetite alone was negligible (Fig. S3); hence, changes in the inactivation rate could be mainly related to

(1) The isoelectric points (IEP) of hematite and magnetite were 8.8 and 6.6, respectively (Table S1). Thus, under the experimental conditions (CBS, pH 8), hematite and magnetite were positively and negatively charged, respectively. However, the surface of MS2 is negatively charged (Giannakis et al., 2017); owing to the electrostatic attraction, the interactions between hematite and MS2 are higher, and the adsorption of viruses on the surface of the semiconductor is essential for efficient inactivation based on a pure photocatalytic process. In contrast, owing to the electrostatic repulsion effect, there were fewer interactions between magnetite and virus.
(2) Hematite has a larger specific surface area (62 m^2/g) than magnetite (10 m^2/g) (Table S1), which provides more photoreactive sites for related reactions and reactive species generation.
(3) Iron-MS2 complexes were formed during the reaction. Previous study has reported that owing to the interaction between the negatively-charged MS2 virions and positively-charged Fe cations, a 'virus-metal interaction' would occur in the iron oxide semiconductor photocatalytic process, where light-sensitize iron-MS2 complex undergoes ligand-to-metal charge transfer (LMCT) process (Ortega-Gómez et al., 2015). Owing to the difference in the surface charges of the two iron oxides and MS2, as well as the larger specific surface area, there are more chances for hematite and MS2 to form an iron-MS2 complex, thus leading to higher inactivation than magnetite.

H_2O_2 alone resulted in 6-log U inactivation within 20 min, which could be attributed to the direct oxidative stress exerted by H_2O_2. The inactivation efficacy was further improved when H_2O_2 was combined with UVA, with total inactivation achieved within 10 min. Based on Eq. (1), a synergistic effect was observed in the UVA/H_2O_2 system, with a calculated factor of 2.1, which could be ascribed to the fact that under UVA irradiation, the virus becomes more sensitive to oxidation (Anan-thaswamy and Eisenstark, 1976).

$$S_{oxidant/UVA} = \frac{k_{oxidant/UVA}}{k_{oxidant} + k_{UVA}} \quad (1)$$

When iron oxides were combined with H_2O_2, inactivation occurred, but it was 10 min longer than that in the sole H_2O_2 exposure (20 min) in both magnetite/H_2O_2 and hematite/H_2O_2 systems. This demonstrates that under the experimental conditions, the heterogeneous Fenton and Fenton-like processes did not contribute to virus inactivation, possibly because H_2O_2 was consumed in non-effective reactions (e.g., surface Fe^{3+} reduction). When the light was turned on, the inactivation efficacy of both heterogeneous photo-Fenton processes dramatically increased, with 6-log U inactivation achieved in both systems within 5 min (shortest sampling time), indicating that the two iron oxides-mediated heterogeneous photo-Fenton processes worked in this study.

3.2.2. Hematite/Magnetite-driven PMS-assisted processes

In the case of PMS groups, as shown in Fig. 2, PMS alone attained 2.6-log inactivation within 120 min, and the inactivation was enhanced when UVA was irradiated, with the total inactivation time reduced by 30 min, which could be ascribed to the synergistic effect of PMS and UVA light, as the calculated synergy factor was 1.7, based on Eq. (1). When combining iron oxides and PMS in the dark, the Fenton-like systems did not work; the inactivation efficiencies of both iron oxide-mediated systems were only 2.3-log and 1.9-log, respectively, indicating that iron oxides could not activate PMS effectively in the dark under the

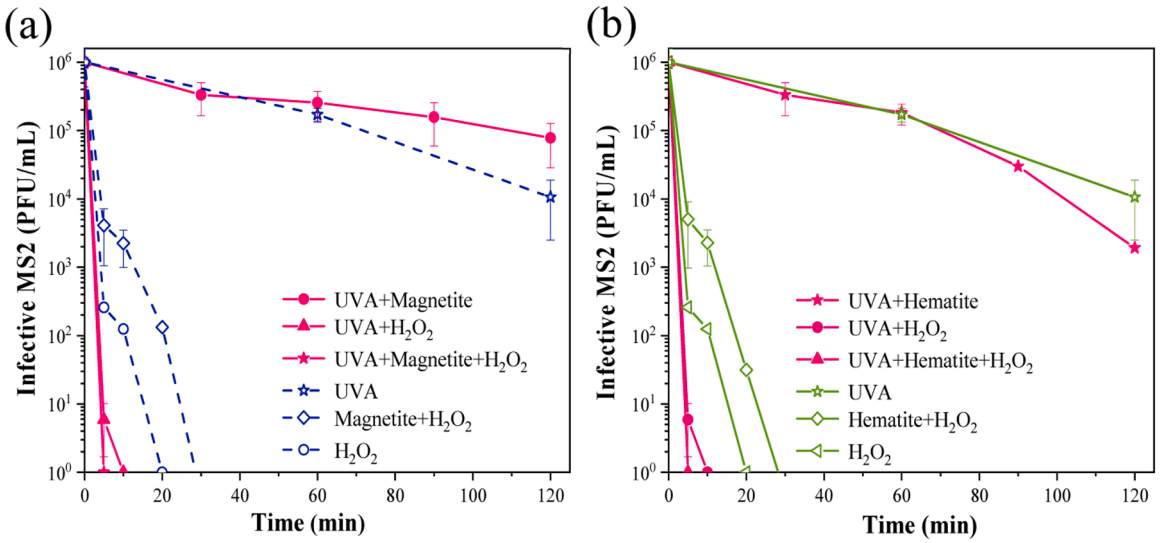

Fig. 1. MS2 bacteriophage inactivation by iron oxide in the presence or absence of UVA and H_2O_2 for (a) magnetite and (b) hematite. Experimental conditions: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [pH]=8. Experiments were performed in triplicate (standard error of ~ 5 %).

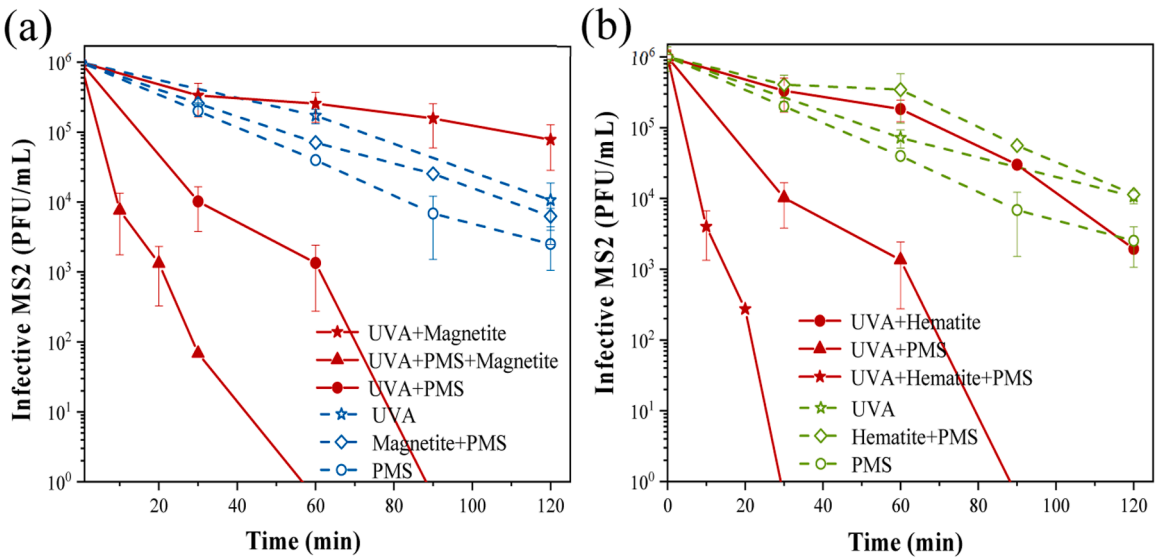

Fig. 2. MS2 bacteriophage inactivation by iron oxide in the presence or absence of UVA and PMS for (a) magnetite and (b) hematite. Experimental conditions: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [pH]=8. Experiments were performed in triplicate (standard error of ~ 5 %).

experimental conditions. When the light was turned on, the inactivation efficacy of the proposed Fenton-like systems showed a significant improvement, with total inactivation achieved within 60 min (magnetite group) and 30 min (hematite group), demonstrating that under UVA irradiation, the two iron oxides successfully mediated the heterogeneous photo-Fenton-like processes for MS2 inactivation.

3.2.3. *Hematite/Magnetite-driven PDS-assisted processes*

For the PDS group, it can be seen in Fig. 3 that under the experimental conditions, PDS alone could barely inactivate the virus. Although this process is thermodynamically similar to that of H_2O_2 (close potentials), apparently the kinetics governing the reaction of the viral capsid components with PDS are slower than those of H_2O_2. When irradiated by UVA light, the inactivation performance of PDS was enhanced, with approximately 2.9-log U inactivation attained within 120 min. According to Eq. (1), the calculated synergistic impact factor was 1.3. Thus, the improved inactivation efficacy of the UVA/PDS system was attributed to the synergistic effect of PDS and UVA light, as discussed previously. Similar to H_2O_2 and PMS, the Fenton-like systems using iron oxides and PDS were also not effective in killing the virus, implying that under experimental conditions, iron oxides could not activate PDS. When all three factors were present, the inactivation efficacy significantly improved, with total inactivation achieved within 90 min (magnetite group) and 60 min (hematite group). Based on previous study, the degradation contributions of different processes could be obtained by calculating the ratio of the reaction rate constants (Song et al., 2020). In this work, although the contribution of iron oxides as photocatalysts to corresponding photo-Fenton-like processes was only 12.7 % (magnetite, 0.02 min^{-1} (UVA/magnetite)/0.158 min^{-1} (UVA/magnetite/PDS)) and 20.8 % (hematite, 0.05 min^{-1} (UVA/hematite)/0.24 min^{-1} (UVA/-magnetite/PDS)), respectively, the synergistic factors (based on Eq. (2)) of the two photo-Fenton-like processes were 2.7 (magnetite group) and 3.9 (hematite group), respectively, indicating that effective synergy occurred in both iron oxide-mediated photo-Fenton-like processes.

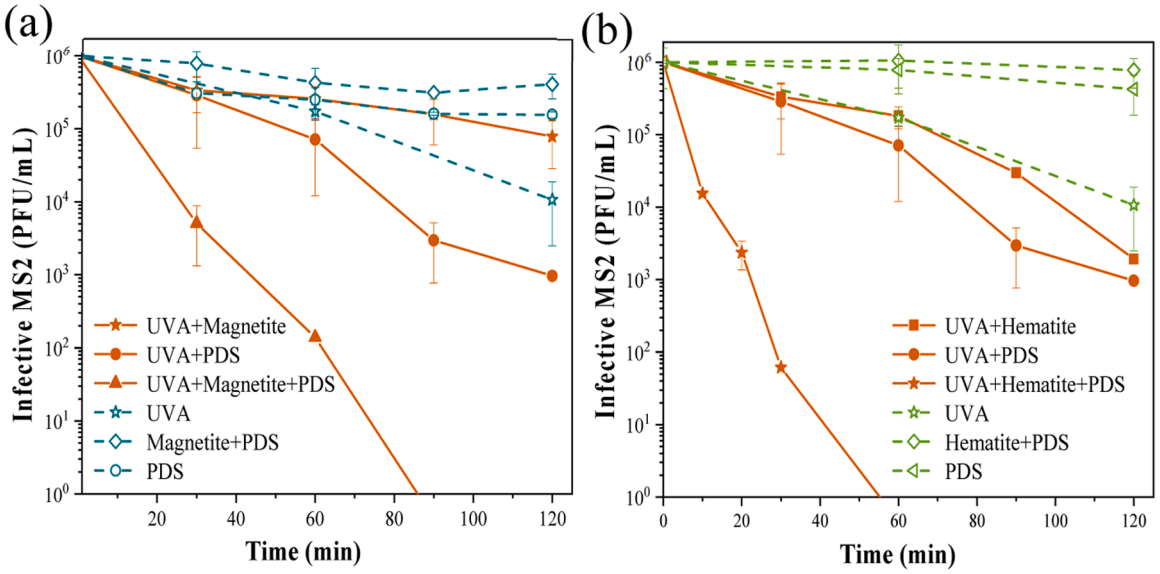

Fig. 3. MS2 bacteriophage inactivation by iron oxide in the presence or absence of UVA and PDS for (a) magnetite and (b) hematite. Experimental conditions: [iron oxide]=1 mg/L, [oxidant]=10 mg/L, [pH]=8. Experiments were performed in triplicate (standard error of ~ 5 %).

$$S_{iron\ oxides/oxidants/UVA} = \frac{k_{iron\ oxides/oxidants/UVA}}{k_{iron\ oxides} + k_{oxidants} + k_{UVA}} \quad (2)$$

3.2.4. Delineating the constructed heterogeneous photo-Fenton(-like) process

Before further analyzing the inactivation process, a point worthy of mentioning is the ineffective dark processes. The reason may be ascribed to that under the pH condition of this study (pH=8), the two iron oxides were easily agglomerate since the IEP of hematite and magnetite 8.8 and 6.6, respectively, the formed clumps may be 'engulfing' viruses and preventing them from inactivation by oxidants. In addition, the experimental matrix is CBS, which can partially scavenge the produced hydroxyl radicals to form carbonate radicals and active chlorine species, which are longer-living but weaker and more selective.

The improved inactivation efficiencies of the investigated heterogeneous photo-Fenton-like system can be mainly attributed to the following factors:

(1) Under UV light irradiation, iron oxides produce photogenerated electron-hole pairs (Eqs. (3-4), as electron acceptors, the three oxidants could react with the electrons generated in the conduction band (CB) of iron oxides; on one hand, the photogenerated electron-hole pairs were separated; on the other hand, the oxidants were also activated to produce the reactive species for MS2 inactivation (Eqs. (5–7)).

(2) Iron-oxidant complexes are formed when iron oxides contact with oxidants (Ruales-Lonfat et al. 2015). These complexes are photosensitive and can drive a ligand-to-metal charge transfer (LMCT) process to generate reactive species for MS2 inactivation. Note that, although no dissolved iron was detected using the spectrophotometric ferrozine method, this could be attributed to the filtering of the samples prior to testing. During a series of redox reactions between iron oxides and oxidants, Fe^{2+} and Fe^{3+} will be generated and exist on the surface of iron oxides in form of 'surface iron', the reaction mechanism at the solid-liquid interface can be considered similar to that in solution, this provides a great possibility for the formation of iron-complex.

(3) Fe^{2+} and Fe^{3+} on the surface of iron oxides can react with oxidants to produce reactive species (Eqs. (8–13)) ($\equiv$ indicates a reaction on the surface of the oxides) (López-Vinent et al., 2022).

$$Fe_2O_3 + h\nu \rightarrow Fe_2O_3\ (e^- + h^+) \quad (3)$$

$$Fe_3O_4 + h\nu \rightarrow Fe_3O_4\ (e^- + h^+) \quad (4)$$

$$e^-_{CB} + H_2O_2 \rightarrow OH^- + \cdot OH \quad (5)$$

$$e^-_{CB} + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \quad (6)$$

$$e^-_{CB} + HSO_5^- \rightarrow SO_4^{\bullet-} + \cdot OH \quad (7)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + HO^- + \cdot OH \quad (8)$$

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{2+} + HO_2\cdot + H^+ \quad (9)$$

$$\equiv Fe^{2+} + S_2O_8^{2-} \rightarrow \equiv Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \quad (10)$$

$$\equiv Fe^{3+} + S_2O_8^{2-} + 1/2O_2 \rightarrow \equiv Fe^{2+} + SO_4^{\bullet-} + SO_4^{2-} + FeO^{2+} \quad (11)$$

$$\equiv Fe^{2+} + HSO_5^- \rightarrow \equiv Fe^{3+} + SO_4^{\bullet-} + OH^- \quad (12)$$

$$\equiv Fe^{3+} + HSO_5^- \rightarrow \equiv Fe^{2+} + SO_5^{\bullet-} + H^+ \quad (13)$$

(4) In addition to the fact that the holes can directly oxidize the virus, they may also activate oxidants such as H_2O_2 and PMS to generate reactive species for virus inactivation (Eqs. (14-17)) (Machreki et al., 2024; Ruales-Lonfat et al., 2014).

$$H_2O_2 + h^+_{VB} \rightarrow O_2^{\bullet-} + 2H^+ \quad (14)$$

$$h^+_{VB} + O_2^{\bullet-} \rightarrow {}^1O_2 \quad (15)$$

$$HSO_5^- + h^+_{VB} \rightarrow SO_5^{\bullet-} + H^+ \quad (16)$$

$$2SO_5^{\bullet-} + H_2O \rightarrow 2HSO_5^- + {}^1O_2 \quad (17)$$

Based on the above results, it can be concluded that both hematite- and magnetite-mediated photo-Fenton-like systems achieved satisfactory virus inactivation results, although the inactivation efficacy of PMS- and PDS-mediated processes was lower than that of H_2O_2. In sunny areas, both PMS and PDS could be used as alternatives to H_2O_2 because the observed reaction times are acceptable.

3.3. Influence of the presence of bacteria on virus inactivation

The above experiments were conducted using only a virus as the target; however, microorganisms coexist in actual matrices, and they may exert an important influence on each other's life cycles and, by extension, on their inactivation. Therefore, to explore whether the proposed system can be applied to a real scenario, experiments were conducted in reactors containing both MS2 bacteriophages and *E. coli*.

As shown in Fig. 4, when viruses and bacteria coexisted, except for PMS-involved systems, virus inactivation in PDS- and H_2O_2-involved systems was greatly inhibited, and the time for total inactivation of both iron oxide-mediated H_2O_2-involved systems prolonged from 5 to 30 min, and PDS groups were extended by 30 min. Under these conditions, bacteria would compete with viruses, resulting in delayed viral inactivation. Interestingly, the inactivation efficacy of the PMS-containing systems improved when *E. coli* was introduced to the system, achieving total inactivation within 5 min and 10 min for magnetite and hematite-mediated systems, respectively. There are a few possible reasons for this intriguing observation:

(1) Similar to the iron-MS2 complex mentioned previously, iron can also form complexes with bacteria (mainly through broken bacterial cell wall components, e.g., carboxylic acids), where the bacterial cell wall is a sacrificial electron donor, leading to an LMCT process (Eq. (18)) (López-Vinent et al., 2022).

$$[Fe(COO-R)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^{\cdot} \quad (18)$$

The generated Fe^{2+} continued to activate the oxidants, where the rate constants of the Fe^{2+}- H_2O_2 and Fe^{2+}- PDS reactions are 63–76 M^{-1} s^{-1} and 12–27 M^{-1} s^{-1}, respectively, which are much lower than those of Fe^{2+}- PMS ($k = 3.0 \times 10^4$ M^{-1} s^{-1}), resulting in a higher inactivation efficacy than that of H_2O_2- and PDS-involved systems (López-Vinent et al., 2022). Hence, bacteria may fuel the generation of reactive species that inactivate the viruses. It should be noted that based on the test of dissolved iron, it can be safely assumed that the contribution of this case to the significant inactivation differences among different systems is small.

(2) The significant differences among the oxidants could be related to the reactive species generated. H_2O_2 predominantly generates ·OH, PDS generates $SO_4^{\bullet-}$ (·OH as the product of a secondary water-related reaction), and PMS can produce either ·OH or $SO_4^{\bullet-}$. However, there is an increasing body of literature concerning the generation of other species such as singlet oxygen ($^1O_2$), especially when organic compounds are present and activate PMS (Pignatello et al., 2006). Although all three oxidants are peroxides, the asymmetric structure (O—O bond) of PMS can impose different reactivities. Hence, $^1O_2$ was almost certainly involved in the PMS system. Although it has been reported that ·OH is highly toxic to microbes (approximately 10 times faster with biomolecules than $SO_4^{\bullet-}$) (Anipsitakis et al., 2008), $^1O_2$ is more selective and reactive with bacterial components (e.g., proteins, lipids, and nucleic acids) because of its longer lifetime (3–5 μs) and is also highly effective against viruses (Jiang et al., 2023; Giannakis et al., 2022). Combined

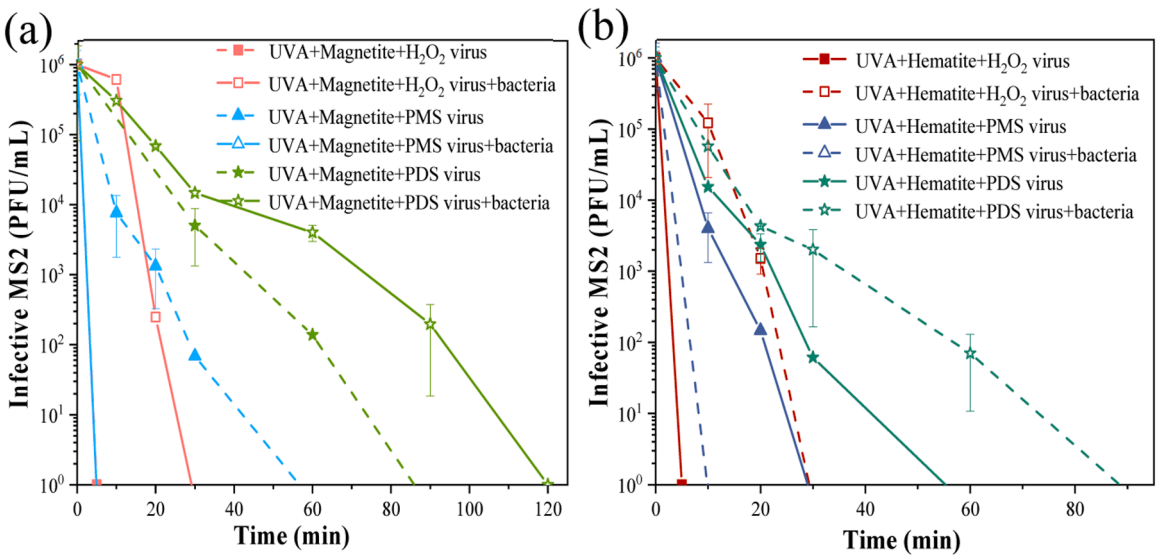

Fig. 4. Inactivation of MS2 bacteriophages in the presence of *E. coli* in (a) magnetite and (b) hematite photo-Fenton-like systems. Experimental conditions: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [pH]=8. Experiments were performed in triplicate (standard error of ~ 5 %).

with a recent report (Tian et al., 2024), it can be proposed that PMS is further activated by cell debris in solution or by bacterial cell wall components to produce $SO_4^{\bullet-}$ as well as $^1O_2$, and under the continuous action of $^1O_2$, virus inactivation is enhanced.

It is important to state here that the second hypothesis will be investigated by EPR and scavenging tests later, and the first hypotheses are transferred from the relevant literature but are plausible explanations for the occurrence of this phenomenon.

In addition, the proposed photo-Fenton-like systems were also used against the sole bacteria, and sole virus and their kinetics were investigated and compared with those of coexisting bacteria and viruses. As shown in Fig. 5, the kinetics of virus inactivation were always faster than those of bacteria, which could be because virions have a simpler structure and are much smaller (one or two orders of magnitude) than bacteria (Marjanovic et al., 2018). Therefore, despite the higher surface area of bacteria that can receive significantly more attacks than the virion, an identical amount of reactive species generated in the reaction system would inactivate more individual viruses, whereas multiple attacks would be needed to damage a single cell of *E. coli*. Moreover, the inactivation modes of the two microorganisms contributed to the inactivation results. The virus can be inactivated after an attack on its attachment protein (A) or destruction of the capsid before genome damage. While for *E. coli*, besides the known intracellular events driven by H_2O_2, either added or self-generated (Marjanovic et al., 2018), on the extracellular side, attacks from the heterogeneous photo-Fenton process would have to destroy the continuity of the membrane, causing lysis and leakage of the intracellular material. Also, it is important to note that previous studies have found that coat proteins of the viral capsid possess higher reactivity than biomolecules of the *E. coli* cell wall, leading to faster inactivation of the virus (Zhang et al., 2020). Similar to the trend of inactivation efficacy, the kinetics of H_2O_2- and PDS-involved systems for the mixed microorganism trials was much smaller than that for the sole virus, but higher than that of the sole bacteria. For the PMS system, the kinetics of both iron oxides were much higher than those of the sole virus system and sole bacterial system, implying the potential application for dealing with mixed microbes in practice.

Although the inactivation efficacy and kinetics of PDS groups for the mixed microorganisms were lower than those of PMS-involved ones, it can also be considered a good alternative to H_2O_2, since the time required for complete inactivation was within 120 min, which is acceptable for areas with intensive sunshine exposure.

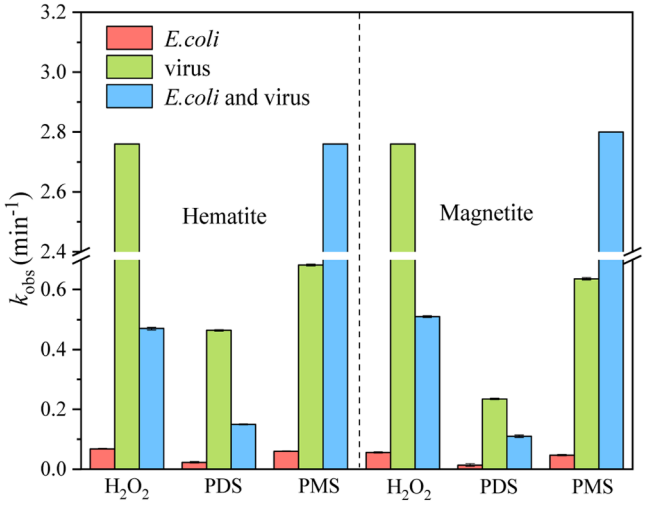

Fig. 5. The k_{obs} of the sole *E. coli*, sole virus, and virus coexist with *E. coli* inactivation in different photo-Fenton-like systems. Experimental conditions: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [pH]=8. Experiments were performed in triplicate (standard error of ~ 5 %).

3.4. *Humic acid-incorporated iron oxide-mediated photo-Fenton(-like) processes for MS2 bacteriophage inactivation*

Humic acids (HA) are important components of natural organic matter (NOM). The complex composition gives to HA peculiar adsorption, redox, and complexation characteristics (Niu et al., 2011). A previous study reported that HA can complex iron/iron oxides via different functional groups (Rose and Waite, 2003), and can promote (Colón et al., 2008) or inhibit (Gonçalves et al., 2020) the degradation of organic pollutants. HA-coated magnetite was successfully synthesized in a previous study and was found to play a positive role in the heterogeneous photo-Fenton process for organic pollutant removal (Pignatello et al., 2006). Nevertheless, the performance of the HA-modified iron oxide-mediated photo-Fenton-like process for the inactivation of viruses in water remains unclear. Hence, MS2 bacteriophage inactivation in HA-incorporated iron oxide-mediated photo-Fenton(-like) processes was also investigated, the details are presented in TextS3.

3.5. Reactive species identification experiment

3.5.1. EPR tests

First, EPR experiments were performed to identify the reactive species in each combined system. Based on previous studies (Pino-Sandoval et al., 2023; Li et al., 2018), it can be safely concluded that ·OH is the main radical in the H_2O_2-involved system. Therefore, EPR tests were conducted only for PMS- and PDS-containing systems. As shown in Fig. 6, when DMPO was used as the spin-trapping reagent for both $SO_4^{\bullet-}$ and ·OH, the characteristic peaks of the DMPO—OH and DMPO-SO_4 adducts were observed in both PDS-involved systems, indicating the presence of $SO_4^{\bullet-}$ and ·OH. However, no DMPO-SO_4 or DMPO—OH adducts were detected in the PMS systems; instead, the characteristic signals of the DMPOX adducts appeared (Fig. 6c). A previous study reported that the reaction of $^1O_2$ with DMPO could induce the formation of DMPOX (Gonçalvesa et al., 2021). To confirm this, TEMP was employed as a spin-trapping reagent for $^1O_2$ in EPR experiments. As shown in Fig. 6d, triplet signals with intensities of 1:1:1, corresponding to TEMP-$^1O_2$ adducts, were observed, implying that $^1O_2$ existed in the PMS-involved systems. No characteristic peaks of TEMP-$^1O_2$ adducts were observed in the H_2O_2- and PDS-involved systems (data not shown), indicating that the production of $^1O_2$ in the H_2O_2- and PDS-involved systems was negligible. In addition, no DMPO—$O_2^{\bullet-}$ adducts were observed in any of the combined systems (data not shown).

3.5.2. Scavenger experiments

Quenching experiments were conducted to further confirm the presence of the reactive species. Owing to their different reaction rate constants, isopropanol (IPA) and *t*-butanol (TBA) were first employed to identify $SO_4^{\bullet-}$ and ·OH, respectively (Kohn and Nelson, 2007). As depicted in Fig. 7a, when TBA was added to the H_2O_2-involved system, the total inactivation time of both systems was prolonged from 5 to 30 min. Combined with the results shown in Fig. 1, the inactivation performance of both H_2O_2-involved systems could be considered completely suppressed. This indicates that ·OH was the main radical in H_2O_2-involved systems. It should be noted that the inhibition of virus inactivation with the two concentrations of TBA was almost the same, indicating that even 0.1 mM TBA was enough to quench all the ·OH in the system, and the added TBA concentration did not cause viral inactivation. However, a concentration of 0.5 mM in the following tests was adopted to cover for any variations.

With PDS, when TBA was added, the inactivation efficiencies of UVA/hematite/PDS and UVA/magnetite/PDS systems at 120 min was only 2.9-log U and 2.6-log U, respectively (Fig. 7c and d), which was in sharp contrast to the control groups (6-log U achieved by UVA/hematite/PDS and UVA/magnetite/PDS systems at 60 and 90 min, respectively). The inactivation performance of the two systems was further inhibited when IPA was added to the system, with virus inactivation limited to 1.7-logU (UVA/hematite/PDS) and 1.8-logU (UVA/magnetite/PDS), respectively. As the UVA group alone could cause 1.9-log inactivation (Fig. 1), it could be concluded that both ·OH and $SO_4^{\bullet-}$ contributed to virus inactivation in the PDS groups, and ·OH played a more important role than $SO_4^{\bullet-}$.

For the PMS systems, when IPA was added, the inactivation efficiencies of the UVA/magnetite/PMS and UVA/hematite/PMS systems were 3.5-log and 3.9-log within 120 min (Fig. 7e and f), respectively,

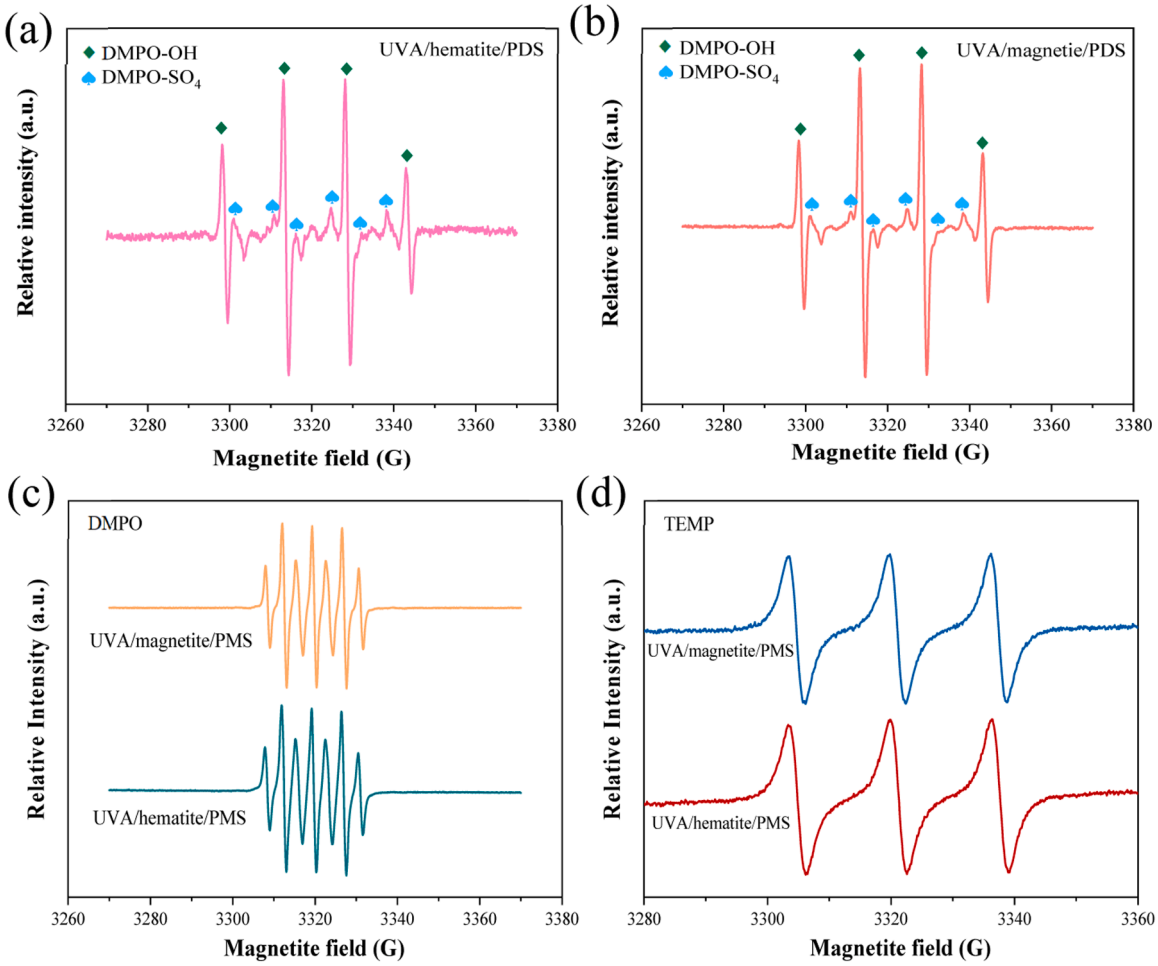

Fig. 6. EPR experiments in different systems. The experimental conditions were as follows: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [pH]=8.

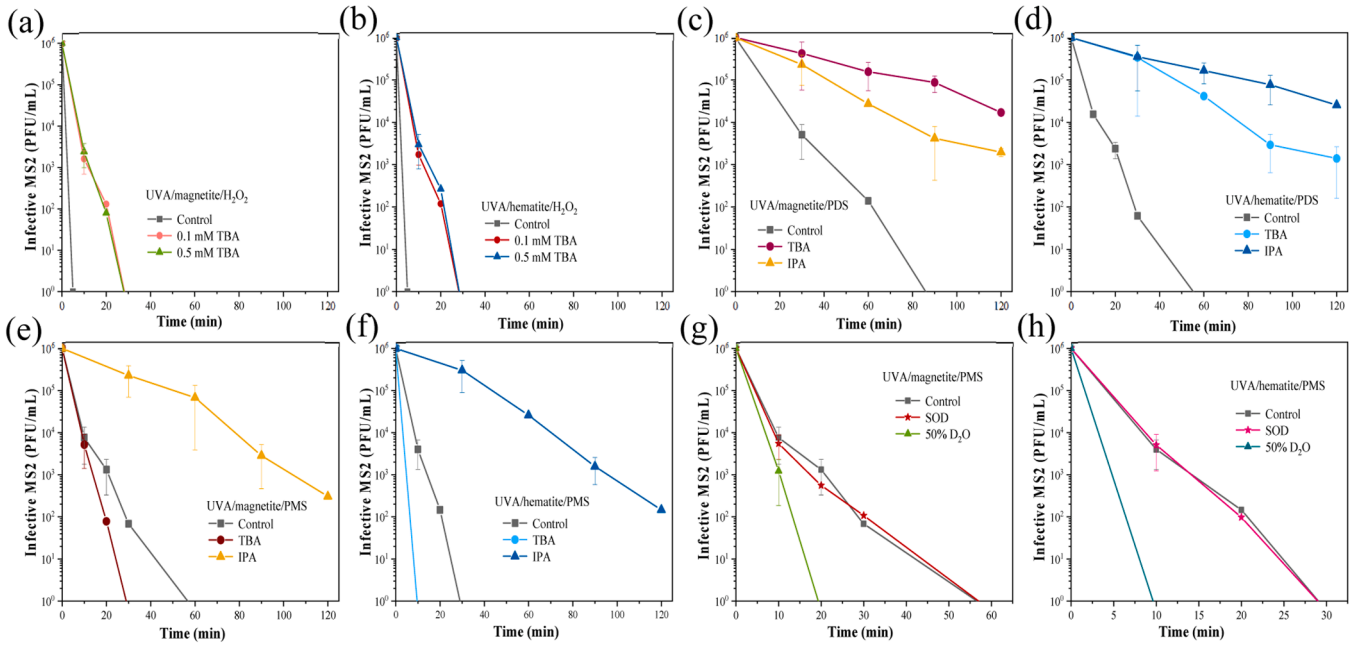

Fig. 7. Quenching experiments for the different systems studied. Experimental conditions: [iron oxides]=1 mg/L, [oxidants]=10 mg/L, [TBA]=[IPA]=0.1–0.5 mM, [SOD]=50 units/mL, [pH]=8. Experiments were performed in triplicate (standard error was ~ 5 %).

which were much lower than those of the control system (6-log inactivation within 60 and 30 min for UVA/magnetite/PMS and UVA/hematite/PMS systems, respectively). However, when TBA was introduced into the system, the inactivation performance of both systems was significantly improved, with total inactivation achieved within 10 and 30 min for the UVA/hematite/PMS and UVA/magnetite/PMS systems, respectively. Since TBA at the two concentrations would not inactivate the virus, other reasons must be responsible for this phenomenon. EPR results have shown that $^1O_2$ is formed in PMS-involved systems, and inactivation may be attributed to the long lifetime of $^1O_2$ and the absence of a corresponding anti-oxidation enzyme for $^1O_2$ in bacteria (Villén et al., 2006; Qiao et al., 2012). $^1O_2$ is more selective and sensitive to bacterial moieties, such as proteins, lipids, and nucleic acids (Dong et al., 2021). Analogously, $^1O_2$ has a similar effect on viruses. In general, $O_2^{\bullet-}$ is considered a precursor of $^1O_2$; however, EPR did not detect $O_2^{\bullet-}$. Moreover, when SOD (a scavenger of $O_2^{\bullet-}$) was introduced into the PMS-involved system, the inactivation efficacy of both systems was almost unaffected (Fig. 7g and h), indicating that $^1O_2$ was not derived from $O_2^{\bullet-}$, thus ruling out the possibility of Eq. (15). As discussed above, $SO_5^{\bullet-}$ can induce the generation of $^1O_2$; thus, Eqs. (13) and (16–17) were operative during the PMS experiments. In addition, the dismutation of PMS (eventually catalyzed by iron oxides) could also lead to the direct formation of $^1O_2$.

Based on the above analysis, it is possible to hypothesize that when IPA was added to the system, it was directly oxidized by PMS, in this way, PMS was consumed and decreased the generation of $^1O_2$. For TBA, it was speculated that some oxidizing intermediates might be formed during the reaction between TBA and PMS and then exert a synergistic effect with $^1O_2$.

3.6. *Inactivation mechanism in the constructed photo-Fenton-like systems*

Based on the above results and previous studies (Ortega-Gómez et al., 2015; S. Giannakis et al., 2017), the MS2 bacteriophage inactivation mechanisms in the iron oxide-mediated photo-Fenton-like systems were proposed (Fig. 8), and the corresponding inactivation pathways are as follows:

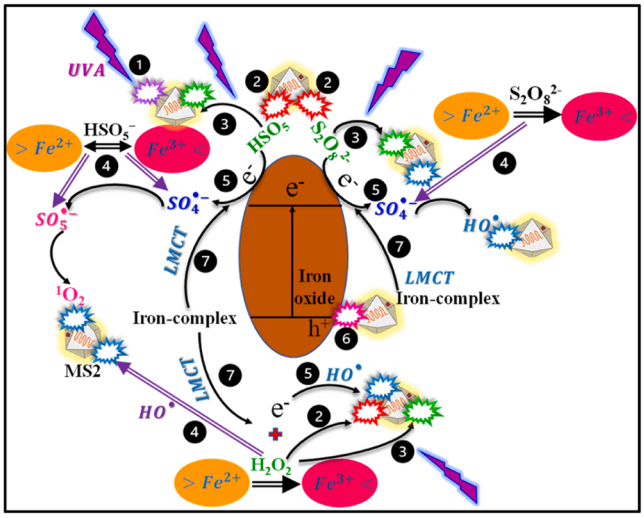

Fig. 8. Integrated mechanistic proposition for the inactivation of MS2 bacteriophages in the proposed photo-Fenton-like system.

(1) UVA can impair viral infectivity by directly disrupting the viral genome and causing damage to the coat protein of the virus, resulting in inactivation of the virus (pathway 1).
(2) Oxidative stress exerted by oxidants can directly cause viral death, and different oxidants can cause varying degrees of inactivation (pathway 2). The inactivation performance was enhanced under UVA irradiation due to the synergistic effects of UVA light and oxidants (pathway 3).
(3) Under UVA irradiation, the iron oxide-mediated heterogeneous photo-Fenton(-like) processes worked and played a major role in the inactivation of virus, as discussed in 3.2.4 (pathway 4). In addition, although iron oxide as a photocatalyst had little effect on virus inactivation, it should also be considered that the photogenerated electrons could activate the oxidants to form reactive species (pathway 5), and the holes could directly cause the death of the virus (pathway 6).

(4) Iron oxide-oxidant complexes and iron oxide-MS2 complexes may be formed and drive LMCT processes to produce reactive species for virus inactivation (pathway 7).

4. Conclusions

The inactivation performance of low reagent concentrations of iron oxides (1 mg/L, hematite, and magnetite) and three oxidants (10 mg/L, H_2O_2, PDS, and PMS) involved in photo-Fenton-like systems for MS2 bacteriophage inactivation at near-neutral pH was systematically investigated and compared, and the results are summarized as follows:

(1) Under UVA irradiation, the investigated heterogeneous photo-Fenton-like systems could effectively inactivate the MS2 bacteriophage, although the necessary time for total inactivation in the PDS-involved systems was longer than in those with PMS. In sunny areas, this could also be acceptable because the longest total inactivation time of PDS was within 120 min.
(2) In addition to H_2O_2, the inactivation performance of the hematite-mediated photo-Fenton-like system was better than that of magnetite-containing systems. Even so, magnetite-mediated photo-Fenton-like systems could attain complete inactivation using only 30 min longer than that of hematite. Moreover, considering that magnetite is easy to separate and recover owing to its magnetic characteristics, it could represent a low-cost photocatalyst for water disinfection in more advanced contexts/applications than point-of-use water disinfection systems.
(3) When bacteria were added to the matrix, the inactivation performance of both the H_2O_2 and PDS systems was inhibited, whereas it exerted a positive effect on the PMS system, implying the great potential of PMS involving photo-Fenton-like systems for mixed microbe treatment.
(4) HA incorporated iron oxide has been reported to play a positive role in the photo-Fenton-like processes for organic pollutants degradation, in this work, the positive effect was also found in hematite mediated PMS photo-Fenton-like process for bacteria inactivation. However, it inhibited the inactivation in H_2O_2- and PDS-based systems. The promoting or inhibiting effect is closely related to the reactive species generated in each system as well as the positive and negative charges on the surface of the iron oxide.
(5) EPR and radical quenching experiments indicated that ·OH was the main radical responsible for virus inactivation in H_2O_2- and PDS-involved systems, while $^1O_2$ was the primary reactive species that caused virus death in PMS-involved systems.

Overall, this study showed an effective process for MS2 bacteriophage inactivation. The proposed photo-Fenton-like systems were economically viable because the concentrations of iron oxides and oxidants were low. Moreover, the proposed system exhibited excellent virus inactivation performance at near-neutral pH, which is important for the treatment of pathogenic microorganisms in drinking water.

CRediT authorship contribution statement

Jialin Jia: Writing – original draft, Methodology, Investigation, Formal analysis. **Marco Minella:** Writing – review & editing. **Mercedes Cid Ruiz:** Methodology, Investigation. **Jeremie Decker:** Methodology, Investigation. **Dong Li:** Writing – review & editing, Methodology. **Nuno P.F. Gonçalves:** Writing – review & editing, Methodology. **Alessandra Bianco Prevot:** Writing – review & editing. **Tao Lin:** Funding acquisition, Writing – review & editing. **Stefanos Giannakis:** Conceptualization, Validation, Writing – review & editing.

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.

Data availability

No data was used for the research described in the article.

Acknowledgments

This work was supported by funds from the National Key P&D Program of China (2022YFC3203702), the Science and Technology Development Plans of the Ministry of Housing and Urban-Rural Development (2021-K-131), and the Six Talent Peaks Project in Jiangsu Province (JNHB-004). China Scholarship Council (202006120369), Jiangsu Funding Program for Excellent Postdoctoral Talent (2023ZB646), and the Hohai University full-time postdoctoral research fund (2016–423278). National Natural Science Foundation of China for Youth (22306101). Stefanos Giannakis would like to acknowledge the REDDIS project, 'Procesos reductivos como el Talón de Aquiles bacteriano en la desinfección de aguas residuales y en aguas naturales', which received funding from the Agencia Estatal de Investigación (Spain), 'Proyectos Consolidación Investigadora 2022′(CNS2022–135728), as well as the DETRAS Project, 'Desinfección-Descontaminación de Efluentes Contra la Transmisión de la Resistencia en Antibióticos' (APOYO-JOVENES-21-UXUKHL-88-WQWWQF), funded by the Comunidad de Madrid through the call 'Research Grants for Young Investigators from Universidad Politécnica de Madrid'. Nuno Gonçalves acknowledges funding from the European Union's Horizon Europe Research and Innovation Programme under the Marie Skłodowska-Curie Actions PF grant agreement No 101065059. Marco Minella and Alessandra Bianco Prevot acknowledge support from the Project CH4.0 under the MUR program 'Dipartimenti di Eccellenza 2023–2027′ (CUP: D13C22003520001).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121760.

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