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Ru(III)-catalyzed permanganate oxidation of bisphenol A

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ABSTRACT

This study employed Ru(III) as catalyst in permanganate oxidation of bisphenol A (BPA) for the first time. Ru(III) could significantly improve the reaction rate of BPA oxidation by 1.2–6.3 times with its concentration varying from 2.5 to 15 μM. The oxidation of BPA by Ru (III)-catalyzed permanganate followed pseudo-first order with respect to BPA or permanganate and second order with respect to Ru(III). BPA removal by Ru-catalyzed permanganate oxidation was heavily dependent on pH, which may be associated with the variation of permanganate oxidation potential with pH. The effect of temperature on BPA removal by Ru(III)-catalyzed permanganate was investigated, and the activation parameters were calculated. BPA removal in the catalytic oxidation was enhanced in the presence of 1–10 mg C L^{-1} humic acid. Although the catalytic ability of Ru(III) in tap water was inferior to that in DI water, the presence of 5 μM Ru(III) did increase the second-order rate constant of BPA oxidation from 36.7 to 40.8 $M^{-1}s^{-1}$ in tap water. The degradation by-products of BPA in catalytic permanganate oxidation were identified. Finally, the catalytic mechanism was tentatively proposed.

Keywords: Kinetics; Byproducts; Mechanism; Catalysis; Electron shuttle

1. Introduction

Permanganate has been widely used in potable water treatment for enhancing coagulation and removing micropollutants and in remediation of contaminated groundwater [1,2]. Compared with other oxidants, permanganate is preferred because of its relatively low cost, ease of handling, effectiveness over a wide pH range, and producing no harmful disinfection products [3,4]. Recently, there has been rising concerns in the application of permanganate to control endocrine disrupting chemicals (EDCs) and chlorophenols during wastewater treatment, for its specific selectivity for phenolics [5–7]. However, the reactivity of permanganate toward phenolics was much lower compared to ozone and hydroxyl radicals and thus catalyzing this process is becoming a necessity.

Unfortunately, the reports about catalyzed permanganate oxidation were very few. Mn(II) and other reduced metals (e.g. As(III) and Cr(III)) can enhance permanganate oxidation in acid or alkaline solution, respectively [5,8,9]. MnO_2 enhanced Mn(VII)

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oxidations of triclosan notably in the pH range of 5.0–6.0 but negligibly at pH 7.0–9.0 [10]. Among the catalysts which have potential for use in selective oxidations, ruthenium takes a special position owing to its versatility. Ruthenium can catalyze numerous oxidative transformations: the oxidation of alkanes, the cleavage of double bonds, the asymmetric epoxidation of alkenes, the oxidation of alcohols and ethers, and the oxidation of amines and phenols [11]. The aqueous Ru(III) has been successfully applied into the degradation of L-leucine, L-isoleucine, L-arginine, and D-panthenol by alkaline permanganate [12–15]. The removal rate of atenolol by alkaline permanganate oxidation was increased by 300% due to the presence of Ru(III) [15]. The reaction rates of Ru(III)-catalyzed oxidative degradation of amitriptyline—an antidepressant drug—by acid permanganate were increased eightfold than its uncatalyzed counterpart [16]. But there was no report about the application of Ru(III) in permanganate oxidation at environmentally relevant pH level.

Therefore, the objectives of this study were to investigate the removal kinetics of bisphenol A (BPA), a typical EDC, by Ru(III)-catalyzed permanganate oxidation and to determine the influences of pH, temperature, and co-existing chemicals on this process. The degradation byproducts of BPA during Ru(III)-catalyzed permanganate oxidation were identified and the catalytic mechanism was proposed.

2. Experiment and materials

2.1. Reagents and chemicals

BPA and $KMnO_4$ of reagent grade were purchased from Tianjin Chemicals Reagent Co. Ltd, and used without further purification. The $KMnO_4$ crystals were dissolved in DI water to make a 10 mM stock solution. The stock solution of BPA (1 mM) was prepared by dissolving a pre-determined quantity of BPA in 0.002 M NaOH. The $RuCl_3$ was purchased from Acros Co., and dissolved into 0.2 M HCl to prevent oxidation of Ru(III). The stock solution of $Na_2S_2O_3$ (scavenger) (0.1 M) was prepared by dissolving a certain quantity of $Na_2S_2O_3$ crystals in DI water. A commercial humic acid purchased from Jiangxi Reagent Co. Ltd, China, was used as a surrogate of humic substance and purified by repeated pH adjustment, precipitation, and centrifugation to remove ash, humin, and fulvic acid, completely following the procedure described by Kilduff and Weber [17]. The stock solutions of $CaCl_2$, $Mg(NO_3)_2$, and $NaHCO_3$ were prepared from the corresponding analytical reagent chemicals to determine the influence of co-solutes on Ru(III) catalytic ability. Experiments were also conducted to test the effects of background matrices in real water on Ru(III)-catalyzed BPA oxidation by dosing BPA into tap water. The tap water ($DOC = 2.4\,mg\,C\,L^{-1}$, $[HCO_3^-] = 0.34\,mM$, $[Ca^{2+}] = 1.2\,mM$, and $[Mg^{2+}] = 0.9$ mM) was collected in our lab. After vacuum filtered through 0.45 μM cellulose membrane filters, tap water was stored at 4℃ and used within two days.

2.2. Batch experiments

All experiments on the kinetics of BPA oxidation by $KMnO_4$ in the presence of Ru(III) were conducted in brown glass bottles with stopples. In a typical experiment, brown glass bottles containing 200 mL of BPA, Ru(III), and 30 mM NaCl (as background electrolyte) were put in water bath (20℃). The experiments were initiated after adding an aliquot of the permanganate stock solution into the reactor. At fixed time intervals, 10 mL of sample was rapidly transferred with a syringe to a small beaker containing 100 μL of $Na_2S_2O_3$ (0.1 M) to terminate the reaction immediately, and was then filtrated with a membrane filter (0.22 μm). The concentration of residual BPA was analyzed directly by HPLC. No buffer was used at pH 4.0–7.0, and borate buffer was used at pH 8.0–9.0. The pH values remained almost constant (±0.1) during the whole process. The residual trace amount of MnO_2 after filtration and ionic strength (30 mM NaCl) had scarcely any effects on the BPA degradation (not shown). It should be notified that the initial concentration of permanganate was controlled at 10 μM in order to keep consistent with the pilot application in the experiments to verify the influences of co-existing chemicals on BPA oxidation by permanganate. All experiments were run in duplicates or triplicates, and all points in the figures are the mean of the results and error bars represent standard deviation of the means.

2.3. Analytical methods

The concentration of BPA was quantified by HPLC on a Waters e2695 instrument with a Symmetry C18 column (2.1 mm × 150 mm, 3.5 μm) and UV-visible detector (Waters 2,489) set at 280 nm. The mobile phase, water/methanol (30/70, v/v), was run in an isocratic mode and the flow rate was $0.5\,mL\,min^{-1}$. The concentration of humic acid (DOC, mg C L^{-1}) was examined with a TOC-VCPH analyzer (Shimadzu). Ultra performance liquid chromatography together with electrospray ionization quadruple time-of-flight tandem mass spectrometry (UPLC-ESI-QTOF MS), Waters Acquity UPLC-Xevo G2 QTOF, was used

Table 1
Details of the LC–MS/MS gradient program

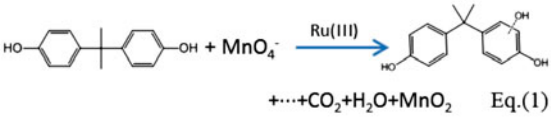
Time (min)	Milli-Q water (%)	Methanol (%)
0	99	1
3	99	1
15	80	20
25	50	50
28	50	50
30	99	1
32	99	1

to detect the intermediates of BPA degradation. In this study, the mass spectrometer was operated in the m/z 50–800 range for LC–MS/MS. The eluent was delivered at 0.5 mL min^{-1} by a gradient system (Table 1) from UPLC and partitioned by a Waters column Acquity UPLC BEH C18 column 2.1 mm × 100 mm, 1.7 µm.

3. Results and discussion

3.1. Stoichiometry and reaction orders

The reaction mixture containing an excess of permanganate (100 µM) over BPA (5 µM), and Ru(III) (5 µM) was allowed to react for 10 min at pH 7.0 and 20°C. The formation of MnO_2 (reduction product of permanganate) may interfere in the quantification of remaining permanganate by UV-vis scanning at 526 nm, therefore, consumption of permanganate was determined in the first five minutes of the reaction. The remaining BPA in the first five minutes of reaction was then analyzed by HPLC. The result indicated that one mole of MnO_4^- consumed one mole of BPA, according to Eq. (1). The main reaction products were identified and listed in Section 3.5.



Eq.(1)

It was proved that the reaction between BPA and permanganate was of second order in total and first order with respect to each reactant with a molar ratio of permanganate to BPA ≥ 5:1 without Ru(III) [18] and can be expressed as

$$-\frac{d[\mathrm{BPA}]}{dt}=k_U[\mathrm{Mn(VII)}][\mathrm{BPA}] \tag{2}$$

As Ru(III)-catalyzed permanganate oxidation of BPA in aqueous solution is expected to occur in parallel paths with contributions from both the catalyzed and uncatalyzed pathways (Eq.(3–5)).

$$\mathrm{Ru(III)}+\mathrm{Mn(VII)}\rightarrow\mathrm{Ru(oxidized)}+\mathrm{MnO_2} \tag{3}$$

$$\mathrm{Ru(oxidized)}+\mathrm{BPA}\rightarrow\mathrm{Ru(III)}+\mathrm{BPA(oxidized)} \tag{4}$$

$$\mathrm{Mn(VII)}+\mathrm{BPA}\rightarrow\mathrm{MnO_2}+\mathrm{BPA(oxidized)} \tag{5}$$

Thus, the total reaction rate constant (k_T) is equal to the sum of the reaction rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions. In the presence of Ru(III), the loss of BPA followed the pseudo-first-order kinetics within the time scales investigated, as illustrated in Fig. 1(a), suggesting that the reaction was first order with respect to BPA (Eq. (6)). For a constant concentration of BPA (5 µM), the pseudo-first-order rate constant (k_T^*, s^{-1}) increased progressively as increasing Mn(VII) concentration from 25 to 150 µM at pH 7.0 (Fig. 1(a)), demonstrating the order with respect to Mn(VII) was unity (Eq. (6) and Fig. 1(b)). Therefore, the catalyzed oxidation kinetics of BPA by Mn(VII) could be described by a second-order rate law:

$$\begin{aligned}-\frac{d[\mathrm{BPA}]}{dt}&=k_T^*[\mathrm{BPA}]=k_T[\mathrm{Mn(VII)}][\mathrm{BPA}]\\&=(k_U+k_C)[\mathrm{Mn(VII)}][\mathrm{BPA}]\end{aligned} \tag{6}$$

Fig. 1(c) and Table 1 revealed that k_T is also a function of the concentration of Ru(III), which has no relationship with the k_U. Therefore, the reaction orders of Ru (III) can be determined from the slopes of lnk_C vs. ln [Ru(III)] plots by varying the concentrations of Ru(III), while keeping the other parameters constant according to Eq. (7).

$$k_C=k_C^*\times[\mathrm{Ru(III)}]^p \tag{7}$$

where p is the reaction order for Ru(III), k_C^* is the reaction rate constant with respect to Ru(III). Therefore, it can be concluded that

$$\ln k_C=\ln\ k_C^*+p\ln\ [\mathrm{Ru(III)}] \tag{8}$$

The linear fitting in Fig.1(d) displayed a slope of 2.1. Therefore, the reaction order p was approximately 2.0. The k_C^* was determined to be 8.07 × 1.0^{14} M^{-3} s^{-1} by the intercept (Fig.1(d)). Finally, based on all the calculated reaction rate constants, the reaction law can be written as

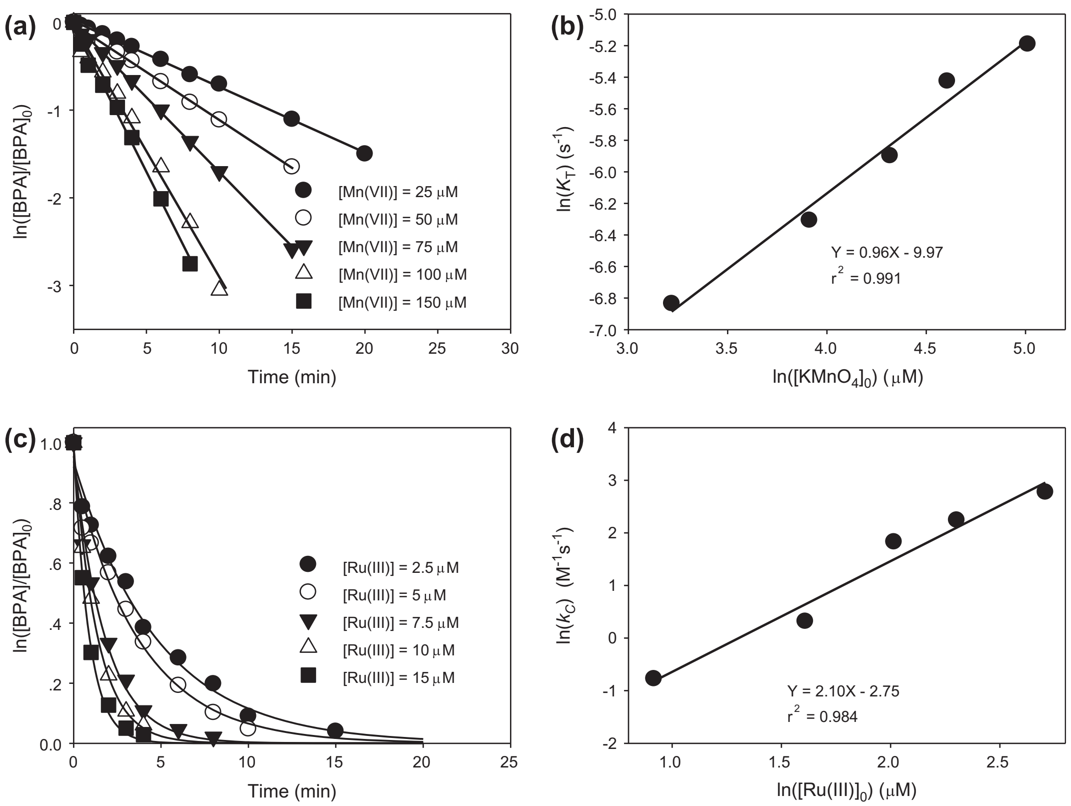


Fig. 1. (a) Time course of BPA (5 μM) oxidation by permanganate of different concentration in the presence of Ru(III) (5 μM) at pH 7.0; (b) linear relationship between measured first-order rate constants (K_T, s^{-1}) and permanganate concentrations at pH 7.0; (c) effects of Ru(III) concentration on BPA (5 μM) oxidation by permanganate (100 μM) at pH 7.0; and (d) linear relationship between measured catalytic rate constants (k_C, M^{-1} s^{-1}) and Ru(III) concentration at pH 7.0.

$$-\frac{d[\mathrm{BPA}]}{dt} = (28.53\mathrm{M}^{-1}\mathrm{s}^{-1} + 8.07 \times 10^{14}\mathrm{M}^{-3}\mathrm{s}^{-1}[\mathrm{Ru(III)}]^2)[\mathrm{Mn(VII)}][\mathrm{BPA}] \qquad (9)$$

3.2. Effect of pH

The oxidation kinetics of BPA (pK_a 9.6 and 10.2) by permanganate in 20-fold excess in the absence or presence of Ru(III) at different pH are shown in Fig. 2. It was obvious that the total reaction rate constant k_T, uncatalyzed reaction rate constant k_U, and catalyzed reaction rate constant k_C were heavily dependent on pH (Fig. 2). A parabola-like shaped pH-k_T profile for Ru(III)-catalyzed permanganate oxidation was observed with the minimum BPA removal achieved between pH 6.0 and 7.0 (Fig. 2(b)). Under acidic condition, k_C played a major role in the removal of BPA, while the uncatalyzed reaction became more important under alkaline condition. This phenomenon can be attributed to the variation of permanganate oxidation potential under different pH levels. With pH increasing from 4.0 to 7.0, the oxidation potential of permanganate decreased from 1.38 to 1.15 V, leading to the decreased oxidation of Ru(III) (Eq. (3)). The high oxidation potential of permanganate was essential to the formation of Ru(oxidized), which may be more reactive than permanganate and can serve as a co-oxidant to enhance BPA removal [18]. The values of k_U increased largely with pH increasing from 5.0 to 9.0, and reached its maximum at pH 9.0. This phenomenon was also reported by Du et al. that the degradation rates of phenol and chlorophenols reached their maximum at the pH around their pK_a [7]. The k_T/k_U decreased from 8.35 to 1.45 with an increase in pH from 4.0 to 7.0, while negligible enhancement was observed at pH 8.0 (i.e. $k_T/k_U \approx 1$) and even negative effect at pH 9.0.

3.3. Effect of temperature

The reaction rate was measured at five different temperatures while keeping other conditions constant. It was found that Ru(III)-catalyzed BPA oxidation by

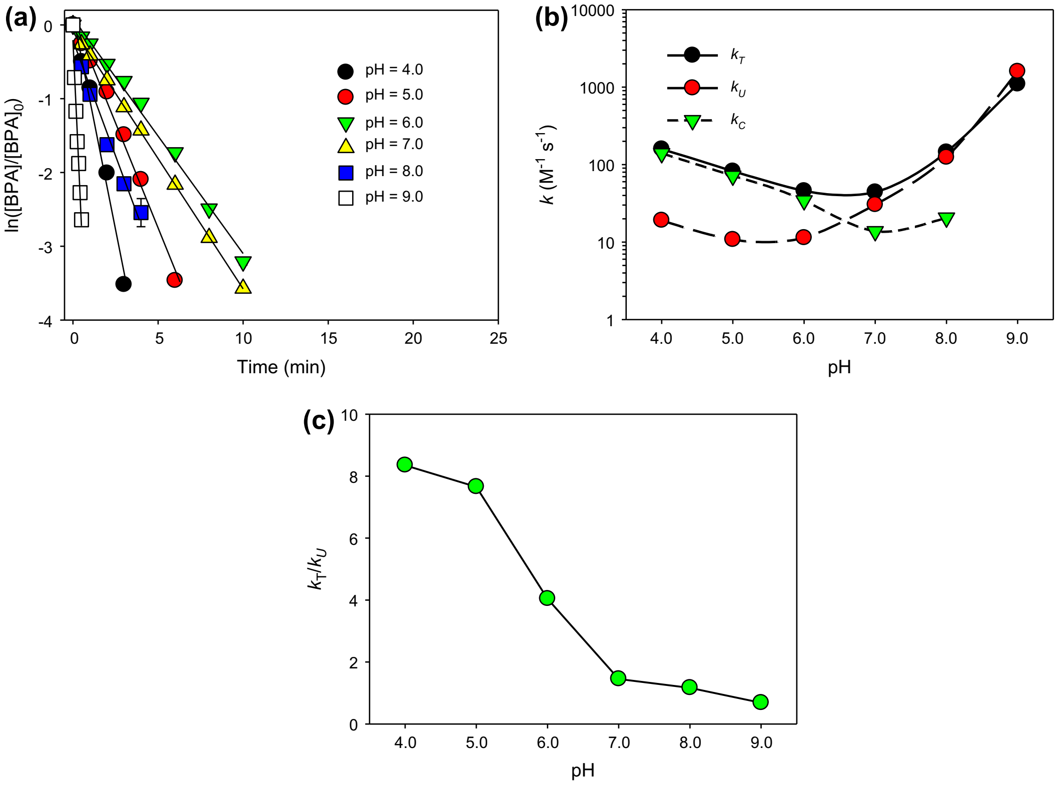


Fig. 2. (a) Ru(III)-catalyzed BPA degradation by permanganate at pH 4.0–9.0; (b) tendency of second-order reaction rate k_T, k_U, and k_C; and (c) pH-dependence of the oxidation enhancement k_T/k_U. Reaction conditions: $[BPA]_0$ = 5 μM, $[Mn(VII)]_0$ = 100 μM, and $[Ru(III)]_0$ = 0 or 5 μM.

permanganate was strongly dependent on temperature since the k_T of BPA destruction by permanganate increased significantly from 29.7 to 134.8 $M^{-1}\,s^{-1}$ with increasing temperatures from 10 to 30℃, as shown in Table 1.

$$\ln k = \ln A + \frac{E_a}{RT} \tag{10}$$

According to the Arrhenius equation (Eq. (10)), plotting $\ln(k_T)$ vs. $1/T$ would yield a linear curve, and the activation energy (E_a) was determined to be 56.6 kJ mol^{-1}. This E_a value was smaller than that in the absence of Ru(III) (67.8 kJ mol^{-1}) [18]. Thus, the presence of Ru(III) lowered the energy barrier of permanganate oxidation of BPA (Table 2). The activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$) were calculated according to Eyring plot ($\ln(k_T/T)$ vs. $1/T$), yielding the activation parameters $\Delta H^{\neq} = 54.2$ kJ mol^{-1} and $\Delta S^{\neq} = -25.9$ J $mol^{-1}\,K^{-1}$. Then, the activation Gibbs free energy $\Delta G^{\neq}$ was calculated to be 61.8 kJ mol^{-1} based on $\Delta H^{\neq}$ and $\Delta S^{\neq}$. According to the complexation theory at the transition state, the negative $\Delta S^{\neq}$ would be bound to that when the Ru(oxidized) attacks the benzoic ring with BPA forming a more ordered pentagon ring and the loss of degrees of freedom by formation of a rigid transition state (Table 3).

3.4. Effect of co-existing chemicals

As presented in Fig. 3, the presence of Ca^{2+} slightly decreased the removal of BPA by Ru(III)-catalyzed permanganate from 62.4 to 49.7% by increasing its concentration from 0 to 7.5 mM. However, further increase in Ca^{2+} concentration from 7.5 to 10.0 mM resulted in a slight enhancement in BPA removal rate from 49.7 to 55.0%. But the mechanisms were still ambiguous and needed further investigation. Both Mg^{2+} and bicarbonate had negligible effect on BPA removal by Ru(III)-catalyzed permanganate.

However, BPA removal by Ru(III)-catalyzed permanganate oxidation was strongly influenced by the presence of HA. As shown in Fig. 3(d), the BPA removal rate was enhanced from 62.4 to 92.3% by increasing humic acid concentration from 0 to 2.5 mg C L^{-1} as DOC. This phenomenon can be attributed to

Table 2
Effect of of Ru(III) concentration, temperature, and pH on the Ru(III)-catalyzed oxidation kinetics of BPA by permanganate

[Mn(VII)] (μM)	[BPA] (μM)	[Ru(III)] (μM)	T (°C)	pH	k_T ($\mathrm{M^{-1}\,s^{-1}}$)	k_U ($\mathrm{M^{-1}\,s^{-1}}$)	k_C ($\mathrm{M^{-1}\,s^{-1}}$)
100	5	2.5	20	7.0	34.9	30.3	4.6
100	5	5	20	7.0	44.0	30.3	13.7
100	5	7.5	20	7.0	92.2	30.3	61.9
100	5	10	20	7.0	124.1	30.3	93.8
100	5	15	20	7.0	190.1	30.3	159.8
100	5	5	10	7.0	29.7	16.3	13.4
100	5	5	15	7.0	39.7	24.5	15.2
100	5	5	20	7.0	44	30.3	13.7
100	5	5	25	7.0	103.4	72.2	31.2
100	5	5	30	7.0	134.8	102.9	31.9
100	5	5	20	4.0	158.3	19.0	139.3
100	5	5	20	5.0	82.1	10.7	71.4
100	5	5	20	6.0	45.7	11.3	34.4
100	5	5	20	7.0	44.0	30.3	13.7
100	5	5	20	8.0	144.4	123.8	20.6
100	5	5	20	9.0	1090.2	1591.1	–

Table 3
Activation parameters of the Ru(III)-catalyzed and uncatalyzed reactions

Activation parameters	E_a ($\mathrm{kJ\,mol^{-1}}$)	$\Delta H^{\neq}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta S^{\neq}$ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$\Delta G^{\neq}$ ($\mathrm{kJ\,mol^{-1}}$)
Catalyzed	56.6	54.2	−25.9	61.8
Uncatalyzed [18]	67.8	65.4	8.9	62.8

the non-covalent interactions of humic acid with phenols, which were related to the formation of π–π interactions between the monoaromatic ring of substrates and humic acid aromatic components. The π–π interaction with humic acid could enhance the density of the electron cloud of phenol, which could result in the enhancement of BPA oxidation by Ru(oxidized) and permanganate [19,20]. However, further increasing humic acid concentration from 2.5 to 10.0 $\mathrm{mg\,C\,L^{-1}}$ resulted in a decline in BPA removal from 92.3 to 87.4%, which may be attributable to the fact that humic acid of high concentration exerted a significant permanganate or Ru(oxidized) demand, and then reduced the mass of oxidant available for the destruction of BPA. The influence of humic acid on BPA removal by Ru(III)-catalyzed permanganate was similar to that in the absence of Ru(III) [18].

BPA degradation by Ru(III)-catalyzed permanganate in natural water was also examined by spiking BPA into tap water. Apparently, compared to the uncatalyzed oxidation kinetics obtained in DI water, BPA oxidation was accelerated in all of the other three water matrices (Fig. 4). The higher removal rate of BPA in tap water compared to that in DI water was probably due to the co-existing humic acid of concentration 2.4 $\mathrm{mg\,C\,L^{-1}}$ and 0.34mM of bicarbonate . However, Ru(III) showed less catalyzing reactivity toward BPA oxidation by permanganate in tap water than that in DI water, which may be associated with the inhibitive influence of Ca^{2+} present in tap water (~1.2 mM) and the other unknown negative effects. The reduced species in tap water may exhaust the newly formed Ru(oxidized), and thus depress its oxidative ability. Although the catalytic ability of Ru(III) was inferior to that in DI water, the Ru(III) did increase the second-order rate constant of BPA oxidation from 36.7 to 40.8 $\mathrm{M^{-1}\,s^{-1}}$ in tap water. Consequently, Ru(III)-catalyzed permanganate oxidation is a promising process for eliminating BPA from real water.

3.5. BPA byproducts in Ru(III)-catalyzed permanganate oxidation

According to previous studies, different oxidation mechanisms may generate different oxidation products [21–23]. Both permanganate and ozone attack the phenol and chlorophenols by [3 + 2] addition (forming a penta ring) [18,24], and four of the initial byproducts of BPA in these two reactions were in complete agreement [18,21]. The participation of Ru(III) in the reaction between BPA and permanganate might induce different degradation pathways and thus

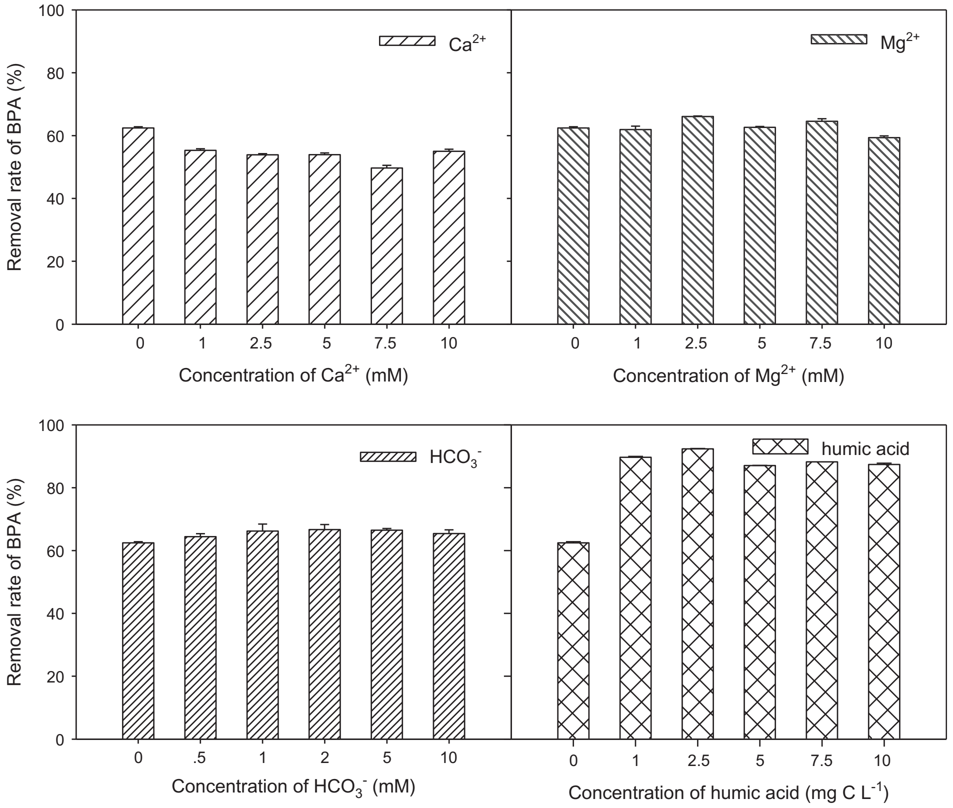


Fig. 3. Influences of Ca^{2+}, Mg^{2+}, HCO_3^-, and humic acid on BPA (5 μM) removal by permanganate (10 μM) in the presence of Ru (5 μM).

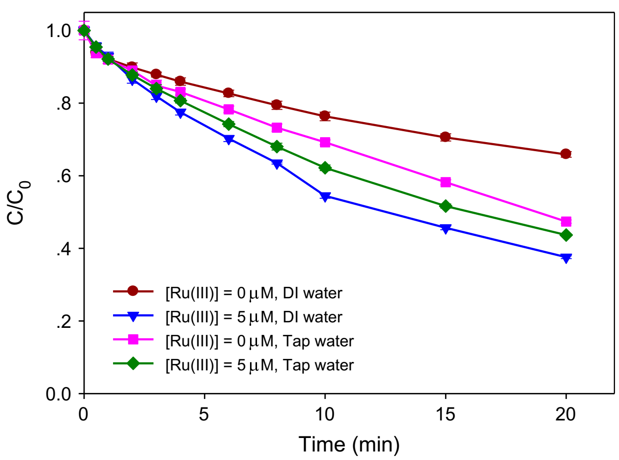


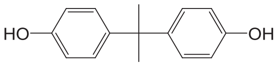
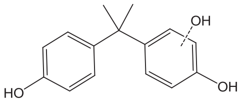
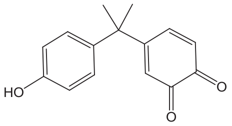
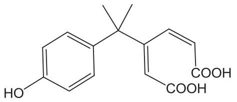
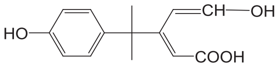
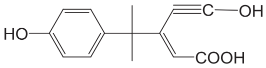
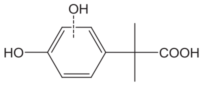
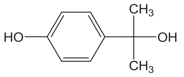
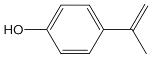
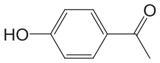
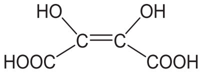
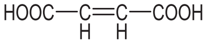
Fig. 4. The degradation of BPA (5 μM) by permanganate (10 μM) in DI water or tap water with or without Ru(III) (5 μM) at pH 7.0.

resulted in the appearance of some new intermediates and oxidation products. Therefore, the degradation products of BPA by permanganate oxidation in the absence of Ru(III) were compared with those in the presence of Ru(III) by LC–MS/MS. Eleven products, from *m/z* 115 to 275, were detected and summarized in Table 4. The oxidation products of BPA detected in the Ru(III)-catalyzed permanganate oxidation process and those in the noncatalyzed process were identical [18]. Therefore, it was speculated that BPA was also degraded by Ru(III)-catalyzed permanganate via [3 + 2] addition as permanganate and ozone did. Eight of the eleven intermediates had been observed in other oxidation processes while the other three, with *m/z* 247, 245, and 195, were only reported by our previous study [18]. All the intermediates eluted earlier than BPA, indicating that they were more polar than their parent compound. The initial degradation by-products (*m/z* 243, 241, 275, and 152) of BPA verified in permanganate oxidation process showed no change on the alkyl group, as listed in Table 4, indicating that the benzoic ring was the reaction site at early stage of BPA oxidation by permanganate and Ru with higher oxidation states.

3.6. Proposed catalytic mechanism

The mechanism of permanganate oxidation catalyzed by Ru(III) was tentatively proposed based

Table 4
Oxidation products of BPA detected by LC–MS/MS

Product #	ESI(-) MS *m*/*z*	ESI(-) MS/MS *m*/*z*	Proposed structure	Rt (min)
BPA	227	227, 212, 211, 133, 93		20.29
1	243	243, 227		19.04
2	241	241, 239		19.10
3	275	275, 231, 187, 133		17.16
4	247	204, 133, 93		9.58
5	245	202, 133, 93		21.58
6	195	195, 133		10.66
7	151	151, 133		9.20
8	133	133, 117, 93		8.11
9	135	43， 93		8.36
10	149	149, 117		1.11
11	115	115	 $\mathrm{HOOC{-}\underset{H}{C}{=}\underset{H}{C}{-}COOH}$	1.29

on above discussion, as shown in Fig. 5. Permanganate oxidizes Ru(III) to its higher oxidation state (Ru(oxidized)) [25] and it was reduced to MnO_2. The Ru(oxidized) formed *in situ* was much more reactive than permanganate and could oxidize BPA rapidly with the regeneration of Ru(III). The identical degradation byproducts in the catalytic and uncatalytic reactions indicated that the behavior of oxidized Ru species were very similar to that of permanganate, which was also reported by Greenwood [26]. In a short, Ru(III) could enhance permanganate oxidation and played a role of electron shuttle in BPA conversion under environmentally relevant conditions.

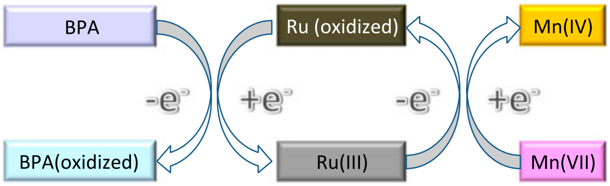


Fig. 5. Catalytic role of Ru(III) in permanganate oxidation of BPA.

This speculation was consistent with the catalytic activity of Ru(III) at different pH. Fig. 2 revealed that the catalytic activity of Ru(III) was strongly pH dependent with greater activity achieved at lower pH. This should be associated with the fact that the oxidation potential of permanganate decreased with increasing pH. At lower pH, Ru(III) could be easily oxidized by permanganate with higher oxidation potential, and form Ru(oxidized) to decompose organics. The negligible catalytic activity under alkaline conditions was probably due to the fact that oxidation potential of alkaline permanganate was too low to oxidize Ru(III) to Ru(oxidized). Therefore, the high-enough oxidation potential of permanganate was essential for the formation of Ru(oxidized) and the enhanced removal of BPA in the presence of Ru(III). The determination of real species of Ru(oxidized) is also needed and this is also our key task in further study.

4. Conclusions

This paper for the first time investigated the kinetics of Ru(III)-catalyzed permanganate oxidation of BPA. The reaction followed pseudo-first order with respect to BPA and permanganate, respectively, and second order with respect to Ru(III). It was found Ru (III) significantly improved the degradation of BPA under acid condition, but had negligible effect under alkaline conditions. This phenomenon can be attributed to the higher oxidation potential of permanganate under acid condition, which led to the formation of a larger amount of of Ru(oxidized) when compared to the case under alkaline conditions. Ru (III) decreased the activation energy in catalytic oxidation. The Ca^{2+} and some unknown chemicals had some negative effects on this catalytic system, while the presence of humic acid enhanced BPA removal. The degradation products of BPA during Ru(III)-catalyzed permanganate oxidation were identified. The catalytic mechanism of Ru(III) in permanganate oxidation of BPA was proposed. It should be noted that the toxicity of Ru in water is still unknown, and its cost is rather expensive. Moreover, the addition of Ru(III) into permanganate oxidation system is far from practical application. The ultimate objective of our study is to invent an environmentally friendly and inexpensive catalyst to replace Ru(III) in homogenous permanganate oxidation process or to develop Ru(III)-loaded solid catalyst to catalyze permanganate oxidation and thus the catalyst can be used repeatedly.

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