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Kinetics study on the oxidation of chlorophenols by permanganate

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ABSTRACT

The kinetics of the oxidation of chlorophenols (CPs) by potassium permanganate was studied in the present study, along with the changes in oxidant dosage, pH, temperature, and real water matrices. The reactions between permanganate and three kinds of CPs, i.e. 4-chlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP), are second order overall and first-order with respect to each reactant. The degradation rates of the CPs increase with increasing permanganate dosage or temperature. pH plays an important role during permanganate oxidation. With the increase in pH from 4.0 to 10.0, the reaction rates of 4-MCP and 2,4-DCP decrease first and then increase, and finally decrease rapidly when pH > pK_a, while the rates of 2,4,6-TCP decrease continuously. The degradation rates of the CPs are obviously higher in real water than in pure water. The reaction rate follows the order of 2,4,6-TCP > 2,4-DCP > 4-MCP under acidic conditions, and follows the reverse order under alkaline conditions in both pure water and real water.

Keywords: Chlorophenol; Permanganate; Kinetics; Real water

1. Introduction

Chlorophenols (CPs) are a kind of widespread organic pollutants in environments, due to their extensive use in dyes, pharmaceuticals and pesticides production, wood preservatives, waste incineration, etc. as well as by-products formed during chlorination of drinking water for disinfection [1–3]. Most of the CPs are recalcitrant to natural biotic and chemical degradation, and some are known toxins, mutagens, and carcinogens [4,5]. Their toxicity, recalcitrance, bioaccumulation, strong odor emission, and persistence can directly impact the health of humans and wildlife and have a potential threat through the contamination of water bodies [6,7]. Therefore, due to these public health and environmental concerns, effective control methods for their removal from waters where they are present are needed.

The recalcitrant nature of CP molecules to natural degradation mechanisms necessitates the need for a more aggressive chemical approach. Chemical agents with CP oxidation potential mainly include O_3 [1,8], UV/O_3 [9], Fenton's reagent, UV/Fenton reagents [10], H_2O_2, UV/H_2O_2 [11], and permanganate. Hydroxyl radicals and ozone have been shown to rapidly oxidize aromatics and selected CPs. Peroxide oxidation has also been previously demonstrated by others. Permanganate, however, has achieved little attention probably for its inability to oxidize benzene which is the basic building block of most organic pollutants and its inferior ability to mineralize organics. Actually,

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potassium permanganate ($KMnO_4$) works well for water-soluble compounds and is easy, robust, inexpensive, and reproducible. It can oxidize various kinds of organics, including organics with C=C (e.g. chlorinated ethenes) [12], ether, ketone, trinitrotoluene (TNT), pesticides (e.g. aldicarb and dichlorvos) [13], polycyclic aromatic hydrocarbons (PAHs) (e.g. benzo (a)pyrene and phenanthrene) [14], and phenolic organics like bisphenol A and CPs [15-17]. Although permanganate probably does not efficiently mineralize these organic pollutants, it possibly oxidizes them to other organics that can be readily mineralized by other methods (e.g. photo-degradation) [18].

The previous studies on the permanganate oxidation of CPs mainly focused on monochlorinated phenol (MCP) and/or dichlorinated phenol (DCP). The reactions between permanganate and CPs were always determined as pseudo-first order. However, the reported reaction kinetics for oxidation of them is inconsistent. For example, pseudo-first-order reaction rates were reported as 2,6-DCP > 2,4,6-trichlorophenol (TCP) > 2,4-DCP > 2-MCP > 4-MCP by He et al. [19], while others found the following order of 2-MCP > 2,6-DCP > 4-MCP > 2,4-DCP > 3-MCP [20]. Actually, pH has an important effect on permanganate oxidation of phenolic compounds and therefore on their reaction rates. Thus, the reaction sequence might totally be different at different pH conditions, which are not well understood. Moreover, most of these studies were conducted in pure or synthetic water systems. So, it is difficult to predict their actual removals and the reaction rates during real water treatment processes. Therefore, in order to gain a better understanding of the degradation of these chemicals by permanganate, more detailed information is necessary.

The aims of this study are: (1) to determine the reaction rates between $KMnO_4$ and three kinds of CPs both in pure water and in real water; (2) to investigate the effects of oxidant dosage, pH, and temperature.

2. Materials and methods

2.1. Chemicals

Analytical grade of 4-MCP, 2,4-DCP, and 2,4,6-TCP are all Aladdin reagents (Shanghai, China), had a purity of 99%, at least. High-performance liquid chromatography (HPLC) grade of methanol is Honeywell Burdick & Jackson solvent. HPLC grade of phosphoric acid (H_3PO_4) is an Aladdin reagent. Other chemicals including $KMnO_4$ and ascorbic acid are of analytical grade and used without further purification.

Pure water used in the experiment is Milli-Q water. The natural water used was taken from the Yangtze River, China. Natural water samples were filtered through glass fiber filters with a pore size of 1 μm (Whatman) to remove suspended solids and then stored at 4℃. The main water quality parameters of the filtered natural water are as follows: dissolved organic carbon (DOC), $3.9\ \text{mg L}^{-1}$; conductivity, $160\ \mu\text{S cm}^{-1}$; pH 8.0; UV_{254}, 0.067; turbidity, 1.3 NTU.

The stock solutions of individual CP (5.061–7.778 mM) were prepared with ultrapure water and stored in amber glass bottles at 4℃ and diluted to working solutions using Milli-Q water or the filtered surface water before experiments. Potassium permanganate working solution (6.328 mM), ascorbic acid working solution (5.678 mM), and other reagents were freshly prepared with Milli-Q water every four to seven days and stored in dark bottles to avoid light exposure.

2.2. Analytical methods

The concentrations of the CPs in water samples were analyzed by a Waters HPLC system equipped with a Waters 1525 series binary pump, a Waters Symmetry C18 column (150 × 4.6 mm, 5 μm particles), a Waters 2707 auto-injector, and a Waters 2489 dual λ UV detector. The mobile phase was run in an isocratic mode, with Milli-Q water or H_3PO_4 solution (1 mM) used as mobile phase A and methanol as mobile phase B. The proportions of A/B were 30/70, 20/80, and 10/90 for the detection of 4-MCP, 2,4-DCP, and 2,4,6-TCP, respectively. The total flow rate of A and B was $1.0\ \text{mL min}^{-1}$. The injection volume was 50 μL for each sample. The detection wavelength was set at 280 nm. The temperature of the column was maintained at 30℃ during detection.

The concentrations of the CPs were quantified by external standard quantification procedure. The systems were calibrated using standard solutions at five concentration levels by serial dilutions from the stock solutions. The peak area vs. injected amount chart was obtained as standard curve with a regression coefficient value (r^2) over 0.99. The detection limit is $5\ \mu\text{g L}^{-1}$ for three kinds of CPs.

2.3. Permanganate oxidation experiment

An appropriate volume (100 mL) of the CP working solution (2 μM) was placed in cylindrical glass vials, which were immersed in a thermostatic water bath to maintain temperature and to perform batch oxidation experiments. Magnetic stirrer was used under the water bath. The oxidation reactions were initiated by injection of 158–948 μL of $KMnO_4$ working solution ($[KMnO_4]_0 = 10–60$ μM). Samples were collected at several time intervals, and quenched immediately with ascorbic acid working solution. The concentrations of residual CPs were analyzed directly by HPLC. Each experiment was performed in duplicate and the mean value was used.

3. Results and discussion

3.1. Kinetics of the reactions between permanganate and CPs

The oxidation experiments were conducted in pure water (pH 5.8) without buffer at 25℃. Note that the pH changes did not exceed 0.3. The reactions between permanganate and each CP were considered as a second-order reaction overall and first-order with respect to the CPs ([CP]) and permanganate ($[KMnO_4]$) concentrations. The rate of the CPs′ degradation could be expressed as:

$$-\mathrm{d}[\mathrm{CP}]/\mathrm{d}t = k_2[\mathrm{CP}][\mathrm{KMnO_4}] \tag{1}$$

where k_2 is the second-order kinetic constant.

As permanganate was in large excess and its decrease in concentration was smaller than 20% of its initial concentration, it could be considered constant. The rate of the CPs′ degradation can then be expressed as:

$$-\mathrm{d}[\mathrm{CP}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{CP}] \tag{2}$$

$$k_{\mathrm{obs}} = k_2[\mathrm{KMnO_4}]_0 \tag{3}$$

where k_{obs} is the pseudo-first-order kinetic constant. The first-order reaction rates with respect to each CP are confirmed in Fig. 1, where $\ln([CP]_0/[CP])$ vs. time is shown for experiments performed at varied permanganate dosage. The values of k_{obs} in these experiments were calculated by linear regression analysis and are summarized in Table 1. k_{obs} values as a function of the initial concentrations of permanganate are presented in Fig. 2. A straight line was also obtained, confirming the rate of the CPs′ degradation is also first-order with respect to the concentration of permanganate. The reaction rates increase with increasing permanganate concentrations, confirming the independence of the second-order rate constants (k_2) from the reagent concentrations. After linear analysis of the data shown in Fig. 2, the k_2 value at 25℃ of 2.53, 5.14, and 20.23 $M^{-1}\ s^{-1}$ can be calculated for 4-MCP, 2,4-DCP, and 2,4,6-TCP, respectively.

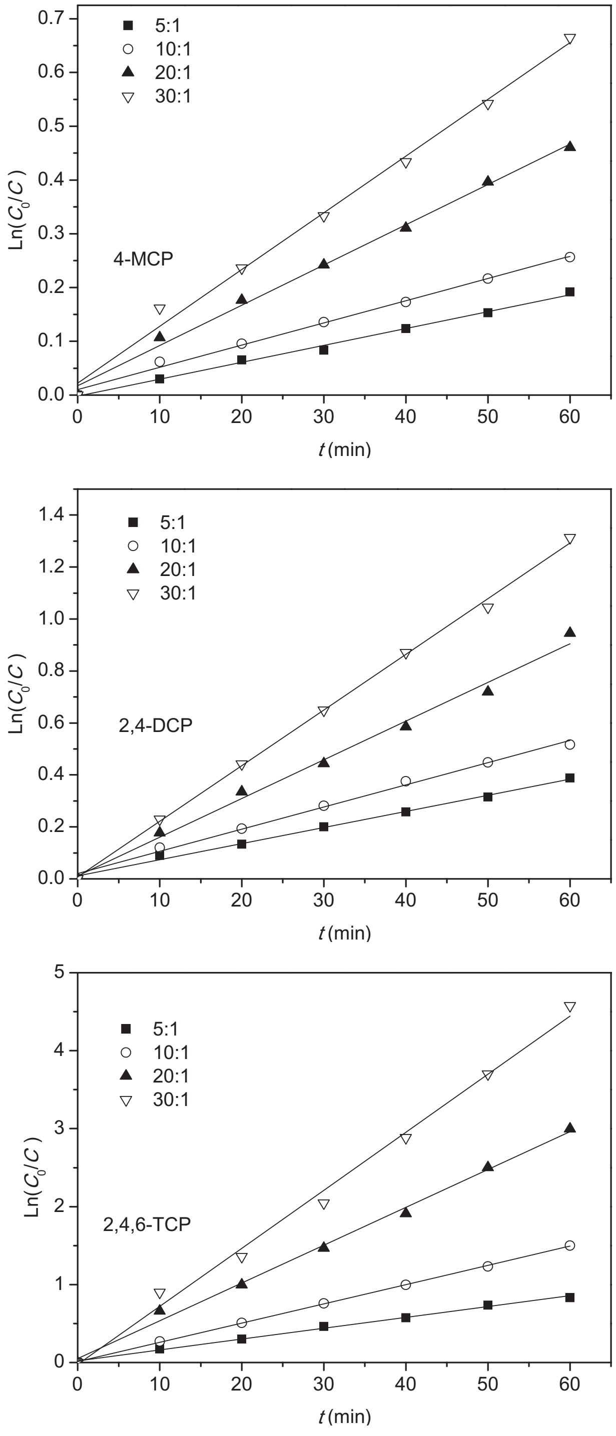

Fig. 1. Pseudo-first-order kinetic plots for CPs′ degradation under different $KMnO_4$ dosages. Conditions: $[CP]_0 = 2$ μM, $[KMnO_4]_0 = 10–60$ μM, pH 5.8, 25℃.

Table 1
Rate constants for CPs' degradation under varied initial concentrations of permanganate ($[CP]_0$ = 2 μM, 25℃)

CP	$[KMnO_4]_0$ (μM)	k_{obs} ($\times 10^{-5}$ s^{-1})	r^2
4-MCP	10	5.23	0.9911
	20	6.88	0.9905
	40	12.48	0.9915
	60	17.58	0.9905
2,4-DCP	10	10.33	0.9927
	20	14.22	0.9911
	40	24.83	0.9921
	60	35.72	0.9974
2,4,6-TCP	10	23.18	0.9942
	20	41.13	0.9995
	40	80.90	0.9949
	60	124.13	0.9939

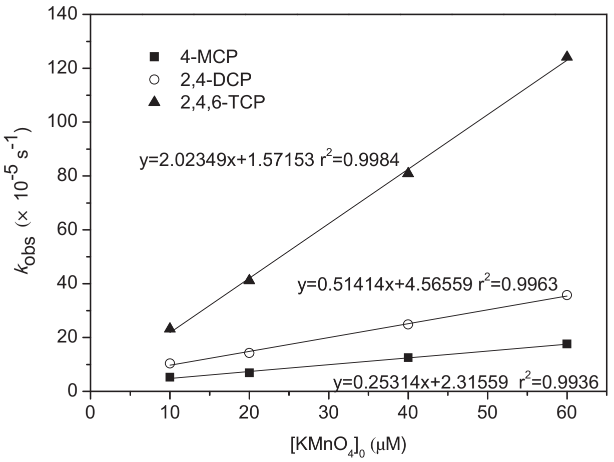

Fig. 2. Relationships of k_{obs} values of the degradation of three CPs by permanganate and permanganate dosages. Conditions: $[CP]_0$ = 2 μM, pH 5.8, 25℃.

The k_2 values achieved in our study are similar to that of 8.38–19.41 M^{-1} s^{-1} reported by He et al. [19] for the three CPs and 3.8–4.2 M^{-1} s^{-1} for 4-MCP and 2,4-DCP reported by Hossain and McLaughlan [20].

The result reveals that the chlorine substituent on the aromatic ring obviously affects the reaction rates of the CPs. The rates of the CPs increase with the increase in the amount of the substituted chlorines and present a sequence of 2,4,6-TCP > 2,4-DCP > 4-MCP (see Table 1). This is in accordance with the theory that a certain number of halogens increase the reaction rate of CPs by electron-donating capabilities [21]. But the increase is limited to a certain degree of halogenation. When the number of halogens increases, the σ-electron-withdrawing effect increases to such an extent that it counteracts the π-electron-donating effect, reaction rates become slower. The reaction rates are affected by not only the halogen number but also their substitution position. It is proposed that the oxidation kinetics of CPs may be affected by the interaction of electron-withdrawing chlorine and hydroxyl groups, the resonance of the phenolic anion, the steric effect of chlorine, and the acidities of CPs [21,22].

3.2. *Effect of temperatures*

The effect of temperatures on the reactions between permanganate and the CPs was determined at 10, 20, 30, and 40℃ in pure water at $[KMnO_4]_0/[CP]_0$ of 10. Pseudo-first-order constants of $(2.98 - 17.63) \times 10^{-5}$ ($r^2 = 0.9957 \pm 0.0017$), $(4.40 - 24.47) \times 10^{-5}$ ($r^2 = 0.9969 \pm 0.0007$), and $(2.11 - 8.68) \times 10^{-4}$ ($r^2 = 0.9978 \pm 0.0008$) s^{-1} were also calculated by linear regression analysis at studied temperature ranges for 4-MCP, 2,4-DCP, and 2,4,6-TCP, respectively. The relationship between the rate constants and temperatures is shown in Fig. 3. The rates of all these compounds increase slowly at lower temperature ranges, whereas the rates increase rapidly at higher ranges. The k_{obs} follows the order of 2,4,6-TCP > 2,4-DCP > 4-MCP at different temperatures ($p < 0.05$). The second-order rate constants of 1.49–8.82, 2.20–12.23, and 10.53–43.40 M^{-1} s^{-1} were calculated according to Eq. (3) at studied temperature ranges for 4-MCP, 2,4-DCP, and 2,4,6-TCP, respectively. Therefore, the activation energy (E_a) of these chemicals can

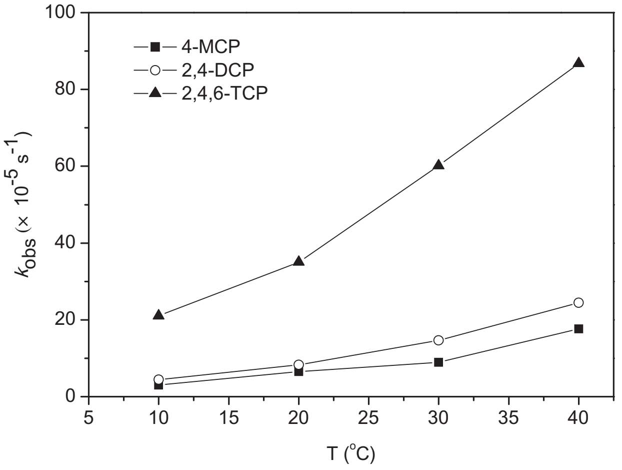

Fig. 3. Rate constants for the degradation of three CPs by permanganate under different temperatures. Conditions: $[CP]_0$ = 2 μM, $[KMnO_4]_0$ = 20 μM, pH 5.8.

be calculated using the linearized Arrhenius equation (Eq. (4)):

$$\ln k_2 = \ln A - E_a/RT \tag{4}$$

After linear regression analysis, the E_a values of 41.61 (r^2 = 0.9791), 42.14 (r^2 = 0.9998), and 35.31 kJ mol^{-1} (r^2 = 0.9968) were calculated for 4-MCP, 2,4-DCP, and 2,4,6-TCP, respectively. Among these CPs, 2,4,6-TCP has a lower E_a value because of its higher susceptibility to permanganate oxidation at pH 5.8.

3.3. Effect of pH

Fig. 4 shows the effects of pH on k_{obs} of the degradation of the CPs by permanganate at [KMnO$_4$]$_0$/[CP]$_0$ of 10. The pH of the aqueous solutions was adjusted with 0.1 mol L^{-1} of HClO$_4$ or NaOH solution for pH 6.0–7.0, and buffered with sodium acetate–acetic acid solution (10 mM) for pH 4.0–5.0, borate solution (10 mM) for pH 8.0–9.0, and borax sodium hydroxide solution (10 mM) for pH 10.0, respectively. The reaction rates of the CPs vary with the pH changes. For both 4-MCP and 2,4-DCP, the rates first decrease as pH increased from 4.0 to 5.0, and then increase slowly as pH increased from 5.0 to 9.0. But finally, the rates decrease fast as pH > pK_a (the pK_a values of 4-MCP, 2,4-DCP, and 2,4,6-TCP are 9.2, 7.8, and 6.0, respectively [8,19]). The minimum rate takes place at pH 5.0 in the studied pH range. The rate of 2,4,6-TCP decreases at the studied pH range because of its lower pK_a value vicinal to 5.0.

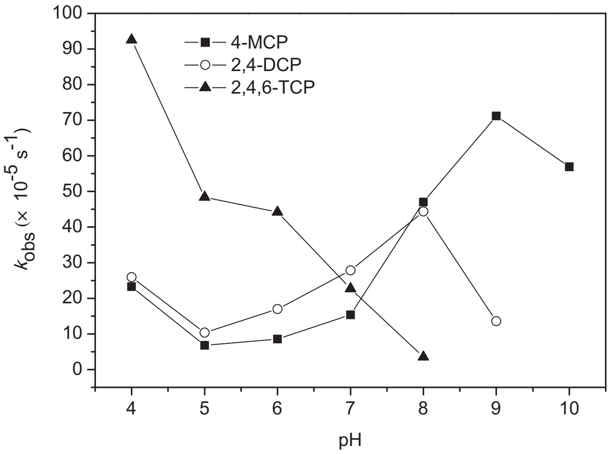

Fig. 4. Rate constants for the degradation of three CPs by permanganate under varied pH values. Conditions: [CP]$_0$ = 2 μM, [KMnO$_4$]$_0$ = 20 μM, 25˚C.

The pH dependence of the CPs' degradation could be explained by both of the oxidative ability of permanganate and its reactive manganese intermediates and the present forms of the CPs varying with pH in aquatic system. Permanganate reacts with phenolic compounds by electron transfer [15] and usually undergoes a three-electron exchange at pH 3.5–12 (Eq. (5)):

$$\mathrm{MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O} \tag{5}$$

It is reported that the reactive manganese intermediates, including manganese oxide (Mn(IV)), hypomanganate (Mn(V)), manganate (Mn(VI)), and trivalent manganese ion (Mn(III)), formed during permanganate oxidation together with permanganate ion (Mn (VII)), are all involved in the degradation of phenolic compounds (Eqs. (6)–(11)) [15,23–25]:

$$\mathrm{MnO_4^- + 2e^- \rightarrow Mn(V)} \tag{6}$$

$$\mathrm{MnO_4^- + 4e^- \rightarrow Mn(III)} \tag{7}$$

$$\mathrm{2Mn(V) \rightarrow Mn(IV) + Mn(VI)} \tag{8}$$

$$\mathrm{3Mn(V) \rightarrow Mn(VII) + 2Mn(IV)} \tag{9}$$

$$\mathrm{Mn(VII) + Mn(V) \leftrightarrow 2Mn(VI)} \tag{10}$$

$$\mathrm{2Mn(III) \rightarrow Mn(II) + Mn(IV)} \tag{11}$$

Mn(VI) and Mn(III) are mainly present under alkaline (pH > 12) and strong acidic ([H$^+$] > 1 M) conditions, respectively. Though Mn(V), Mn(VI), and Mn(III) have strong oxidative capacity, they are very unstable and disproportionate under weakly acidic conditions (Eqs. (8)–(11)), and therefore their effect on the degradation of these CPs is negligible [26,27]. But the *in situ* formed MnO$_2$ could oxidize phenols and even autocatalyze permanganate oxidation and therefore enhance the removal efficiency of phenolic chemicals in weakly acidic conditions [28,29]. Moreover, the redox potential (E^0) of permanganate is 1.70 V under acidic conditions higher than that under alkaline conditions (E^0 = 0.59 V) [30]. So both MnO$_2$ and Mn (VII) might be responsible for the faster degradation of the CPs at pH 4.0. However, the oxidative and catalytic capability of MnO$_2$ decreases with the increase in pH, and MnO$_2$ even shows no effect on permanganate oxidation and Mn(V) might be involved in the removal of phenolic compounds under weakly alkaline conditions [15,31]. Thus, the evolution and replacement of the reactive manganese intermediates with pH might induce the decrease in the rates of the CPs at pH 4.0–5.0 and a slight increase when pH > 5.0.

Except for the variation of the oxidative abilities of permanganate and these manganese intermediates with pH, some researchers explicated the pH–rate profile of phenol oxidation by permanganate from the phenols' present form under different pH conditions. It is the fact that the acidic organic compounds, like these CPs whose relative existence form, non-dissociated, and dissociated form depend on the pH of solution, present different reactivity toward oxidant agents with the change in pH. Therefore, their reaction rates depend on the degree of dissociation, and consequently, on the pH of the reaction system. Du et al. [32,33] supposed that the dissociated CPs react much more easily with permanganate than the undissociated CPs. This might contribute to the higher oxidation rates of the CPs at pH close to their $\mathrm{p}K_\mathrm{a}$. Moreover, they suggested a proton transfer mechanism for permanganate oxidation of CPs and their phenolates:

$$\mathrm{ArOH} + \mathrm{MnO_4^-} \rightarrow \text{products} \tag{12}$$

$$\mathrm{ArOH} \leftrightarrow \mathrm{ArO^-} + \mathrm{H^+} \tag{13}$$

$$\mathrm{ArO^-} + \mathrm{MnO_4^-} \leftrightarrow \text{intermediates} \tag{14}$$

$$\text{Intermediates} + \mathrm{H^+} \rightarrow \text{products} \tag{15}$$

The undissociated CPs are directly degraded by permanganate oxidation to generate products (Eq. (12)). However, the dissociated CPs first form phenolate–permanganate intermediates (Eq. (14)), and then, the intermediates combine with $\mathrm{H^+}$ and finally decomposed to products (Eq. (15)). The reaction rates of the undissociated CPs decrease with increasing pH, while the rates of the dissociated CPs exhibit a bell-like shape in the pH range of 5–9 because the oxidation of the phenolates requires the participation of protons (Eq. (15)). Therefore, the overall rates of CPs exhibit a parabola-like shape at pH 5–9.

The results shown in Fig. 4 also reveal that the reaction rates of the CPs present different sequences under different pH conditions. The sequence of 2,4,6-TCP > 2,4-DCP > 4-MCP ($p < 0.05$) is always valid under acidic conditions, which is different to that of 2-MCP > 2,6-DCP > 4-MCP > 2,4-DCP > 3-MCP at pH 5.3–6.2 as reported by Hossain and McLaughlan [20]. The rate order is 2,4-DCP > 2,4,6-TCP > 4-MCP at pH 7.0 in the present study, which is also different to those of 4-MCP > 2,4-DCP > 2,6-DCP at pH 7.2 and 2.6-DCP > 2,4,6-TCP > 2,4-DCP > 2-MCP > 4-MCP at pH 7.0 achieved by Zhang et al. [21] and by He et al. [19], respectively. However, it seems that the sequence is totally reversed to 2,4,6-TCP < 2,4-DCP < 4-MCP in weakly alkaline conditions comparing to that under acidic conditions. This aspect has also been previously pointed out by other researchers. For example, Benitez et al. [8] observed a similar reverse trend for the non-dissociated CPs and their phenolate ions during ozonation. Besides the effect of the reactivity of Mn(VII) and the reactive manganese intermediates toward phenols and phenolates varying with the change of pH, the chlorine substituents on the aromatic ring might also be accounted for the different rate sequence of the CPs in the course of permanganate oxidation under various pH conditions. It is reported that there exists weak intramolecular hydrogen bonding between the hydroxyl group and the ortho-substituted chlorine in protontated CPs, and the length of the bond decreases with the increase in the amount of the ortho-substituted chlorines [34]. As a result, the bond shifts the redox potential of the CPs to lower potentials and facilitates the CPs' oxidation. As a result, the oxidation rates of the CPs by permanganate increase with the increase in the amount of the ortho-substituted chlorines as 2,4,6-TCP > 2,4-DCP > 4-MCP under weakly acidic conditions. But for the dissociated CPs, their oxidation by permanganate is mainly determined by electrophilic attack, and their stability depends on the delocalization of the negative charge. Han et al. [22] stated that the inductive effect strengthened with the increase in the chlorine substituents and the change in the chlorine position from meta to ortho, accounts for the major variations in the stability of the phenoxide anions of all CPs. As a result, the susceptibility of the negative phenolates to permanganate oxidation decreases with the increase in chlorine substituents. This might contribute to the reversed rate sequence of the CPs under alkaline conditions compared with that under acidic conditions.

Our results reveal the influence of pH on the reactions has a considerable importance for the control of CPs during water treatment processes. The value of pH must be keep at an appropriate range to get a good or rapid removal of them.

3.4. The degradation of CPs in real water background

As the characteristics of natural waters may affect the permanganate oxidation of CPs, experiments were therefore conducted in spiked real water with excess permanganate concentration ($[\mathrm{KMnO_4}]_0/[\mathrm{CP}]_0 = 10$). All these CPs were not detected in the natural water mentioned above. In consideration of the significance of pH, experiments were also performed in natural water whose pH was adjusted to 5.8 by 0.1 mol L^{-1} of $HClO_4$ solution. As shown in Fig. 5, the removals at pH 8.0 are higher than at pH 5.8 for both of 4-MCP and 2,4-DCP, while the removal of 2,4,6-TCP is far higher at pH 5.8 than at pH 8.0. Additionally, the order of their reactivity toward permanganate in real water is the same as that in pure water. This is evident that the pH influence on the permanganate oxidation of the CPs in real water is the same as that in pure water.

Though the pH mechanism of the CPs' degradation by permanganate is the same under different water backgrounds, the reaction rates of the CPs are obviously different in different water backgrounds. Pseudo-first-order constants were calculated for the data shown in Fig. 5 by linear regression analysis ($r^2 = 0.9838 \pm 0.0120$) and the result is shown in Table 2. The rate constants in pure water are also listed in Table 2 in order to facilitate comparison. The value of Δ is the k_{obs} difference between real water and pure water. Three CPs have higher degradation rates in real water than in pure water both under acidic and alkaline conditions. This indicates that the matrices of the real water could promote the permanganate oxidation of the CPs. Some researchers reported that some ligands, i.e. humic acid (HA), phosphate, and EDTA, could accelerate the reaction between phenolic compounds and permanganate [28,35]. It was also confirmed in our previous study that HA could greatly promote the permanganate oxidation of nine kinds of phenolic endocrine-disrupting chemicals over a wide pH range [36]. HA is the major component of natural organic matter (NOM) that consisted up to 90% of DOC in surface waters. The DOC of the real water used in our experiment was 3.9 mg L^{-1}; thus, HA in the real water probably plays a dominant role in the enhancement of the reaction rates of the CPs in the course of permanganate oxidation. All these previous studies confirmed that the presence of HA facilitating the formation of *in situ* MnO_2 contributes to the enhancement of the oxidation of phenols by permanganate. In addition, the promotive effect of HA is not only dependent on pH of the aquatic system but also associated with the structures of phenolic compounds [35,36]. The oxidative ability of the *in situ* formed MnO_2 decreases with the increase in pH and takes effect for oxidation of phenols by permanganate under acidic and neutral pH conditions, while it decays and even shows no effect under alkaline conditions. This might be the reason that the enhancement of k_{obs} (the Δ value) is obviously higher at pH 5.8 than at pH 8.0 for both of 2,4-DCP and 2,4,6-TCP. Sun et al. [35] also proposed that the influence and the mechanism of the chlorine substituents on the aromatic ring on the susceptibility of the oxidation of CPs by MnO_2 are similar to those of permanganate. The intramolecular hydrogen bonding plays a decisive role in determination of the reactivity of the undissociated ortho-substituted CPs with MnO_2. As a result, the reaction rates of CPs with MnO_2 or permanganate increase with the increase in the amount of ortho-substituted chlorine, which might lead to the enhancement sequence of 2,4,6-TCP > 2,4-DCP > 4-MCP at pH 5.8 as shown in Table 2. Similarly, the enhancement sequence is reversed to 2,4,6-TCP < 2,4-DCP < 4-MCP under weakly alkaline conditions. Some researchers also stated that HA could interact with phenols besides its ability of inducing formation of *in situ* MnO_2, and the level of the binding increases with the increase in the proportion of the undissociated form of phenols [35,37]. The interaction could enhance the density of the electron cloud of CPs and thus accelerate CPs' oxidation by permanganate.

Table 2
Rate constants (k_{obs}) for permanganate oxidation of three CPs in different water matrices ($\times 10^{-5}$ s^{-1})

CP	Real water	Pure water	Δ
4-MCP (pH 5.8)	42.00	6.88	35.12
4-MCP (pH 8.0)	94.67	47.02	47.65
2,4-DCP (pH 5.8)	51.50	14.22	37.28
2,4-DCP (pH 8.0)	51.83	44.40	7.43
2,4,6-TCP (pH 5.8)	86.17	41.13	45.04
2,4,6-TCP (pH 8.0)	5.00	3.50	1.50

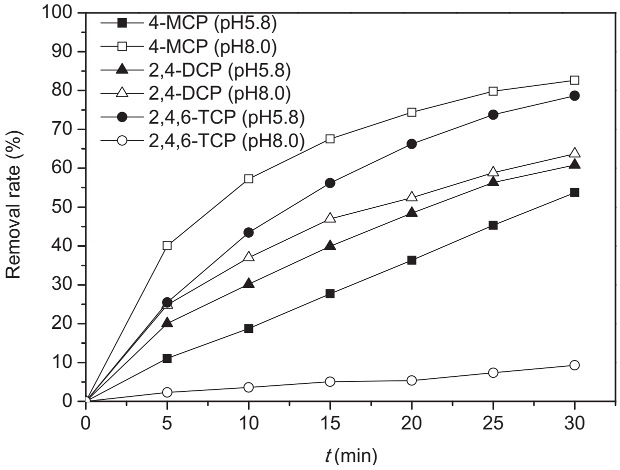

Fig. 5. Removal rates of three CPs by permanganate oxidation in real water matrices. Conditions: $[CP]_0 = 2$ μM, $[KMnO_4]_0 = 20$ μM.

Thus, the lower enhancement of the reaction rates of the CPs in the presence of HA under weakly alkaline conditions is mainly related to the interaction between the CPs and HA. The interaction of the CPs with HA might exist but be masked by the strong reactivity of the *in situ* formed MnO_2 under acidic or neutral pH conditions. Because the undissociated form is dominant for 4-MCP at pH 8.0, the interaction between HA and 4-MCP might induce the highest enhancement of k_{obs} for 4-MCP at pH 8.0.

Our results suggest that permanganate oxidation might be an optional method to control CPs or other phenolic compounds during water treatment processes. Actually, permanganate oxidation has already been used to control iron, manganese, taste and odor, cyanotoxins, etc. in many city waterworks of China. The concentration of permanganate usually does not exceed $3\,\mathrm{mg\,L^{-1}}$ (18.984 μM) in order to ensure the concentration of residual manganese ion blowing the guideline value of $0.1\,\mathrm{mg\,L^{-1}}$ set by the Chinese Government. Moreover, permanganate is always applied as a pre-oxidant to enhance the efficiency of the succeeding coagulation and filtration processes [38] and to control the formation of trihalomethanes (THMs) and other disinfection by-products [39].

4. Conclusions

CPs are an important class of compounds widely used in industrial production. There is growing evidence that they are a threat to human health and aquatic ecosystem. Permanganate oxidation was therefore used to eliminate these chemicals in the study. The reaction between three kinds of CPs and permanganate fits overall second-order kinetics, and first-order with respect to each CP and permanganate. The reactions are oxidant dose and temperature dependent. With the increase in permanganate concentrations or temperatures, the removal rates accelerate for all the CPs. pH and chlorine substituents strongly influence the substrate reactivity. Consequently, the order of the reaction rates of the CPs is totally different under different pH conditions. The removals of the CPs by permanganate oxidation are obviously higher in real water than in pure water. It means that permanganate oxidation might be a selectable method in controlling CPs during water treatment processes. An appropriate increase in the oxidant dosage or temperature enhancement could facilitate their removals. But the pH of the reaction system must be carefully treated in order to achieve higher or rapid removals.

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