UV-activated permanganate process for micro-organic pollutant degradation: efficiency, mechanism and influencing factors

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ABSTRACT

Ultraviolet-activated permanganate (UV/PM) process is a novel advanced oxidation process (AOP), but its application potential remains to be evaluated. This work investigates the degradation of refractory organic pollutant by UV/PM in terms of efficiency, mechanism, and influencing factors. The target compound benzoic acid (BA), which is a micro-organic pollutant and is resistant to PM and UV treatment, can be efficiently degraded by UV/PM. The electron paramagnetic resonance spectra directly supported the formation of hydroxyl radical (HO•) and superoxide radical (O2•−) from UV photolysis of PM. Competitive kinetics experiments verified that O2•− acted as precursor of HO• and the good degradation performance of BA was due to the involvement of HO• and manganese(V). The rate constants of BA degradation showed a positive linear relationship with PM dosage in the range of 0.5–20 mg·L−1, and the degradation process was significantly influenced by solution pH and natural organic matters but insensitive to chloride and bicarbonate at environmentally relevant concentrations. Compared to the typical UV-based AOP UV/hydrogen peroxide, UV/PM is a little inferior, indicating that optimization and enhancement is needed for this process before its possible practical application.

Key words | active manganese species, hydroxyl radical, permanganate, UV activation

HIGHLIGHTS

- The mechanism of HO• generation from photolysis of PM was parsed.
- The effects of operating parameters (e.g. PM dosage, pH, natural organic matters, alkalinity, and chloride) on UV/PM process were investigated.
- UV/PM process was compared with UV/H2O2.
- Optimization and enhancement is needed for UV/PM process before its possible practical application.

INTRODUCTION

Permanganate (PM), as a green oxidant, is widely used in water treatment to control algae, color, odor, heavy metals, emerging organic pollutants, disinfection by-products, coagulant demand, and chlorine demand. The attractive characteristics of PM are its chemical stability, convenient storage and delivery, effectiveness over a wide pH range, and little second-pollution (Guan et al. 2010). PM is a selective oxidant which tends to react with organic pollutants bearing electron-rich moieties such as phenols and olefins, but it shows a slow reaction kinetics with some other contaminants such as trimethoprim, lincomycin, and ciprofloxacin (Hu et al. 2010). Moreover, due to its moderate oxidation potential (+1.51 V) at neutral pH, PM degrades micro-organic pollutants slowly, and the degradation process is usually accompanied with the formation of many intermediates which may keep partial or whole biotoxicity relative to the
parent molecule or even display stronger biocytotoxicity than their parent molecule (Zhang et al. 2014).

To enhance the degradation capacity of micro-organic pollutants by PM, researchers have tried to activate PM to produce secondary oxidants such as manganese (Mn(III), Mn(IV), Mn(V), and Mn(VI)). The reported activation methods of PM include reduction activation (bisulfitte (Sun et al. 2015), Mn(II) (Luther et al. 1994), hydrogen peroxide (H₂O₂) (Davies 1969)), ligand-induced activation (pyrophosphate (PP), ethylenediaminetetraacetic acid, and nitrilotriacetic acid) (Jiang et al. 2010), photoactivation (Lee et al. 1987), and sonar activation (Hu et al. 2018). Reduction and ligand-induced activation methods involve the addition of chemical reagents, which are toxic or increase the organic carbon, and thus are not suitable to be used in water treatment. Sonar activation is energy-exhaustive. Ultraviolet (UV) radiation is a promising water treatment technology and has been used to activate oxidants such as peroxides, chlorine, ozone, and ferrate to produce highly reactive radicals such as hydroxyl radical (HO•), chlorine radical (Cl•), and sulfate radical for the destruction of micropollutants (Talaiekhozani et al. 2016; Wang & Liu 2019; Gao et al. 2020; Zhang et al. 2021). Recent work reported that UV irradiation can also be used to activate PM (Guo et al. 2018). In this work, HO• and Mn(V)-peroxo complex (MnO₂(NO₃⁻/O₂)²⁻) were proposed to be the main active species responsible for pollutant degradation, and manganese dioxide (MnO₂) is the final product of PM photodecomposition. Little is known, however, about how the HO• is generated during photolysis of PM or the effects of operating parameters (e.g. PM dosage, pH, natural organic matters (NOM), alkalinity, and chloride) on UV-activated PM (UV/PM) process. This information is believed to be important to push forward the application of UV/PM in practical water treatment.

Thus, benzoic acid (BA), a PM-resistant and UV-resistant organic pollutant, was selected as the target compound. To provide some suggestions on technical feasibility, UV/PM was compared with UV/H₂O₂, one of the most widely used advanced oxidation processes (AOPs) in practice, in terms of BA degradation efficiency and energy cost. This study tries to throw some light on the formation mechanism of reactive species (especially HO•) in the UV/PM system and evaluate the possible effects caused by operating parameters.

**METHODS**

**Chemicals and reagents**

BA, potassium permanganate, ascorbic acid, sodium bicarbonate, sodium chloride, and phenol were obtained from Sinopharm Chemical Reagent Co. Ltd. Sodium pyrophosphate, 4-hydroxytetramethyl-piperidine-1-oxyl (TEMPOL), tert-butanol (TBA), and humic acid (HA) were ordered from Aladdin Reagent Co. Ltd. Boric acid, sodium tetraborate decahydrate, potassium pyrophosphate, and 5,5-dimethyl-1-pyrrrole N-oxide (DMPO) were purchased from Sigma-Aldrich. Ultrapure water (18.2 MΩ·cm) was used to prepare solutions.

**Experimental procedures**

The experiment was carried out in a sealed glass reactor (800 mL, inner diameter 4.0 cm) which was covered by aluminum foil to block light. A low-pressure mercury UV lamp (Heraeus, GPH212T5 L/4, 10 W, ozone-free), with a peak spectrum line at 254 nm, was placed in a quartz tube located at the center of the reactor. The photon flux in the photoreactor was determined to be 6.3 × 10⁻⁸ Einstein·s⁻¹. BA at designed concentration (1 mg·L⁻¹) was first prepared, and the pH value was adjusted using 10 mM phosphate/borate buffer from 5.0 to 9.0 if necessary. A designed volume of freshly prepared potassium permanganate (K₂MnO₄) stock solution (calibrated concentration 1,122.0 mg·L⁻¹) was then added. The mixture was vigorously stirred with a magnetic stirrer during the whole reaction process. The temperature of the reaction slurry was maintained at the set point via water bath. The timing started as soon as the UV light baffle was opened. Excessive ascorbic acid was immediately added after sample drawing. Each experiment under one condition was conducted in triplicate and the means were used.

**Analysis methods**

BA was quantified by an Agilent 1,200 high-performance liquid chromatograph (HPLC) equipped with an Agilent Eclipse XDB-C18 column. HPLC grade methanol/0.1% phosphoric acid (55/45, v/v) was used as the mobile phase at 30 °C with a flow rate of 1 mL·min⁻¹. The detection wavelength was set at 227 nm. The concentration of HA and mineralization rate of BA in different treatment processes were determined via a Shimadzu total organic carbon (TOC) analyzer.

To determine the degradation intermediates of BA, samples (500 mL) were concentrated on a Gilson GX-271 ASPEC apparatus and analyzed with an Agilent 6,460 triple quadruple HPLC-MS equipped with an electrospray ionization (ESI) source. The mass spectrometric measurements were carried out using an ESI in positive ion mode. BA and its intermediates were separated isocratically with
a 55/45 (v/v) acetonitrile/0.1% formic acid mobile phase at the flow rate of 0.3 mL·min⁻¹.

Qualitative analysis of HO⁻ and superoxide radical (O₂⁻) was done through a Bruker A200 electron paramagnetic resonance (EPR) 300E instrument. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of Mn at the surface of the suspended particles. Anhydrous samples for XPS analysis were freshly prepared by filtering 100 mL reaction solution at 10-min reaction time with 0.2 μm membrane and lyophilizing under vacuum.

**Determination of Mn(III)**

To monitor Mn(III) produced during the degradation process of BA by UV/PM, PP was added into the degradation system before the reaction started to capture unstable Mn(III) and form a stable complex. The Mn(III) complex shows a characteristic absorption at 260 nm. A water sample was drawn at the reaction time of 15 min. Two control experiments, single PM oxidation in presence of PP and UV/PM degradation without PP addition, were performed in parallel.

**RESULTS AND DISCUSSION**

**Degradation efficiency of BA by UV/PM**

Comparative abatement of BA was examined by PM oxidation, direct UV photolysis, and UV/PM (Figure 1). Direct UV photolysis and PM oxidation showed poor BA degradation performance for 20-min reaction time (<10.0%), while UV/PM exhibited an obviously improved BA degradation (52.6%). One can find that the degradation rate of BA by UV/PM was much higher than the sum of that of direct UV photolysis and PM oxidation. Thus, there should be newly formed active species contributing to BA degradation. Additionally, UV/PM was compared with UV/H₂O₂ to roughly rank it among the AOPs applied in practice (Figure 1). The results indicated that the pseudo-first-order rate constant of UV/H₂O₂ was almost twice as fast as that of UV/PM (insert in Figure 1) and the mineralization rate in UV/H₂O₂ was 10.1% higher than that in UV/PM. From the perspective of energy required for 90% destruction of pollutant (EE/O), EE/O value of UV/PM was 10.4 times as high as that of UV/H₂O₂ (Text 1S and Table 1S in Supporting Information). Since BA was resistant to UV, PM, and H₂O₂, such comparison illustrates that UV/PM should be further optimized or enhanced from the perspective of oxidizing capacity.

**Verifying the formation of reactive species and quantifying their contributions**

It has been reported that UV photolysis of PM follows a two-step photodecomposition pathway (Thornley & Bitterwolf 2015): (1) PM first transforms to an excited state (MnO⁴⁻) which quickly converts to Mn(V) (MnO₂(η²-O₂⁻)) or reverts to PM (Equations (1) and (2)); (2) Mn(V) then decomposes to Mn(III) (MnO₂) and O₂ or MnO₂ and HO⁻ (Equations (3) and (4)). XPS analysis of the particles generated during the reaction process was performed to identify whether MnO₂ was produced. As shown in Figure 2, there were two characteristic peaks with binding energies of 653.7 eV (Mn2p₁/₂) and 642.3 eV (Mn2p₃/₂) and MnO₂ and HO⁻ (Equations (3) and (4)). XPS analysis of the particles generated during the reaction process was performed to identify whether MnO₂ was produced. As shown in Figure 2, there were two characteristic peaks with binding energies of 653.7 eV (Mn2p₁/₂) and 642.3 eV (Mn2p₃/₂), respectively, in the sample, suggesting the existence of Mn(IV). The formula
of the test sample was finally confirmed to be MnO\textsubscript{2} based on the XPS quantitative analysis, which found the atomic ratio of Mn:O was about 1:2.

\begin{align*}
\text{MnO}_4^- & \xrightarrow{\text{hv}} \text{MnO}_4^{2+} \\
\text{MnO}_4^{2+} & \rightarrow \text{MnO}_2(\eta^2-\text{O}_2)^- \\
\text{MnO}_2(\eta^2-\text{O}_2)^- & \xrightarrow{\text{hv}} \text{MnO}_2 + \text{HO}^* \\
\text{MnO}_2(\eta^2-\text{O}_2)^- & \xrightarrow{\text{hv}} \text{MnO}_2^- + \text{O}_2
\end{align*}

The MnO\textsubscript{2} formed \textit{in situ} usually exists as a stable reduction product of PM and it was proven to demonstrate poor reactivity toward BA. Reactive Mn species, Mn(III) and Mn(V), are therefore considered to possible contributors to enhanced BA degradation. In summary, Mn(III), Mn(V), and HO\textsuperscript{-} were suspected of participating in BA degradation.

Given the possible roles of Mn(III), Mn(V), and HO\textsuperscript{-}, efforts were made to verify whether these three active species were produced. Electron paramagnetic resonance (EPR) spectroscopy was used to directly determine the formation of HO\textsuperscript{-} in UV/PM and the observation of a typical 1:2:2:1 quartet signal of the adduct of HO\textsuperscript{-} with DMPO confirmed the existence of HO\textsuperscript{-} (Figure 3). Meanwhile, the obtained EPR spectrum showed a 14-line spin signal, which was interpreted as an adduct of DMPO with O\textsubscript{2}\textsuperscript{-} (Clément et al. 2005). Considering that the complex of Mn(III) and PP show a characteristic peak of UV absorbance at 260 nm (Guo et al. 2018), we also monitored the UV–Vis absorbance spectra of the reaction solution to ascertain whether Mn(III) was generated (Fig. 1S in Supporting Information). The featured peak of Mn(III) at 260 nm was not detected. The role of Mn(III) is thus excluded, and Mn(V) was speculated to be the active Mn species involved in BA degradation. In addition to UV photolysis, HO\textsuperscript{-} and O\textsubscript{2}\textsuperscript{-}, and Mn(V) are suspected to be responsible for BA degradation in UV/PM systems.

Extensive research works have verified that UV\textsubscript{254} photolysis of aqueous organics does not follow a HO\textsuperscript{-} mechanism (Luo et al. 2018). Based on the simultaneous detection of HO\textsuperscript{-} and O\textsubscript{2}\textsuperscript{-}, we speculated that O\textsubscript{2}\textsuperscript{-} was generated from decomposition of MnO\textsubscript{2}(\eta^2-\text{O}_2)^- (Equation (5)) and acted as the precursor of HO\textsuperscript{-} (Equations (6) and (7) (Hayyan et al. 2016)). Nevertheless, O\textsubscript{2}\textsuperscript{-} is much less reactive toward BA than HO\textsuperscript{-} (Moon et al. 2017), resulting in its minor role during the BA degradation process.

\begin{align*}
\text{MnO}_2(\eta^2-\text{O}_2)^- & \xrightarrow{\text{hv}} \text{MnO}_2^- + \text{O}_2^- \\
2\text{O}_2^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 & \xrightarrow{\text{hv}} 2\text{HO}^*
\end{align*}

To further quantify the respective contribution of UV photolysis, HO\textsuperscript{-}, and Mn(V), a competitive kinetics method was used. TEMPOL (scavenger of O\textsubscript{2}\textsuperscript{-}) and TBA (scavenger of HO\textsuperscript{-}) were added into the UV/PM system. As shown in Figure 4, the presence of TBA decreased the degradation rate of BA by 25.9% compared to that without scavenger addition, indicating that HO\textsuperscript{-} participated in the degradation process. The presence of TEMPOL caused the BA degradation rate to decrease by 28.7%. The negligible difference (2.8%) in inhibition rate for TBA and TEMPOL.
revealed that HO• arose from O$_2^-$ conversion. The Mn(V)-
induced BA decomposition is responsible for the difference
of degradation curves for UV alone and UV/PM in presence
of TBA (scavenger of HO•). Thus, the contributions of HO•,
Mn(V), and UV photolysis are calculated to be 49.2%,
33.3%, and 17.5%, respectively.

**Identification of Mn(V)-induced degradation products**

The transformation products of a pollutant are usually
associated with the active species involved in the degra-
dation process, besides the chemical structure of the
pollutant. Therefore, degradation products of BA induced
by Mn(V) were qualified (Figure 5). Four hydroxylated
products (m/z = 158, 154, 112, and 94) were identified.
The detected hydroxylated products of BA are consistent
with the formation of active Mn species (Mn(V)) because
(1) direct photolysis of aromatic organics are mainly
through a nucleophilic reaction (ring opening) and/or
bond-scission (Bonvin et al. 2013), which usually do not
generate hydroxylated products; and (2) active Mn species
usually react with organics through β-elimination, intra-
molecular redox, hydrogen atom abstraction, and
electron transferring, yielding hydroxylated products as
the main products (Waldemer & Tratnyek 2006; Hu
et al. 2017). These hydroxylated products further verify
the formation of Mn(V).

**Effects of several operational parameters**

To ascertain whether there is an optimum dosage of PM, BA
degradation by UV/PM under different PM dosage was
investigated. As shown in Figure 6(a), BA degradation
improved with the increase of PM dosage. Additionally,
the degradation process obeyed a pseudo-first-order kinetics.
A two-stage linear relationship was shown between the reac-
tion rate constants (k$_{obs}$) and the PM dosage (insert in
Figure 6(a)). In relation to the color produced by PM
(Figure 6(b)) and with reference to the dosage applied in
drinking water plants, a PM dosage of 4 mg·L$^{-1}$ was selected
for the followed experiments.

Figure 7(a) shows the degradation performance of BA
under different pH. A deterioration of the BA removal was
observed with the pH variation from 5.0 to 9.0. Note that
the existing form of PM will not change in the pH range
of 5.0–9.0 because its molar extinction coefficient at 254 nm is constant and the absorption of UV photons by
PM will not be affected. Guo et al. (2018) considered that
pH can influence the degradation process as H$^+$ involved
in the formation of HO• in UV/PM. It is well known that
PM tends to decompose into manganese (MnO$_2^-$) and
oxygen under moderate or strong alkaline pH conditions
(Lott & Symons 1960). The conversion of PM to MnO$_2^-$
may influence the formation of Mn(V) and HO• and could
lead to a deteriorating degradation. In addition, the oxida-
tion potential of HO• will decrease from 2.51 V to
2.29 V (Xiao et al. 2016), which may also slow BA degradation.

Figure 7(b) shows the degradation performance of BA under different concentrations of HA (representative of NOM). Generally, 0.5–5.0 mg·L⁻¹ HA displayed a suppression effect on BA degradation. HA, even at a very low concentration (0.5 mg·L⁻¹), reduced BA degradation rate by 6.9%. When the concentration of HA increased to 5.0 mg·L⁻¹, 28.8% inhibition was observed. HA contains a large number of electron-rich moieties (reductive moieties) such as olefins and aromatic rings, which can compete with BA for HO• and Mn(V) and accelerate PM decomposition through a pathway without reactive species formation. As a light filter, HA will compete with PM for UV photons. On the other hand, HA can act as a ligand to stabilize Mn intermediates to enhance pollutant oxidation by PM (Jiang et al. 2010). Based on the observed phenomena, HA competitive consumption of HO• and Mn(V) appears to prevail over its enhancement effect induced by its ligand role.

In addition to NOM, background impurities such as bicarbonate (HCO₃⁻) and chloride (Cl⁻) in the water matrix can also affect the HO• concentration level. Bicarbonate can react with HO• to generate carbonate radical (CO₃²⁻), a relatively weak oxidative radical with oxidation potential of 1.59 V. Similarly, chloride can capture HO• to produce reactive chlorine species (RCSs; Cl·, Cl₂⁻, and ClO⁻) (Wang & Liu 2019). These RCSs are selective and show weak oxidation power compared to HO•. Thus, the effects of HCO₃⁻ and Cl⁻ on BA degradation by UV/PM were investigated. As shown in Figure 7(c)–7(d), the presence of HCO₃⁻ (1–8 mM) and Cl⁻ (0.5–4 mM) inhibited BA degradation as expected. The inhibition effect of HCO₃⁻ was stronger than that of Cl⁻. Because the pKa of the reaction product of HO• with chloride (ClOH•⁻, Equation (8)) is 7.2, and the reaction solution pH is 7.4, Equation (9) will outcompete Equation (10). Given that the decomposition rate constant of ClOH•⁻ (6.1×10⁹ M⁻¹·s⁻¹, (Wang & Liu 2019)) is slightly faster than its formation rate (4.3×10⁸ M⁻¹·s⁻¹, (Wang & Liu 2019)), most of ClOH•⁻ are believed to dissociate back to HO•. This may explain the weak influence of Cl⁻ on BA degradation. The reactivity of CO₃²⁻ with organic pollutants is usually about three–four orders of magnitude lower than that for HO• (Dell’Arciprete et al. 2012), which can reasonably account for the strong effect caused by HCO₃⁻.

\[
\begin{align*}
\text{HO}^• + \text{Cl}^- &\rightarrow \text{ClOH}^{•-} \quad (8) \\
\text{ClOH}^{•-} &\rightarrow \text{HO} + \text{Cl}^- \quad (9) \\
\text{ClOH}^{•-} + \text{H}^+ &\xrightarrow{hv} \text{H}_2\text{O} + \text{Cl} \quad (10)
\end{align*}
\]

**CONCLUSIONS**

The UV/PM can degrade BA efficiently. However, it was less efficient than UV/H₂O₂ in terms of degradation rate constant and energy consumption. Both the hydroxyl radical (HO•) and Mn(V) were identified in the UV/PM system and confirmed to play major roles in BA destruction (contributing 82.5%). The precursor of HO• was verified to be a superoxide radical originating from the photodecomposition of Mn(V) (MnO₂(η²–O₂)²⁻)). BA degradation by UV/PM improved with the increase of PM dosage from 0.5 to 20 mg·L⁻¹. The degradation process showed a weak...
dependence on initial pH in the range of 5–9 and the maximal degradation efficiency was obtained at initial pH 7.0. HA over a concentration range of 0.5–5.0 mg·L\(^{-1}\) significantly suppressed BA degradation. By contrast, HCO\(_3\) was confirmed to be a weak inhibitor and Cl\(^-\) almost did not show any influence. These results indicate that UV/PM needs optimization (e.g. optimizing UV wavelength) and enhancement (e.g. improving quantum yield of HO\(^\cdot\) and Mn(V)) for practical application.

Unlike the HO\(^\cdot\)-dominated UV/H\(_2\)O\(_2\) system, UV/PM system features formation of broad-spectrum reactive species (HO\(^\cdot\)) and selective reactive species (Mn(V)). This characteristic allows UV/PM to cope with a variety of pollutants contained in complex matrix waters, such as water with undesirable concentration of HO\(^\cdot\) scavengers (NOM, bicarbonate, chloride, etc.). On the economy scale, this will compensate the cost increase in raw materials to some extent when the commonly used UV/H\(_2\)O\(_2\) switches to UV/PM. However, the generation of MnO\(_2\) particles, one of PM photodecomposition products, determines that a particle removal step should be implemented after UV/PM. Based on the addressed characteristics, UV/PM may find its application in utilizing residual PM from the pre-oxidation unit of waterworks to enhance micro-organic pollutant degradation as a prepositive process of filtration unit.

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DATA AVAILABILITY STATEMENT

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

REFERENCES

Bonvin, F., Omlin, J., Rutler, R., Schweizer, W. B., Alaimo, P. J., Strathmann, T. J., McNeill, K. & Kohn, T. 2003 Direct photolysis of human metabolites of the antibiotic sulfamethoxazole: evidence for abiotic back-transformation. Environmental Science & Technology 47 (13), 6746-6755.

Clément, J. L., Ferré, N., Siri, D., Karoui, H., Rockenbauer, A. & Tordo, P. 2005 Assignment of the EPR spectrum of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) superoxide spin adduct. The Journal of Organic Chemistry 70 (4), 1198-1203.
