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Review

Synergistic Effect of Ferrate with Various Water Processing Techniques—A Review

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Abstract: The use of ferrate has been demonstrated as a highly efficient technique for the removal of pollutants in water and wastewater treatment. While most of the published work about ferrate investigated the treatment performance by ferrate alone, new applications of ferrate expand to the synergistic application of ferrate with other techniques such as membrane separation, sulphur-based chemical use, UV radiation, ozonation, acidification, and other chemical additives. This paper aims to review and explore the treatment performance and reaction mechanisms associated with synergistic applications of ferrate. The main objective of this study is to conduct case studies on the synergistic application of ferrate with other water processes. It was found that the efficiency of water treatment increased significantly by the synergistic application of ferrate, and this is attributed to the alleviation of membrane fouling, the activating the formation of more radical oxidative species, enhanced coagulation, and the potential improvement of micropollutants' biodegradability. Therefore, the stated ferrate technology holds high potential for improving the efficiency of water treatment and other environmental remediation processes. Further studies are required to explore a more feasible combination of ferrate with other techniques and expand the understanding of the working mechanisms of the known synergistic applications of ferrate.

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Keywords: emerging micro-pollutants (EMPs); ferrate; removal efficiency; synergistic application; water treatment

1. Introduction

The assurance of safe, hygienic, and sufficient water supplies is vital to humans and the ecosystem. The deterioration of water quality has generated public concerns in modern society. Figure 1 shows that the primary sources of water contamination include industrial waste effluent, crude sewage and wastewater treatment plant (WWTP) effluent, agricultural waste, the usage of pesticides, and domestic and hospital-related disposal through the water cycling system [1–3]. Since the rapid progression of industrialisation, occurrences and detections of artificial organic chemical pollutants in water have been frequently reported. It was proven that many of those compounds exhibit threats and risks posed to human health and ecological security at a low concentration range. Consequently, the derived health and safety issues gradually became long-standing problems under public debate. The exploration and progression of advanced water treatment technologies are urgently required [4].

Oxidation is an essential procedure in tertiary water processing. According to the oxidation derived from free radicals generated from additives, oxidation can be categorised as non-advanced oxidation processes (non-AOPs) and advanced oxidation processes (AOPs). In the past two decades, the AOPs have been increasing the prevalence of the treatment of contaminants in water and wastewater because of their high redox po-

tential and good performance in trials and practices. Instead of AOPs, ferrate is an innovative technology because of its similarly high redox potential compared to those popular AOPs. Ferrate is regarded as a promising degradation technique in water processing because of the dual functions of its properties, i.e., the oxidation and coagulation of various contaminants [5–8]. The study of ferrate as a water-cleaning reagent has received great interest, and a series of trials on ferrate treatment have been conducted. The major trials have focused on the degradation of specific contaminants with the sole addition of ferrate to prove if ferrate is an alternative oxidation technique.

However, the widespread application of ferrate in water treatment still receives many challenges from various perspectives. The recalcitrancy of many pollutants could limit ferrate treatment's performance [5,6], and the rapid self-decomposition of ferrate inhibits its cleaning efficiency [9–11]. Therefore, the optimization of ferrate treatment with the assistance of other processing techniques is demanded. Moreover, ferrate involved technology can be an option for enhancing the performance of conventional water treatment processes [12–14]. Based on the stated reasons and interests, many studies have investigated the synergistic processes of ferrate coupling with other techniques to improve its treatment efficiency. The previous literature has mainly focused on the case studies about the sole application of ferrate in water treatment but not many detail the synergistic application of ferrate with other processes in water treatment. For this reason, this review paper aims to highlight the recent research on the removal of contaminants in water by the synergistic application of ferrate, which can promote the development of knowledge of ferrate application in water and wastewater treatment. Thus, the objectives of this paper include an evaluation of the recent studies of ferrate's coupling with (1) membrane filtration, (2) sulpho-compounds, (3) UV-radiation, (4) ozonation, and (5) various chemical additives. To achieve the stated aims/objectives, this review mainly focuses on the performance of the synergistic application of ferrate in water treatment and the explanation and discussion of the mechanisms of these treatment processes.

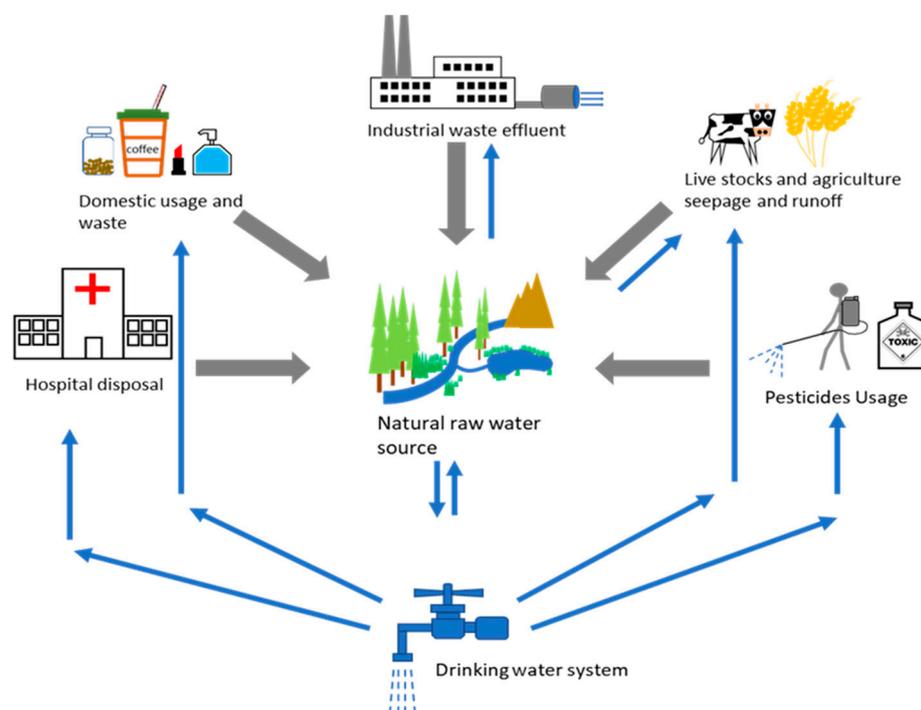


Figure 1. The schematic of water contamination sources and pathways in the water cycle

2. Water Treatment Performance of Synergistic Applications of Ferrate

The application of ferrate alone in water treatment shows a high selectivity and removal efficiency for the treatment of various contaminants. However, a relatively high ferrate dose inhibits its full-scale application due to the high operating costs. Therefore, the synergistic application of ferrate at a decreased dosage is an alternative, practical application of ferrate in water treatment [15]. Meanwhile, ferrate greatly optimises the treatment's efficiency by integrating it into other techniques, including AOPs, membrane separation, and other processes. Table 1 shows the recent trials on the water treatment processes' coupling with ferrate, and each trial is detailed in subsequent sessions.

Table 1. Case studies of removing emerging micro-pollutants (EMPs) through synergising ferrate with other techniques.

| | Synergistic Application of Ferrate | Chemicals | Sample Condition | Removal% | Reference |
|-------------------------------|---|---|-------------------------|---------------------------------------|-----------|
| Ferrate + Persulfate | 5 mM ferrate + 2.5 mM peroxymonosulfate | Atrazine | 46.5 μM | 81.5 | [16] |
| | 90 μM ferrate and 90 μM peroxymonosulfate by following the addition of the 90 μM Hydroxylamine | Ciprofloxacin | 30 μM | 91.5 | [17] |
| | 0.03 mM Ferrate + 0.03 mM peroxy sulfate | Fluoroquinolones | 0.03 mM | 60 (improved from 10 by only ferrate) | [18] |
| | Photo + 0.5 mM Fe^{6+} + 0.5 mM peroxyonosulfate | sulfamethoxazole | 0.1 mM | 80 | [19] |
| Ferrate + sulphite/bisulphite | 0.25 mM Sulphite + 0.05 mM ferrate + photo-activation | Ciprofloaxin | 0.005 mM | >95 | [20] |
| | 100 μM ferrate + 400 sulphite | DEET N, N-diethyk-3-toluamide | 10 μM | 78 | [21] |
| | 100 μM $\text{Fe}(\text{VI})$ + 100 μM sulphite/bisulphite | Flumequine | 20 μM | >40 | [10] |
| | 0.25 mM Sulphite + 0.05 mM ferrate 0 | Tert-butanol (TBA) | 10 mM | > 40 | [20] |
| | 100 μM $\text{Fe}(\text{VI})$ + 100 μM sulphite/bisulphite | Trimethoprim | 2 μM | >90 | [10] |
| | 0.25 mM Sulphite + 0.05 mM ferrate | Sulfamethoxazole | 0.005 mM | >60 | [20] |
| | Ferrate + thiosulphate | [Thiosulphate]:[$\text{Fe}(\text{VI})$] = 1:8 | chloramphenicol | 31 μM | 69 |
| Ferrate + adsorbent | 3 mg L^{-1} ferrate + 0.05 g MgO nanoparticles | Blue-203 dye | 25 mg L^{-1} | > 97 | [23] |
| | 0.5 mM ferrate and 4 g. L^{-1} silicate gel | Caffeine | 0.085–0.089 mM | >95 | [24] |
| | [$\text{Fe}(\text{VI})$]: [$\text{Fe}(\text{III})$] = (3:7) | Chemical weapon agent (Soman) | 0.38 mg.mL $^{-1}$ | 99 | [25] |
| | 6.6 mg mL $^{-1}$ ferrate + 16.6 mg Graphene oxide | Diclofenac | 2.5 mg L^{-1} | 99 | [15] |
| | Simultaneous 0.42 mM Ferrate + 0.12 mM PACl | Humic acids such as NOM | N/A | 37 | [26] |
| | 12 mM ferrate + 625 mg L^{-1} graphene oxide | RHB dye | 0.02 mg L^{-1} | 99 | [15] |
| | Simultaneous application of ferrate and montmorillonite [$\text{Fe}(\text{VI})$]:[R] = 10:1, [montmorillonite] = 100 mg | Sulfadiazine | 0.02 mM | 73.70 | [27] |
| Ferrate + UV | UV- $\text{Fe}(\text{VI})$ 8.96 mg L^{-1} ferrate + 40 mg L^{-1} TiO_2 | Dimethyl phthalate | 11.6 mg L^{-1} | 68 | [28] |

| light intensity = 0.40 mW cm ⁻² , pH 9 | | | | | |
|--|---|---|---|--|---------|
| | 0.1 g L ⁻¹ ferrate + UV fluence rate ¼ 0.198 mW cm ⁻² | phenolic com- pounds | 0.15 mM | 73 | [29] |
| | Ferrate, 0.1 mg L ⁻¹ + O ₃ , 1.2 mg L ⁻¹ | (DMS) N,N-dime- thylsulfamide | 10 µg L ⁻¹ | Completed re- moval and no NDMA for- mation | [30] |
| Ferrate + Ozona- tion | Ferrate 2.0 mg L ⁻¹ + O ₃ , < 2.5 mg L ⁻¹ | Bromination | Bromide concentra- tion in raw water, 500 µg.L ⁻¹ | 88–100 | [30,31] |
| | 0.15 mM ferrate + 10 mg L ⁻¹ ozone | DOC UV ₂₅₄ protein polysac- charide | 7.5 mg L ⁻¹ 0.158 mg L ⁻¹ 4.3 mg L ⁻¹ 5.82 mg L ⁻¹ | 70.5 80.5 25.5 65.5 | [32] |
| | Simultaneous addition of 0.51 µmol L ⁻¹ ferrate and 0.51 µmol L ⁻¹ ozone | tetrabromo- bisphenol-A | 1.84 µM | 85.5 | [33] |
| Ferrate + Other Chemical Addi- tives | 0.1–0.5 mL of 0.5 M HCl in 161.9–569.2 µM Fe(VI) | Acesulfame potas- sium | 49.0–81.4 µM | 95 (from 64 by only ferrate) | [11] |
| | 0.1–0.5 mL of 0.5 M HCl in 161.9–569.2 µM Fe(VI) | Atenolol | 41.6– 56.9 µM | 30 (from 0 by only ferrate) | [11] |
| | 0.1–0.5 mL of 0.5 M HCl in 88.5–634.5 µM Fe(VI). | Caffeine | DW 78.7– 95.3 µM | 60 (from 12 by only ferrate) | [11] |
| | 10 mM ammonia + 0.6 mM ferrate | Flumequine | 0.03 mM | 90 | [9] |
| Ferrate + UF | 2.0 mg L ⁻¹ ferrate + UF | DOC | Approx. 16 mg L ⁻¹ | 41 | [34] |
| Ferrate + ultra- sound Ultrasound | 0.05 mM Fe ⁶⁺ + Ultrasound (Ultrasonic fre- quency: 800 KHz) | Sulfadiazine Sulfamerazine Sulfamethoxazole | 0.02 mM | >95 | [35] |
| Ferrate + Chlorina- tion | 0.25 mM ferrate + 5.0 mg L ⁻¹ chlorinated | | | 80.5 | |
| | 0.25 mM ferrate + 5.0 mg L ⁻¹ chlorami- nated | halo-DBPs | N/A | 72.4 | [36] |

2.1. Mitigation of Membrane Fouling by Ferrate Pre-treatment

One of the major issues restricting ultrafiltration efficiency in water treatment is membrane fouling, mainly caused by the membrane surface accumulation of biopolymer-type substances on which humic acid and lower molecular weight acid compounds are bonded. It has been suggested that the floc-bound extracellular polymeric substances (EPSs) or proteins and polysaccharides play an important role in the formation of biofouling [37,38]. The biopolymer complex of Natural Organic Matter (NOM) particles with electrolytes (Ca²⁺, Mg²⁺, Fe³⁺, CO₃²⁻, SO₄²⁻, and SiO₃²⁻) and microorganisms form a coat on the membrane and decrease the membrane flux, which causes an increase in the backwash cost [34,38]. Coagulation pre-treatment was introduced to mitigate membrane fouling, but the incomplete removal of biopolymers by coagulation is a challenge that water industries face [34,37,38]. The protocol of mitigating the membrane fouling can be summarised as reducing the concentrations of organic matter and inactivating microorganisms. Based on this protocol, ferrate was integrated with membrane filtration, where ferrate could improve the mitigation of membrane fouling compared to only applying ferric-based coagulant [38]. It was demonstrated that the synergistic effect of FeCl₃/Fe⁶⁺ pre-treatment reduced blockage in the cake layer compared to the conventional FeCl₃ pre-treatment [38].

The organic content in the cake layer via $\text{FeCl}_3/\text{Fe}^{6+}$ application is lower than that by individually applying FeCl_3 and ferrate. Similarly, the investigation in [34] shows that UF coupling with 2 mg L^{-1} of ferrate can remove more DOC, increasing from 18% to 40%. The raw water UV_{254} value of 0.150 cm^{-1} was reduced to 0.050 cm^{-1} by ferrate/UF, while this value decreased to 0.112 cm^{-1} by UF alone [34]. Increasing the ferrate dosage could enhance the formation and aggregation of ferric flocs, which were settled and removed readily through the filtration [34]. The study recorded in [37] shows that applying $\text{FeCl}_3/\text{Fe}^{6+}$ pre-treatment can reduce the hydraulically irreversible fouling index.

Specifically, ferrate decomposition resultant ferric (hydro) oxide can form a prefiltration layer on the membrane. This prefiltration layer is characterised as negatively charged, porous, and hydrophilic, which can help the membrane rejection on hydrophilic DOC to alleviate membrane fouling. Tang and coworkers [37] showed that Fe(VI) pre-treatment increased the interaction free energy of the cohesion of foulants, which makes the foulants more hydrophilic and stable; consequently, and then it is difficult for the foulants to deposit on the membrane surface. Thus, the internal foulants in the membrane pores were prevented by delaying the formation of the dense cake layer on the membrane. Moreover, removing the resultant lower-molecular organics via the flocs was also proposed in this case [34,37]. The protein-like substance was the dominant gradient in the internal foulant's layer after the filtration of the raw water, but it can be adsorbed by ferrate-resultant ferric particles or rejected by the membrane and the ferric prefiltration layer on the membrane without entering the membrane pore. Besides the direct inactivation of the microorganism by ferrate oxidation, the assimilable organic matter also decreased by applying 1.5 mg L^{-1} of ferrate, inhibiting the microorganisms' growth in water [34].

The mechanisms of alleviating membrane fouling can be summarized as follows: (1) the synergistic application of $\text{FeCl}_3/\text{Fe(VI)}$ produces larger flocs that are more easily settled, which thereby directly influences the magnitude, composition, and structure of membrane cake layers; (2) aromatic and phenolic carbons in NOM are degraded to smaller molecular organics by ferrate, and this reduces NOMs' ability to attach to the membrane surface; and (3) ferrate inactivates bacteria and microorganisms and thus reduces bio-fouling.

2.2. Ferrate Coupled with Persulfate (SO_5^{2-} , $\text{S}_2\text{O}_8^{2-}$)

Advanced oxidation processes (AOPs) have been regarded as an effective technique for remediating a wide range of pollutants in water due to their high redox potential. Recently, the AOPs based on sulfate radicals have received increasing attention for degrading organic pollutants [16,18]. It was suggested that peroxymonosulfate accepts electrons more readily than peroxydisulfate or hydrogen peroxide (H_2O_2) [16]. Various activators can easily activate peroxymonosulfate due to its asymmetric structure. However, some efficient activators (e.g., cobalt) turned toxic in the leaching process. So, many studies have been conducted to explore the environmental friendly alternatives such as ferrate to these activators [16].

In one study, 0.03 mM of fluoroquinolones in river water was degraded $<10\%$ by solely peroxymonosulfate but by 60% by applying 0.03 mM peroxymonosulfate coupled with 0.03 mM ferrate [18]. It was observed that 0.1 mM sulfamethoxazole can be degraded $>80\%$ when dosing 0.5 mM ferrate mixed with 0.5 mM peroxymonosulfate under solar radiation [19]. Moreover, $46.5 \text{ }\mu\text{M}$ atrazine can be completely degraded by dosing 6 mM ferrate and 5 mM peroxymonosulfate within 20 min [16]. Moreover, it was found that the positive correlations exist between the degradation efficiency and the dosages of ferrate ($0.5\text{--}6.0 \text{ mM}$) and peroxymonosulfate ($1.2\text{--}5.0 \text{ mM}$), as well as the temperature ($15 \text{ }^\circ\text{C}$ to $40 \text{ }^\circ\text{C}$) [10,16]. The high remediation performance of the peroxymonosulfate / Fe(VI) system was attributed to the free radicals and oxidative species derived from the interaction between peroxymonosulfate and Fe(VI) [10,16]. Ferrate decomposition could generate Fe(V) and Fe(IV) species, which contribute to the degradation of atrazine and trime-

thoprim. Then, Fe(III) and Fe(II) (γ -Fe₂O₃/ γ -FeOOH particles), resulting from the decomposition of the ferrate, activated the peroxymonosulfate to produce SO₄^{•-} radicals, which finally react with atrazine and further react with water to produce OH radicals (Table 2 and Figure 2) [10,16,17].

Table 2. Reaction processes involved in the generation of sulphate and hydroxide radicals by the interaction between the ferrate resultant Fe(III)/Fe(II) species and peroxymonosulphate [10,16,17].

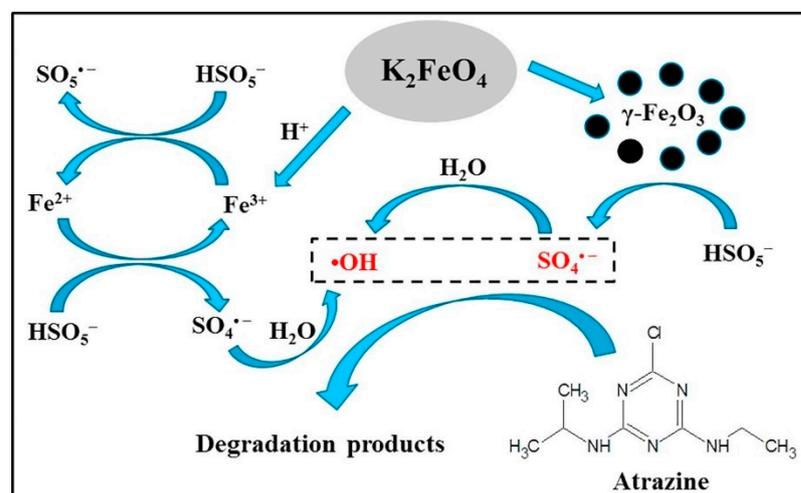
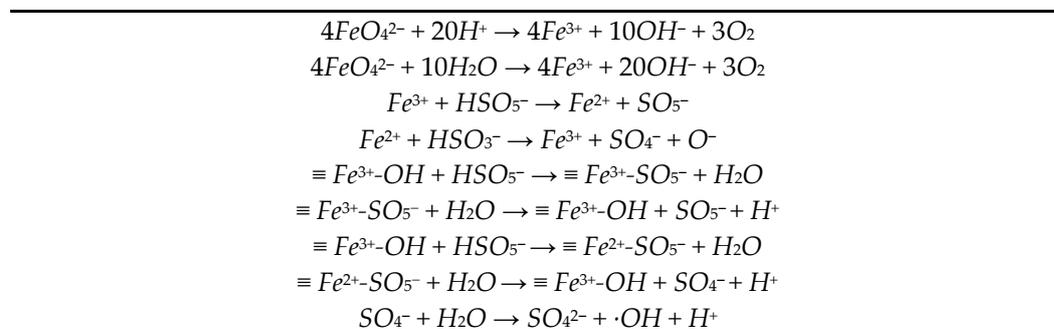


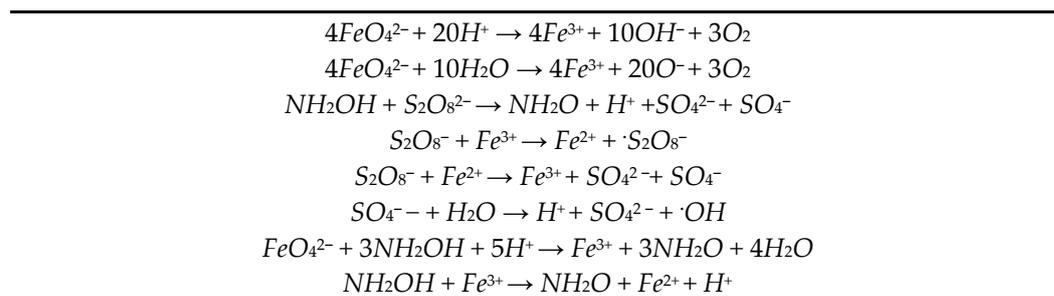
Figure 2. The schematic of interaction between the ferrate and peroxymonosulfate resultant radicals (redraw from [16]).

Due to the complex composition and recalcitrant structure, the mixture of straw waste and cow manure (CCM) was hardly degraded in anaerobic digestion without pre-treatment. Some iron-assisted oxidant has been used as a pre-treatment process, but the ferrous iron could cause the rapid consumption of SO₄ radicals. Wang and his colleagues applied ferrate with peroxymonosulfate in the anaerobic digestion of CCM mixture [39] as a pre-treatment process, which proved beneficial for improving the settling ability and delignifying the lipoprotein of the cell walls to macromolecular substances such as proteins and carbohydrates. The delignification of the CCM mixture was increased by 20–50% and the maximum lignin removal efficiency (50.2%) was obtained. The Peroxymonosulfate /Fe(VI) system significantly increased the removal efficiency of total solids and volatile solids. However, it is worth noting that an overdose of Fe(VI) will cause the formation of Fe(II), which inhibits methanogenesis.

Many trials have been conducted to explore the use of effective reducing agents in the peroxymonosulfate/Fe(VI) system. A study applied hydroxylamine (HA) as an activator to improve the degradation of ciprofloxacin (CIP). After the simultaneous addition of 90 μM ferrate and 90 μM peroxymonoxide following the addition of 90 μM HA, 91.5% of 30 μM CIP was removed at pH4 [17]. In this synergistic system, the ferrate resultant Fe(III)

reacts with HA to produce Fe(II), which then interacts with peroxymonosulphate to produce more radical oxidative species (ROS) (Table 3). The results indicate that Fe(II) was more effective in activating peroxymonosulfate to degrade target organics than Fe(III) [17]. Moreover, the ascorbic acids (AA) and sodium thiosulphate can be used as activators/catalysts to accelerate Fe(III)/Fe(II) cycles; it was reported that the addition of thiosulphate and ascorbic acids achieved a >90% removal of CIP [17].

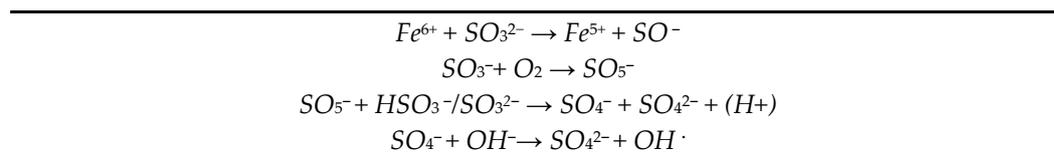
Table 3. Reaction processes involved in the generation of sulphur and hydroxyl radicals by the interaction between the Ferrate resultant Fe(III)/Fe(II) species and peroxymonosulphate with the addition of the hydroxylamine [17].



2.3. Sulphite (SO₃²⁻) + Ferrate

Some studies show that bisulphite and sulphite can act as sulfate radicals after being activated by ferrate [21]. An amount of 2 µM trimethoprim in deionised water can be removed by 90% in 15s with 100 µM ferrate coupled with 100 µM sulphite/bisulphite [10]. The degradation of 0.005 mM ciprofloxacin in deionised water could be improved to >95% by adding 0.25 mM sulphite into ferrate [20]. The 10 mM tert-butanol was degraded by >40% with the same conditional ferrate and sulphite, which exhibits more degradation efficiency than the sole application of ferrate [20]. The activation of ferrate with sulphite increases the oxidative transformation of recalcitrant organic compounds, in which reactive ferrate species such as Fe(V) and Fe(IV) were generated to react with the pollutants [10] (Table 4). The addition of sulphite activates the formation of hydroxyl radicals, which also increases the oxidation efficiency of pollutants [10,21,40] (Table 4). Moreover, the addition of sulphite accelerated the Fe(III) formation by the ferrate decomposition. The rate of converting Fe(VI) to Fe(III) via the activation of excessive sulphite ($k > 10^{12} \text{ M}^{-2} \text{ s}^{-1}$) is higher than that of non-activated ferrate decomposition ($20 \text{ M}^{-2} \text{ s}^{-1}$) [41]. In the ferrate/sulphite system, the resultant activation particulates were instantaneously formed Fe(III) oxide, and the characteristics of the iron particulates were significantly modified. The activation-resultant particulates were less magnetic but more polydisperse/amorphous, which exhibits less crystalline morphology than ferrate's self-decayed particles [41] and improved the oxidation and adsorption of some micro-organic contaminants.

Table 4. Reaction processes involved in forming sulphite radicals in Fe(VI)/sulphite system [21,40,41].



2.4. Thiosulphite ($S_2O_3^{2-}$) with Ferrate

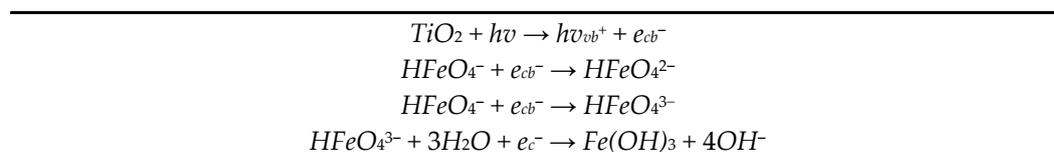
Among the reagents used to activate ferrate, thiosulfate is one of the most popular reductants because of its usability, security, and stability. Chloramphenicol (CAP) is a widely used antibiotic, but it has been banned because of its potential to cause toxicity to human bodies. – However, due to its low cost, it is still being used in some countries [22]. Thiosulfate could significantly accelerate ferrate to degrade chloramphenicol and optimise its removal to 69% when the molar ratio of thiosulphate/ferrate was 1:8 under pH7 [22]. SO_4^{2-} and OH^- free radicals were produced during the $-$ thiosulphate/Fe(VI) reactions, which are the primary reactive oxidation species (ROS). The main oxidation mechanism and ROS production process are based on the equations shown in Table 5 [22].

Table 5. Reaction processes involved in forming thiosulfate radicals in Fe(VI)/sulphite system [22].

| |
|---|
| $Fe^{6+} + CAP \rightarrow Fe^{2+}/Fe^{3+} + CAP$ (oxidized) |
| $Fe^{6+} + S_2O_3^{2-} \rightarrow Fe^{5+}/Fe^{4+} + SO_4^-$ |
| $Fe^{6+} + S_2O_3^{2-} \rightarrow Fe^{2+}/Fe^{3+} + SO_4^{2-}$ |
| $Fe^{5+}/Fe^{4+} + CAP \rightarrow Fe^{2+}/Fe^{3+} + CAP$ (oxidized) |
| $Fe^{5+}/Fe^{4+} + S_2O_3^{2-} \rightarrow Fe^{2+}/Fe^{3+} + SO_4^{2-}$ |
| $SO_3^-/\cdot OH + CAP \rightarrow SO_4^{2-} + CAP$ (oxidized) |

2.5. Ferrate Coupled with Ultraviolet Light (UV) Radiation

UV radiation is an effective AOP technique to remove various pollutants, but it was proved that more emerging organic pollutants are recalcitrant to UV radiation [28,29,42]. The addition of catalysts (H_2O_2 and TiO_2) was regarded as a direct and effective method to improve the degradation efficiency of recalcitrant contaminants. So, many studies experimented with the use of ferrate to assist the treatment of water by UV radiation. The oxidation of profenofos was enhanced up to 19.1% with the synergistic application of UV_{254} and ferrate solution [43]. A 73% removal of phenolic compounds was achieved by the ferrate-UV system, which is higher than that by either an individual application of ferrate or UV radiation [29]. Dimethyl phthalate (DMP) is a refractory endocrine disruptor (EDC), which was degraded by 68% in the UV- TiO_2 -Fe(VI) system; higher than that by the TiO_2 -UV- O_2 system [28]. An almost 100% removal of carbamazepine (CMZ) was achieved by UV radiation-followed by ferrate oxidation. The reduction of DOC from CMZ solution via UV in conjunction with ferrate was greater than the sum of that by UV radiation and ferrate alone [42]. In the ferrate/radiation system, reactive oxygen species (OH^- and O_2^-) and derived ferrate (Fe(IV) and Fe(V)) are the dominant species oxidizing the pollutants; the generation of O_2^- and OH^- free radicals was accelerated in the presence of the air and radiation [29,39]. Therefore, increasing the adsorbed dose of UV radiation can improve the generation of ROS. Moreover, radiation promoted the formation of reactive intermediate species of ferrate (Fe(V), Fe(IV), and Fe(III)), which attack the alkyl-chain of phenolic compounds and contributes to the degradation of pollutants [28]. In the UV- TiO_2 -ferrate system [28,44], the Fe(VI) is relatively effective in scavenging the conduction band electrons from the TiO_2 surface compared to scavenging by oxygen (O_2). Thus, ferrate can act as an electron acceptor to trap electrons produced during the photolytic process [28,29] and it prevents the self-recombination of e^- and h^+ , enhancing the degradation of target organic compounds [28]. The reduction of ferrate and the procedure of the electrons' transference are shown in Table 6.

Table 6. The mechanism of electron transferring and formation of derived ferrate species in UV/Fe(VI) system [28,29].

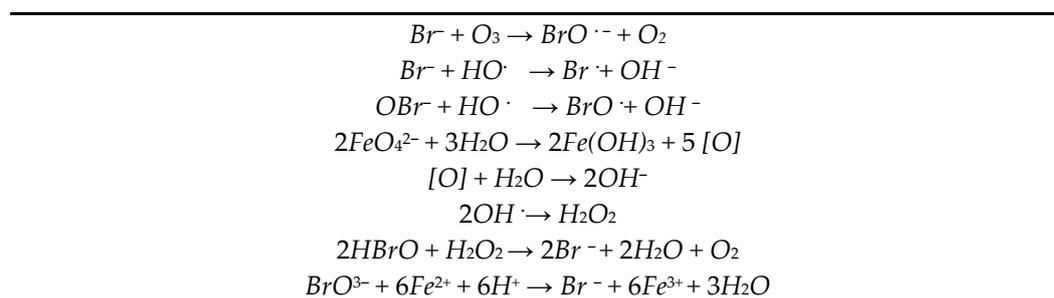
2.6. Ferrate Coupled with Ozonation

Ozone and ferrate are both regarded as high-capacity oxidants, but the sole application of ozonation and ferrate cannot simultaneously achieve the effective degradation of contaminants and control the formation of toxic products [30,31]. Therefore, combining those two oxidants could be a more suitable solution. One study showed that 1.84 μM of tetrabromobisphenol-A was removed by 85.5% by the simultaneous addition of ferrate and ozone—this performance is higher than the removal sum of individual ferrate and ozone (73.1%) [33]. A study reported that the porosity of the fouling layer increased by 25.7% after applying ferrate-peroxidation-ozonation, resulting in the mitigation of membrane fouling with a maximal reduction of the transmembrane pressure (TMP) by 89.5% [32]. The synergistic action of ferrate-ozonation can achieve the maximum removal of DOC, UV₂₅₄, protein, and polysaccharides by 70.5%, 80.5%, 25.6%, and 65.5%, respectively [32]. The high rate of the removal of the pollutants was mainly attributed to the derived oxidative ferrate species (Fe(V) and Fe(IV)) and radical oxidative species (ROS). In particular, the OH^- free radical played the dominant role in the oxidation of pollutants in water. The generation of more OH^- free radicals was mainly based on three proposed procedures in the ferrate-ozone system, as shown in Table 7. Additionally, the intermediates of ferrate species (Fe(V) and Fe(IV)) also facilitated the removal of organics. Nonetheless, the catalytic interaction between ferrate and ozone can be weakened by the sequence of ozone peroxidation, so ferrate peroxidation is the ideal way to sufficiently interact with the ozone and enhance the synergistic effect [33].

In comparison with the use of ozonation and FeCl_3 coagulation, ferrate-ozonation did not significantly result in the formation of N-Nitrosodimethyl-amine (NDMA) after the treatment and could remove 10% more metformin, benzotiazole, and acesulfame, but the process of FeCl_3 in conjunction with ozonation could not achieve the same. Additionally, ferrate-ozonation can effectively inhibit the formation of bromate compared to sole ozonation, and bromination can be greatly inhibited [30]. In another study, ferrate-ozonation was capable of reducing the bromate concentration below the maximum contaminant level (MCL) ($10 \mu\text{g L}^{-1}$) for a bromide concentration of $500 \mu\text{g L}^{-1}$ in raw water [31]. The inhibition mechanism could be attributed to decreasing the oxidation of Br^- and enhancing the reduction of BrO_3^- and BrO in the ferrate treatment followed by ozonation. Ferric and ferrous species derived from the ferrate decomposition can enhance ozone decomposition, reducing the direct reaction of HBrO/BrO^- or BrO_3^- with ozone, and thus reducing the bromate formation. Table 8 shows the combined interaction in the mechanism inhibiting the bromination via the ferrate-ozone system.

Table 7. The mechanism of forming OH^- radicals in the ferrate/ozone system [32].

| | |
|---|--|
| OH^- produced from the direct decomposition of ozone | $\text{O}_3 + \text{OH}^- \rightarrow \text{O}^- + \text{HO}_2^- \rightarrow \text{OH}^-$ |
| OH^- produced from ferrate decomposition and interaction of ferrate species | $\text{Fe(VI)} \rightarrow \text{Fe(V)} \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$ |
| | $\text{Fe(VI)} \rightarrow \text{Fe(IV)} \rightarrow \text{Fe(II)}$ |
| | $\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{Fe(III)}$ |
| OH^- produced from the interaction of surface hydroxyl on resultant ferrate particles ($\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$) | $\text{O}_3 + >\text{OH}^- \rightarrow \text{O}_2^- + \text{HO}_2^- \rightarrow \text{OH}^-$ |

Table 8. The mechanism of inhibiting bromination in the ferrate/ozonation processes [31].

2.7. Ferrate Coupled with Other Additives

2.7.1. Ferrate + Ammonia

In many studies, ammonia/high-valent iron species complexes have been demonstrated to possess high reactivity. By applying 0.6 mM ferrate coupled with 10 mM ammonia, approximately 90% of flumequine was degraded [9]. The addition of ammonia in the ferrate can activate the formation of ammonia/high-valent iron species, which increases the reactivity of the ferrate species. Specifically, the postulated ammonia complexed ferrate species are preferentially consumed by the hydroxylation at the double bond moiety of flumequine, thus enhancing the oxidation rate of flumequine. Moreover, it was found that the oxidation products of flumequine by ferrate coupled with ammonia have less antibacterial activity against *E. coli* and *B. subtilis* than that of ferrate without ammonia; this also could be attributed to the hydroxylation at the C12=C13 double bond of flumequine.

2.7.2. Ferrate + Acids

It is known that the performance of ferrate treatment is significantly pH-dependent; acidic conditions are preferential for the oxidation of pollutants by ferrate. Based on this principle, various acids were tested in the ferrate treatment to reduce the ferrate doses and shorten the reaction time. The acidic activation of ferrate can increase the removal efficiencies of acesulfame potassium, atenolol, and caffeine to 95%, 30%, and 60%, respectively [11]. The improved performance could be attributed to the enhanced participation of the reactive species Fe(V) and Fe(IV), which have been proven to be around 2–4 orders of magnitude more than Fe(VI). Moreover, the O₂ and H₂O₂ are likely formed by the acid-catalysed decomposition of ferrate, and the ferrate is further converted to Fe(IV) and Fe(V) after its reaction with the derived O₂ and H₂O₂ [11].

2.7.3. Ferrate + Quinone

Many transition metals, bases, and acids are widely applied to enhance the electron transfer catalysis in chemical and biochemical reactions. Quinone can be reduced to a semiquinone anion radical and hydroquinone and then further transfer electrons to molecular oxygen to produce superoxide in the presence of oxygen. Consequently, quinone was recently regarded as a promising alternative electron transfer catalyser for enhancing water treatment performance. By adding quinone to the ferrate treatment, the performance was significantly improved, which could be attributed to the quinone activation that promotes the decomposition of ferrate to produce Fe(V) and Fe(IV), and then enhances the treatments' ability to oxidise the pollutants with electron-rich moieties [45].

3. Conclusions and Further Works

3.1. Conclusions

Water treatment performance has been significantly improved by the synergistic application of ferrate with membrane separation, sulphur-based chemicals, UV radiation,

ozonation, acidification, and other chemical additives. The performances and major mechanisms of synergistic ferrate processes are summarised below:

- (1) Ferrate significantly improves membrane processing efficiency and alleviation membrane fouling; macromolecular natural organic matter can be oxidised into smaller organic particles by the ferrate. The properties and structure of flocs and DOC foulants were changed by ferrate oxidation so that the resultant flocs were more easily settled and difficult to deposit onto the membrane.
- (2) The high treatment performance by ferrate/sulphur compounds has mainly been attributed to the oxidative species formed during the interaction between ferrate and sulphur compounds such as Fe(V), Fe(IV), and free radicals such as SO_4^- , SO_5^- , SO_3^- , and OH^- .
- (3) The high performance of ferrate coupled with other additives such as acids, quinone, and ammonia is because these chemical additives activate the ferrate's decomposition, which increases the available electrons equivalence per unit of ferrate and modifies the properties and structure of the resultant ferric flocs, which can improve the efficiency of the adsorption and sedimentation.

3.2. Challenges and Future Work

The many challenges that the synergistic application of ferrate faces have been summarised and the relevant future work has been proposed as follows.

- (1) The membrane-fouling mechanism varies after ferrate pre-oxidation. When the dosage of ferrate is increased to a certain threshold level, the DOC substances can be further degraded to smaller molecular weight substances such as protein and humic-like substances, which can penetrate to the membrane pore, and the accumulation of these substances can cause internal fouling by protein and humic-like substances. The optimisation of the logistics of the synergistic application of ferrate/membrane separation is required in future work.
- (2) On the ferric particles resulting from the sulphite/ferrate system, the crystalline structure of the non-activated particles is easier to prepare but has a low adsorption of pollutants. In contrast, the amorphous structure of the activated particles is more effective in adsorbing the pollutants but has a low precipitation rate. Therefore, future works need to study balanced treatment goals: the high adsorption of pollutants and/or quick precipitation via stoichiometric of sulphite and ferrate ratios.
- (3) In the ferrate/ozonation system, the catalytic interaction between ferrate and ozone can be weakened by the sequence of ozonation, so ferrate pre-oxidation is the ideal way to interact with the ozone and enhance the synergistic effect sufficiently.
- (4) Adding an appropriate amount of quinone could activate the decomposition of the ferrate to produce the reactive ferrate species (Fe(V) and Fe(IV)), which enhanced the ability to oxidise the electron-rich moieties. However, the excessive addition of quinone could weaken the flocculation performance and retard the transformation of iron species. Thus, the logistics of quinone application need to be optimised.

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