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Short communication

The Mn(VII)–H_2O_2 oxidation process: Abatement of electron-deficient N-containing organic compounds

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ABSTRACT

Chemical oxidants applied in water treatment are electrophiles, which preferentially attack sites with higher electron density. This typically results in less efficient oxidative abatement of organic compounds with electron-withdrawing substituents. In this study, we observed that the permanganate-hydrogen peroxide (Mn(VII)–H_2O_2) process can enhance the abatement of some nitrogenous organic compounds with electron-withdrawing groups more significantly compared to Mn(VII) in absence of H_2O_2. A comparison of the oxidation of aniline and 4-chloroaniline, N,N-dimethylaniline and p-cyano-N,N-dimethylaniline, and hydrazine and acethydrazide for Mn(VII) and the Mn(VII)–H_2O_2 process was performed. It was observed that Mn(VII)–H_2O_2 can specifically enhance the oxidative abatement of the paired target compounds containing electron-withdrawing groups. By addition of Ba^{2+}, to block the Mn(VI) reaction, it was demonstrated that Mn(VI) formed in the Mn(VII)–H_2O_2 process, was decisive for inducing the enhanced oxidation. This study reveals an interesting novel application of Mn(VII)–H_2O_2 for oxidative abatement of N-containing electron-deficient organic compounds during water treatment.

1. Introduction

Permanganate (Mn(VII)) is a comparatively stable chemical oxidant for water treatment with a relatively low carbon footprint [4]. It can be applied for the mitigation of disinfection byproducts (DBPs) formation through pre-oxidation, removal of Mn(II) and Fe(II) and inhibition of the growth of invasive species in intake pipes of drinking water treatment plants [6,1,3]. However, Mn(VII) is a selective oxidant for organic compounds and reacts mostly with phenols, anilines and olefins, but only slowly with aliphatic amines and alkanes [13,8,2]. Overall, compared to ozone that also produces hydroxyl radical ($^\bullet OH$), it is considered a mild oxidant with a limited broadband applicability in water treatment [7,12]. To enhance the applicability of permanganate, the oxidation range of Mn(VII) was improved, by combining it with a reductant (e.g. Na_2SO_3 or $CaSO_3$), another technology (e.g., UV), or with reductant-coated heterogeneous catalysts [11,5,9,16]. The purposes of these approaches are to induce the formation of more reactive oxidants such as Mn(III), $SO_4^{\bullet-}$, $^\bullet OH$ and Mn(V), etc., to enhance oxidative abatement of micropollutants.

In a previous study, we reported that a combination of permanganate with hydrogen peroxide (Mn(VII)–H_2O_2) can enhance the abatement of the fluoroquinolone antibiotic ciprofloxacin, compared to Mn(VII) in absence of H_2O_2 [15]. The produced Mn(VI) from the one-electron reduction of Mn(VII) by H_2O_2, was proposed to be the main species responsible for the enhanced oxidation. In addition, superoxide radical ($O_2^{\bullet-}$) was detected in this reaction. Since ciprofloxacin contains an aniline structure, we tested the efficiency of the abatement of other N-containing compounds such as anilines, N,N-dimethylanilines, benzylamines, hydrazides and some organic compounds without nitrogen groups such as benzoic acid, oxalic acid, diphenylmethanol. Specifically, the enhancing effect of electron-withdrawing substituents on the oxidizability of anilines and hydrazides by Mn(VII)–H_2O_2 compared to Mn(VII) was discovered and further investigated in this study.

2. Materials and methods

Potassium permanganate ($KMnO_4$, $\geq$ 99 %) was obtained from Merck, Darmstadt (Germany). H_2O_2 ($\geq$35 %), aniline ($\geq$99.5 %), 4-chloroaniline (98 %), N,N-dimethylaniline (99 %), p-cyano-N,N-dimethylaniline (98 %), p-toluenesulfonyl hydrazide (97 %), hydrazine monohydrate ($NH_2NH_2 \cdot H_2O$, 98 %), acethydrazide ($CH_3CONHNH_2$, 90 %), sodium phosphate dibasic dihydrate ($Na_2HPO_4 \cdot 2H_2O$, 98.5–101.0
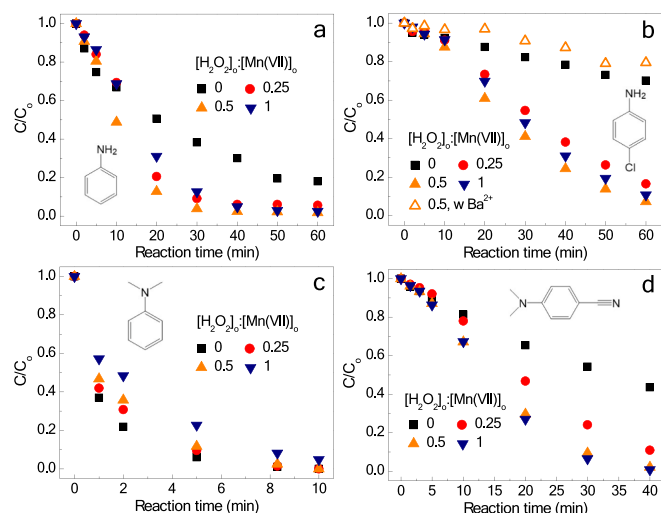
Fig. 1. Oxidative abatement of organic target compounds by Mn(VII) and Mn(VII)–H$_2$O$_2$ at molar concentration ratios [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ = 0–1. Experimental conditions: pH = 7.5, 2 mM phosphate buffer, (a) [Mn(VII)]$_o$ = 100 μM, [H$_2$O$_2$]$_o$ = 0–100 μM, [aniline]$_o$ = 1 μM; (b) [Mn(VII)]$_o$ = 100 μM, [H$_2$O$_2$]$_o$ = 0–100 μM, [4-chloroaniline]$_o$ = 1 μM, [BaCl$_2$]$_o$ = 100 μM; (c) [Mn(VII)]$_o$ = 5 μM (lower concentration because of a very fast reaction), [H$_2$O$_2$]$_o$ = 0–5 μM, [*N,N*-dimethylaniline]$_o$ = 1 μM; (d) [Mn(VII)]$_o$ = 100 μM, [H$_2$O$_2$]$_o$ = 0–100 μM, [*p*-cyano-*N,N*-dimethylaniline]$_o$ = 1 μM. Samples were collected at selected time points and quenched with NH$_2$OH ([NH$_2$OH]$_o$:[Mn(VII)]$_o$ = 25) containing Na$_2$EDTA. The pH varied by less than 0.1 during the experiments.

%), sodium phosphate monobasic monohydrate (NaH$_2$PO$_4$·H$_2$O, ≥ 99 %), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS, ≥ 98 %) and hydroxylamine hydrochloride (NH$_2$OH·HCl, ≥ 99 %) were obtained from Sigma Aldrich. Barium chloride dihydrate (BaCl$_2$·2H$_2$O, ≥ 99 %) was obtained from Scharlau (Spain), and the disodium dihydrate salt of ethylenediaminetetraacetic acid (Na$_2$EDTA·2H$_2$O, ≥ 99 %) was obtained from Fluka.

The absorbance of H$_2$O$_2$ or ABTS$^{\bullet+}$ solution at a specific wavelength was recorded by a UV–Vis spectrophotometer (Cary 100, Agilent, USA) with a 1-cm quartz cuvette (Hellma, Germany). The concentration of the H$_2$O$_2$ stock solution was quantified at A$_{240}$ with ε$_{240 nm}$ = 40 M^{-1} cm^{-1}, and the concentration of the formed ABTS$^{\bullet+}$ was quantified at A$_{728}$ with 14000 M^{-1} cm^{-1} [10,14]. The concentrations of aniline, 4-chloroaniline, *N,N*-dimethylaniline, *p*-cyano-*N,N*-dimethylaniline, *p*-toluenesulfonyl hydrazide and 2-phenylacetohydrazide were quantified by a high-performance liquid chromatograph coupled with a diode array detector (HPLC-DAD, UltiMate 3000, Thermo Scientific, Switzerland) with a 5C$_{18}$-MS-II column (3 × 150 mm, 5 μm particle size, Cosmosil, Japan). To compare between the oxidation efficiency of Mn(VII) and Mn(VII)–H$_2$O$_2$ on aniline/4-chloroaniline, *N,N*-dimethylaniline/*p*-cyano-*N,N*-dimethylaniline and *p*-toluenesulfonyl hydrazide/2-phenylacetohydrazide, Mn(VII) (100 μM) and/or H$_2$O$_2$ (25–100 μM) were added to a solution containing 2 mM phosphate buffer (pH 7.5), the target organic compound (1 μM) under magnetic stirring. Subsequently, samples were taken at selected time points, immediately quenched with NH$_2$OH·HCl (molar ratio [NH$_2$OH]$_o$:[Mn(VII)]$_o$ = 25) containing EDTA (molar ratio [EDTA]$_o$:[Mn(VII)]$_o$ = 2, to mask the formed Mn(II)), to avoid precipitations in the HPLC system. The kinetic data obtained were proven to be stable with representative repeated experiments.

To compare the oxidation ability of Mn(VII)/Mn(VII)–H$_2$O$_2$ on hydrazine/acetohydrazide, Mn(VII) (50 μM) and/or H$_2$O$_2$ (50 μM) were first added to a 2 mM phosphate-buffered solution (pH 7.5) under stirring. Samples were collected after 5 and 9 min, when the Mn(VII)–H$_2$O$_2$ reaction (if present) had reached a plateau, quenched with solutions containing excess ABTS ([ABTS]$_o$:[Mn(VII)]$_o$ = 10), and measured at

A$_{728}$. A$_{728}$ hardly varied for these two time points, indicating a stable formation of ABTS$^{\bullet+}$ from the oxidation by Mn(VII) or Mn(VII)–H$_2$O$_2$. To test the reactivity of hydrazine or acethydrazide, these compounds were added to a Mn(VII)-containing solution or a stabilized Mn(VII)–H$_2$O$_2$ system, after completion of the reaction between Mn(VII) and H$_2$O$_2$. The produced semi-stable oxidative intermediate, Mn(VI), has a long life-time in the Mn(VII)–H$_2$O$_2$ system, beyond the initial fast reaction [15]. Samples were then collected at 0.17–3 min of hydrazine/acethydrazide oxidation time and immediately quenched with solutions containing excess ABTS ([ABTS]$_o$:[Mn(VII)]$_o$ = 10) and then measured at A$_{728}$. The extent of oxidant consumption (ΔA$_{728}$) by hydrazine or acethydrazide for Mn(VII) only or the Mn(VII)–H$_2$O$_2$ system, was semi-quantitatively calculated by the decrease of A$_{728}$ compared to the blank A$_{728}$ (i.e. the average value of A$_{728}$ obtained at 5 and 9 min after Mn(VII) and/or H$_2$O$_2$ addition, when hydrazine or acethydrazide was not added). This decrease is a measure for the consumption of oxidants (Mn(VII), Mn(VII)–H$_2$O$_2$) by the target compounds and can be used to assess the reaction kinetics.

3. Results and discussion

3.1. Abatement of aniline and 4-chloroaniline by Mn(VII)–H$_2$O$_2$

Fig. 1 shows the oxidative abatement of various target compounds by Mn(VII) and the combination of Mn(VII) with H$_2$O$_2$. Fig. 1a shows that the combined Mn(VII)–H$_2$O$_2$ process significantly enhances the oxidative abatement of aniline compared to Mn(VII) alone. The extents of enhancement were similar for molar ratios [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ = 0.25–1.0. Fig. 1b shows that for 4-chloroaniline, an even more pronounced enhancement of the oxidation by Mn(VII)–H$_2$O$_2$ was observed for all [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ ratios. For a reaction time of 30 min and a molar concentration ratio [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ = 1, the degradation efficiency of aniline was enhanced by 42 %, while the degradation efficiency of 4-chloroaniline was enhanced by 193 %. In presence of Ba^{2+}, the enhancement effect of the Mn(VII)–H$_2$O$_2$ process for the abatement of 4-chloroaniline was completely inhibited (Fig. 1b), indicating that Mn(VI), which is quenched by Ba^{2+}, is a critical species for the observed enhancement. This is consistent with the previous observation that Mn(VI) is the first Mn reaction product formed from the reaction of Mn(VII) with H$_2$O$_2$ at molar ratios [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ ≤ 1 [15].

3.2. Abatement of N,N-dimethylaniline and p-cyano-N,N-dimethylaniline by Mn(VII)–H$_2$O$_2$

Fig. 1c shows that compared to Mn(VII) oxidation, the Mn(VII)–H$_2$O$_2$ process did not enhance the abatement of *N,N*-dimethylaniline and even had a slight inhibition effect. In contrast, Fig. 1d shows that Mn(VII)–H$_2$O$_2$ enhanced the oxidative abatement of *p*-cyano-*N,N*-dimethylaniline compared to Mn(VII). For a reaction time of 30 min, the degradation efficiency of *p*-cyano-*N,N*-dimethylaniline was enhanced by 66 %, 98 % and 104 % at molar concentration ratios [H$_2$O$_2$]$_o$:[Mn(VII)]$_o$ = 0.25, 0.5 and 1, respectively. Since the *p*-cyano-*N,N*-dimethylaniline has an electron-withdrawing group on the aniline structure, this indicates again that the combination Mn(VII)–H$_2$O$_2$ can enhance the oxidative abatement of the electron poorer compound, compared to Mn(VII). Moreover, the comparison between the abatement of *N,N*-dimethylaniline and *p*-cyano-*N,N*-dimethylaniline indicates again the selectivity of the oxidation by the combined Mn(VII)–H$_2$O$_2$ system for electron poorer organic compounds.

3.3. Oxidation of aromatic hydrazides by Mn(VII)–H$_2$O$_2$

Based on the results of this and a previous study [15], in which an enhancement of the abatement of ciprofloxacin by the Mn(VII)–H$_2$O$_2$ process was observed, it is hypothesized that *N*-containing compounds with electron-withdrawing groups are susceptible to this oxidation
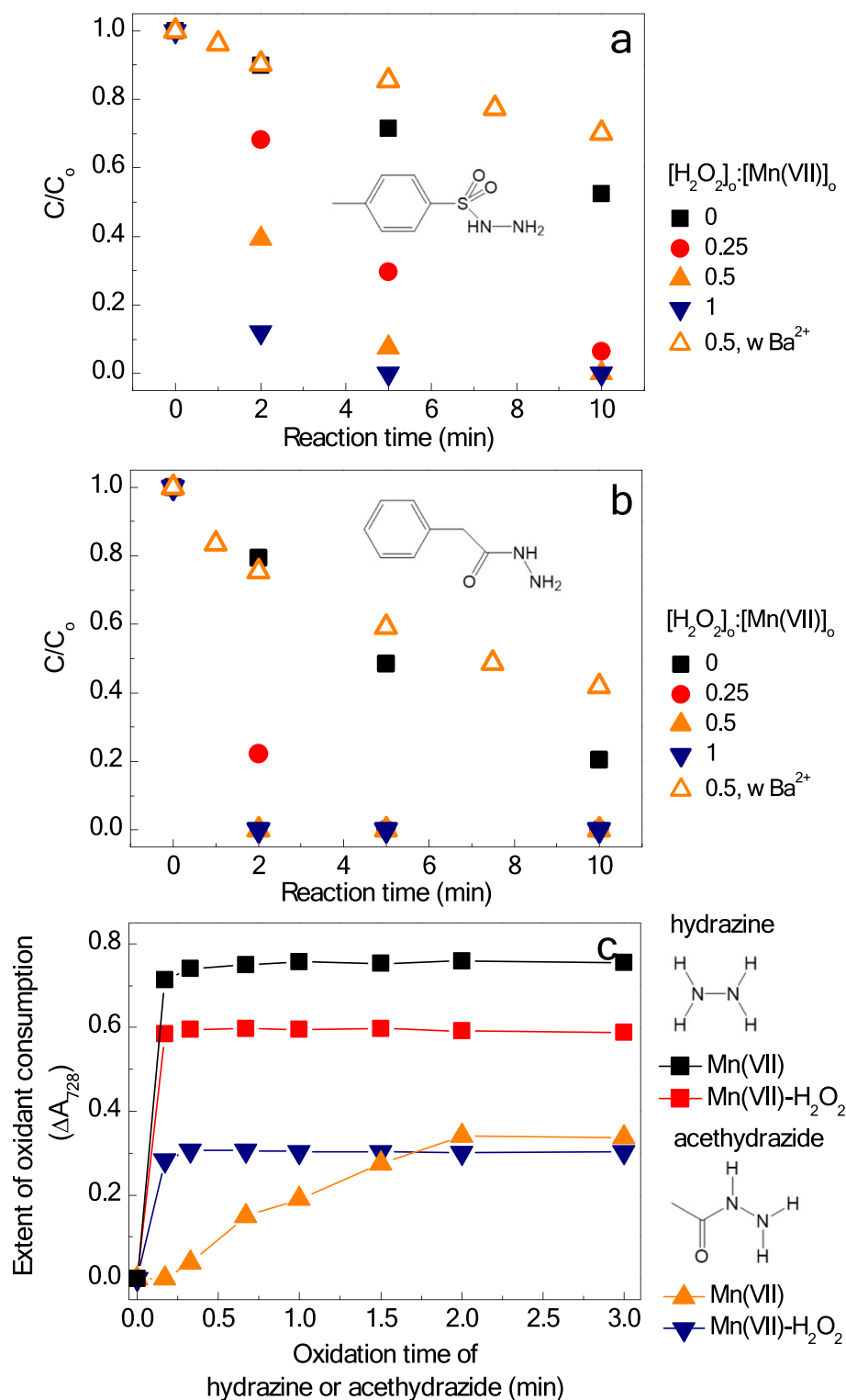
Fig. 2. Oxidative abatement of (a) *p*-toluenesulfonyl hydrazide and (b) 2-phenylacetohydrazide by Mn(VII) and Mn(VII)–H$_2$O$_2$ at molar concentration ratios [H$_2$O$_2$]$_o$: [Mn(VII)]$_o$ = 0.25–1. Experimental conditions: pH = 7.5, 2 mM phosphate buffer, [Mn(VII)]$_o$ = 100 μM, [H$_2$O$_2$]$_o$ = 0–100 μM, [*p*-toluenesulfonyl hydrazide]$_o$ = [2-phenylacetohydrazide]$_o$ = 1 μM, [BaCl$_2$]$_o$ = 100 μM. Samples were collected at selected time points and quenched with NH$_2$OH ([NH$_2$OH]$_o$:[Mn(VII)]$_o$ = 25) containing Na$_2$EDTA. (c) Extent of oxidant consumption (ΔA$_{728}$) of hydrazine or acethydrazide for Mn(VII) only and the Mn(VII)–H$_2$O$_2$ oxidation systems. Hydrazine or acethydrazide was added to the Mn(VII)/Mn(VII)–H$_2$O$_2$ solution prior to the quenching of Mn(VII)/Mn(VII)–H$_2$O$_2$ solution with ABTS. Experimental conditions: pH = 7.5, 2 mM phosphate buffer, [Mn(VII)]$_o$ = 50 μM, [H$_2$O$_2$]$_o$ = 50 μM, [hydrazine/acethydrazide]$_o$ = 20 μM, [ABTS]$_o$:[Mn(VII)]$_o$ = 10. Further details about the experiments and the calculation method of the extent of oxidant consumption (ΔA$_{728}$) are provided in the materials & methods section.

process. Fig. 2a shows that at molar concentration ratios $[H_2O_2]_0$:[Mn(VII)]$_0$ = 0.25, 0.5 and 1, the oxidative abatement of *p*-toluenesulfonyl hydrazide was significantly enhanced compared to oxidation by Mn(VII) only. The abatement efficiency of *p*-toluenesulfonyl hydrazide increased by 212 %, 495 % and 762 % for a reaction time of 2 min for molar concentration ratios $[H_2O_2]_0$:[Mn(VII)]$_0$ = 0.25, 0.5 and 1, respectively, relative to Mn(VII) alone. The presence of Ba^{2+} completely inhibited the enhancement effect (Fig. 2a), indicating again the decisive role of the produced Mn(VI) for the enhanced oxidation. Another compound with a –NH–NH$_2$ structure, 2-phenylacetohydrazide, also underwent an enhanced oxidation during the Mn(VII)–H$_2$O$_2$ process, with an inhibition by Ba^{2+} (Fig. 2b). This indicates that the Mn(VII)–H$_2$O$_2$ oxidation process has also a high efficiency for the abatement of aromatic hydrazides and a large enhancement for electron-poorer compounds.

3.4. Abatement of hydrazine and acethydrazide by Mn(VII)–H$_2$O$_2$

It is noteworthy that on the structures of *p*-toluenesulfonyl hydrazide and 2-phenylacetohydrazide, there are electron-withdrawing moieties (sulfone and ketone groups) next to the hydrazide group. To reveal the effect of electron density on the oxidation of hydrazide by Mn(VII)–H$_2$O$_2$, the oxidations of hydrazine (NH$_2$NH$_2$) and acethydrazide (CH$_3$CONHNH$_2$) by Mn(VII) and Mn(VII)–H$_2$O$_2$ were investigated. The extent of oxidant consumption (ΔA_{728}) of hydrazine or acethydrazide for the Mn(VII) only or the Mn(VII)–H$_2$O$_2$ oxidation systems, as introduced in the materials & methods section, was semi-quantitatively used to evaluate the extent of oxidant consumption induced by these two *N*-containing compounds for Mn(VII) only or the Mn(VII)–H$_2$O$_2$ oxidation system. As shown in Fig. 2c, the oxidant consumption rates induced by hydrazine for Mn(VII) and Mn(VII)–H$_2$O$_2$ systems were similar, and the extent of oxidant consumption for the Mn(VII) system was shown to be higher than for the Mn(VII)–H$_2$O$_2$ system. In contrast, the consumption rate induced by acethydrazide was significantly higher for the Mn(VII)–H$_2$O$_2$ than for the Mn(VII) system. Since there is an electron-deficient acetyl group adjacent to the –NH–NH$_2$ moiety in acethydrazide, it supports the finding that an electron withdrawing group on *N*-containing organic compounds can enhance the oxidation by the Mn(VII)–H$_2$O$_2$ process compared to a Mn(VII) oxidation only.

Overall, this study reveals that for *N*-containing compounds with electron-withdrawing substituents, Mn(VII)–H$_2$O$_2$ leads to a higher relative enhancement of the oxidation compared to Mn(VII) relative to the target compound without an electron-withdrawing substituent. On the one hand, the produced Mn(VI) from the Mn(VII)–H$_2$O$_2$ process may be more reactive towards the electron-deficient *N*-containing organic compounds compared to Mn(VII) oxidation only. On the other hand, the $O_2^{\bullet-}$ which is formed from the Mn(VII)–H$_2$O$_2$ reaction [15], might play a role to activate the electron-deficient sites, by increasing their electron densities and make the corresponding compounds more easily oxidized by the Mn(VII)–H$_2$O$_2$ process. Based on these findings, an addition of H$_2$O$_2$ can be implemented in the second stage of a Mn(VII) oxidation process to target *N*-containing compounds such as anilines and hydrazides with electron-withdrawing substituents. Nevertheless, the target functional groups that can be degraded by Mn(VII)–H$_2$O$_2$ still deserve further investigation, to get a better understanding of a broader applicability of this process. Moreover, the mechanistic understanding related to the effects of electron withdrawing groups needs to be improved. When treating industrial wastewaters containing a variety of organic pollutants and inorganic ions, electron-rich moieties and inorganic constituents will be consumed by Mn(VII) oxidation before H$_2$O$_2$ addition and the induction of the Mn(VII)–H$_2$O$_2$ process. The unique selectivity of the Mn(VII)–H$_2$O$_2$ system can then be an advantage for the abatement of *N*-containing electron-deficient organic compounds in such complex water matrices. It is also noteworthy that even though Mn(VI) was demonstrated to be mainly responsible for inducing the enhancement effects, there might be other Mn species that are produced from Mn(VI) which directly oxidize the micropollutants.

4. Conclusions

Compared to oxidation by Mn(VII), the Mn(VII)–H$_2$O$_2$ oxidation process can enhance significantly the abatement of some nitrogenous organic compounds with electron withdrawing substituents relative to the unsubstituted analogues:

- Compared with aniline and *N,N*-dimethylaniline, the degradations of 4-chloroaniline and *p*-cyano-*N,N*-dimethylaniline were significantly enhanced by Mn(VII)–H$_2$O$_2$ in contrast to Mn(VII) oxidation.
- The aromatic hydrazides, *p*-toluenesulfonyl hydrazide and 2-phenylacetohydrazide, and acethydrazide which all contain electron-withdrawing groups also underwent significantly enhanced oxidations by Mn(VII)–H$_2$O$_2$.
- Mn(VI) was demonstrated to be the main species responsible for inducing the enhanced oxidation.
- Due to the significant enhancement of the oxidation of some target compounds with electron-withdrawing substituents by Mn(VII)–H$_2$O$_2$, the underlying oxidation mechanisms deserve further investigation to better assess a broader applicability of this novel process.

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

Data will be made available on request.

Acknowledgements

References

[1] Balog, G.G., Neimery, T.F., Davis, L.S., 1995. Baltimore City adopts a proactive approach to zebra mussel control using potassium permanganate. Electric Power Research Inst., Palo Alto, CA, U.S.A.

[2] J.S. Du, B. Sun, J. Zhang, X.H. Guan, Parabola-like shaped pH-rate profile for phenols oxidation by aqueous permanganate, Environ. Sci. Technol. 46 (16) (2012) 8860–8867.

[3] R.M. Galvín, J.M.R. Mellado, Potassium permanganate as pre-oxidant in a reverse osmosis water plant, Water SA 24 (4) (1998) 361–363.

[4] X.H. Guan, D. He, J. Ma, G.H. Chen, Application of permanganate in the oxidation of micropollutants: a mini review, Front. Environ. Sci. Eng. China 4 (4) (2010) 405–413.

[5] K.H. Guo, J.S. Zhang, A.L. Li, R.J. Xie, Z.J. Liang, A.N. Wang, L. Ling, X.C. Li, C.H. Li, J.Y. Fang, Ultraviolet irradiation of permanganate enhanced the oxidation of micropollutants by producing HO• and reactive manganese species, Environ. Sci. Technol. Lett. 5 (12) (2018) 750–756.

[6] B. Moyers, J.S. Wu, Removal of organic precursors by permanganate oxidation and alum coagulation, Water Res. 19 (3) (1985) 309–314.

[7] E. Ortenberg, B. Telsch, Taste and odour problems in potable water, Academic Press, Handbook of Water and Wastewater Microbiology, 2003.

[8] Petri, B.G., Thomson, N.R., Urynowicz, M.A., 2010. Fundamentals of ISCO using permanganate. In Situ Chemical Oxidation for Groundwater Remediation, in SERDP/ESTCP Environmental Remediation Technology, 89–146.

[9] D.D. Rao, J. Chen, H.Y. Dong, J.L. Qiao, B.X. Zhou, Y.K. Sun, X.H. Guan, Enhanced oxidation of organic contaminants by Mn(VII)/CaSO3 under environmentally relevant conditions: performance and mechanisms, Water Res. 188 (2021) 116481.

[10] J.V. Rodrigues, C.M. Gomes, Enhanced superoxide and hydrogen peroxide detection in biological assays, Free Radical Biol. Med. 49 (1) (2010) 61–66.

[11] B. Sun, X.H. Guan, J.Y. Fang, P.G. Tratnyek, Activation of manganese oxidants with bisulfite for enhanced oxidation of organic contaminants: the involvement of Mn (III), Environ. Sci. Technol. 49 (20) (2015) 12414–12421.

[12] U. von Gunten, Oxidation processes in water treatment: are we on track? Environ. Sci. Technol. 52 (9) (2018) 5062–5075.

[13] R.H. Waldemer, P.G. Tratnyek, Kinetics of contaminant degradation by permanganate, Environ. Sci. Technol. 40 (3) (2006) 1055–1061.

[14] N. Walpen, J. Houska, E. Salhi, M. Sander, U. von Gunten, Quantification of the electron donating capacity and UV absorbance of dissolved organic matter during ozonation of secondary wastewater effluent by an assay and an automated analyzer, Water Res. 185 (2020) 116235.

[15] K. Xu, U. von Gunten, Permanganate reduction by hydrogen peroxide: formation of reactive manganese species and superoxide and enhanced micropollutant abatement, ACS EST Engg. 1 (10) (2021) 1410–1419.

[16] H.L. Zhang, J. Ma, J. Zhang, T.J. Strathmann, ABNO-functionalized silica as an efficient catalyst for enhancing permanganate oxidation of emerging contaminants, Environ. Sci. Technol. 57 (1) (2023) 635–642.