

Full Length Research Paper

Kinetic investigations of oxidation of chlorophenols by permanganate

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The kinetics of oxidation of various chlorophenols such as 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) by potassium permanganate (0.8-3.2 mM) were studied in un-buffered solution with ionic strength ~ 0.02 M. Experimental results indicated that the reaction of CPs with permanganate was of second-order overall (0.86 to 19.0 M⁻¹s⁻¹) and the reaction is first-order individually with respect to both permanganate and all chlorophenols (CPs) at an initial pH ~ 7.0 and 22°C. The degradation rate of chlorophenols can be accelerated by increasing oxidant concentration. The reaction rates of 4-CP with permanganate did not show any significant change over pH 5.5 to 8.5 and ionic strength ~ 0 to 0.2 M. The determined rate constants allowed us to predict the reaction rates of CPs with KMnO₄ during oxidative treatment of CPs at contaminated sites.

Key words: Chlorophenols, kinetics, oxidation, potassium permanganate, rate constant.

INTRODUCTION

Chlorophenols are used as fungicides, herbicides, insecticides and precursors in the synthesis of other pesticides and can be formed as a by-product during bleaching of pulp with chlorine and in the disinfection of drinking water by chlorination (Ahlborg and Thunberg, 1980). They can be found in ground waters, wastewaters and soils (Wegman and Broek, 1983). Chlorophenols have become a significant environmental issue due to their toxicity and long persistence in the environment (Cortes-Martinez et al., 2007). Most of them have been listed as priority pollutants by the US Environmental Protection Agency (USEPA, 1980). Therefore, effective methods are needed that are suitable for the treatment of chlorophenols from contaminated sites to avoid further spread to the environment and their elimination from contaminated groundwater.

Attempts to treat these toxic compounds into harmless

simple species using advanced oxidation processes such as ozone, ozone and ultraviolet, and Fenton's reagent have been reported to be effective for the destruction of chlorophenols (Pera-Titus et al., 2004), although the cost for such a treatment is high. Oxidizing agents such as ozone, Fenton's Reagent and hydrogen peroxide have significantly shorter residence time in the ground compared to permanganate (Huang et al., 1999). Permanganate has advantages in subsurface remediation due to its persistence, ease of handling, low cost and reactivity over a wide pH range. While permanganate reactivity with chlorophenol has been carried out previously (Waldemer and Tratnyek, 2006; He et al., 2010), the subject remains relatively under researched compared to the other oxidants.

Lee and Sebastian (1981) determined oxidation of 2-CP, 3-CP, 4-CP, 2,4-DCP and 2,4,6-TCP with

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permanganate. They found that permanganate-chlorophenol reaction was second-order in an unbuffered alkaline (0.1M NaOH) environment. While Waldemer and Tratnyek (2006) determined the reaction to be second-order in a neutral, phosphate buffered solution, there is still a lack of kinetic data about the degradation of chlorophenols under various oxidant concentrations at neutral pH in un-buffered solutions. Jiang et al. (2009) found that a phosphate buffer significantly enhanced permanganate oxidation of 2,4-dichlorophenol. Other researchers (He et al., 2010; Hossain and McLaughlan, 2012) have determined second-order rates from pseudo-first-order rates assuming the reaction was second-order based on the work of Lee and Sebastian (1981). The results of research to date show considerable ambiguity in experimentally determined reaction sequences for various chlorophenols with permanganate. For example, Waldemer and Tratnyek (2006) found the sequence 2,4-DCP > 2,4,6-TCP > 2-CP > 3-CP, while Hossain and McLaughlan (2012) found 2-CP > 2,6-DCP > 4-CP ~2,4-DCP > 3-CP and Zhang et al. (2003) found 4-CP > 2,4-DCP > 2,6-DCP. Therefore, this study aims to verify whether the permanganate-chlorophenol reaction is second-order under neutral pH, un-buffered conditions and determine the reaction rates. Clarification on the expected resulting reaction sequence for various monochlorophenols (2-CP, 4-CP, 3-CP), dichlorophenols (2,4-DCP, 2,6-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) will be undertaken.

MATERIALS AND METHODS

Chemicals

Analytical grade 2-CP, 3-CP, 4-CP, 2,4-DCP, 2,6-DCP and 2,4,6-TCP reagents (99%; Sigma- Aldrich Chemical Company) were used. All solutions were prepared with Milli-Q water. Individual stock solutions of chlorophenol ~0.52 to 0.78 mM were prepared and kept in a screw-capped amber colour glass bottle while stored in a refrigerator at 4°C for up to 1 month. KMnO₄, oxalic acid, KCl, Na₂SO₃, NaOH, H₂SO₄ and HCl were analytical grade from Chem-Supply. The ionic strength (I to 0.02 M) was maintained with the addition of KCl. A 10 mM stock solution of permanganate was prepared in an amber colour glass bottle and standardized with oxalic acid.

Analytical method

Chlorophenol and KMnO₄ concentrations were analysed with UV-visible spectrophotometer (Shimadzu, Model UV-1700) using a 10 mm quartz cell. The analysis were carried out using maximum absorption wavelengths at pH 12 for 2-CP (294 nm), 3-CP (292 nm), 4-CP (298 nm), 2,4-DCP (305 nm), 2,6-DCP (299 nm) and 2,4,6-TCP (312 nm) (Hossain and McLaughlan, 2012; Thomas and Burgess, 2007). The calibration plot was constructed for trichlorophenol, dichlorophenols and monochlorophenols over a concentration range 0.0054 to 0.52 mM, 0.0064 to 0.61 mM and 0.0073 to 0.78 mM, respectively, and found absorptivity for 2-CP is 3.42 cm⁻¹ mM⁻¹, for 3-CP is 3.05 cm⁻¹ mM⁻¹, for 4-CP is 2.38 cm⁻¹

mM⁻¹, for 2,4-DCP is 3.60 cm⁻¹ mM⁻¹, for 2,6-DCP is 4.90 cm⁻¹ mM⁻¹ and for 2,4,6-TCP is 5.17 cm⁻¹ mM⁻¹. The required pH for CP analysis was adjusted using 1 M NaOH or HCl. The detection limits were 0.0006 and 0.0008 mM for trichlorophenol, dichlorophenols and monochlorophenols, respectively. The detection limit was determined using the formula (Ermer, 2001): LOD = 3.3*σ/S where σ and S are the standard deviation and slope of the calibration line. The maximum absorption wavelengths for KMnO₄ at pH 5.6 were 525 nm which agrees with Hood et al. (2000). Calibration for permanganate was performed over a range 1 to 1.5 mM, and the measured absorptivity was 2.47 cm⁻¹ mM⁻¹. The calibration data was generated in triplicate and the mean value used. The regression coefficient value (r²) for all the calibration curves were an excellent straight line fit (r² > 0.99).

All samples were centrifuged at 3,000 rpm for 5 min and then filtered using 0.2 μm Whatman filter paper to remove any manganese dioxide precipitates present. The catalytic effect of MnO₂ colloids during KMnO₄ oxidation kinetics of 2,4-DCP is not significant at pH 7 supported by Jiang et al. (2009). Any remaining MnO₂ may oxidize the phenolate ion but at alkaline conditions the rate of reaction is much slower than the permanganate oxidation of CP and therefore has no influence on the kinetics of the initial reaction (Lee and Sebastian, 1981). The filtrate was analysed for residual chlorophenol concentration with the spectrophotometer at pH 12. The absorbance data were converted into CP concentration by use of a previously prepared calibration curve.

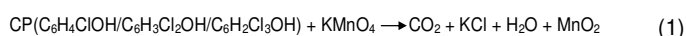
Kinetic methods

Batch experiments were carried out in an aqueous solution by varying the concentration under pseudo-first-order condition where permanganate was in excess. Initial concentrations were varied in the range 0.8 to 3.2 mM for permanganate. Oxidation reaction was initiated by mixing CP and KMnO₄ in a series of screw-capped amber colour glass bottles with ~10% headspace condition. At preselected time intervals 0.1 to 0.15 ml of 2 M Na₂SO₃ solution was added immediately into the vials to quench the reaction. All the reactions were conducted without added pH buffer in duplicate and the reported data was an average of these values. Un-buffered solutions were used since it was believed this would better represent a groundwater environment than a well buffered neutral solution. In other studies a phosphate buffer has been used to minimise flocculation of manganese dioxide (MnO₂) colloids which form as a by-product of the permanganate oxidation reaction (Rodriguez et al., 2007; Waldemer and Tratnyek, 2006).

Previous study was also found that during the oxidation of permanganate with 4-CP creates a reaction by-product of colloidal manganese dioxide (Hossain and McLaughlan, 2012). To minimize the impact of manganese dioxide colloids on absorbance, the vials were centrifuged at 3,000 rpm for 5 min before filtration. The resulting supernatant was then filtered using 0.2 μm Whatman filter paper to avoid interference by light scattering. The residual chlorophenols were analysed directly by UV-visible spectrophotometry. The initial pH of the experiment was 7.0 ± 0.05 and was adjusted using sulphuric acid or sodium hydroxide, as required.

Data analysis

Few studies are available on the oxidation of chlorophenols. It is believed that CP (mono chlorophenol, dichlorophenol and trichlorophenol) and permanganate oxidation proceeded according to Equation 1:



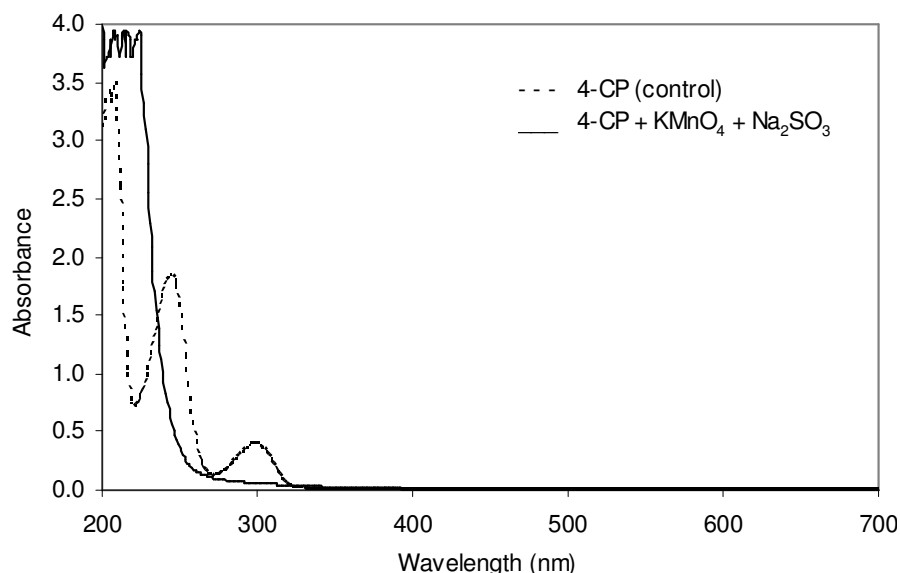


Figure 1. Absorption spectra after reaction of 4-CP (~ 0.16 mM) and KMnO_4 (1.5 mM) using quenching agent Na_2SO_3 , pH 12 (22°C).

According to Equation 1, the oxidation reaction of CP and KMnO_4 can be expressed using rate law (Boekel, 2008) as Equation 2:

$$r = -d[\text{CP}]/dt = k_2 [\text{CP}]^\alpha [\text{KMnO}_4]^\beta \quad (2)$$

Where r is the reaction rate, k_2 represents the second-order rate constant ($\text{M}^{-1} \text{s}^{-1}$), $[\text{CP}]$ is the concentration of chlorophenol (M), $[\text{KMnO}_4]$ is the concentration of permanganate (M), α and β are the reaction orders with respect to $[\text{CP}]$ and $[\text{KMnO}_4]$, respectively.

The reactions are assumed to be second-order overall and first-order with respect to either CP or KMnO_4 based on previous kinetic studies on the oxidation of CP by KMnO_4 (Lee and Sebastian, 1981; Waldemer and Tratnyek, 2006; He et al., 2010). Therefore, the reaction order for both α and β are expected to be one. The Equation 2 can be rewritten as Equation 3:

$$d[\text{CP}]/dt = -k_2 [\text{CP}][\text{KMnO}_4] \quad (3)$$

As the permanganate is present in excess and its concentration is assumed to be constant, the reaction then becomes pseudo-first-order and Equation 3 can be simplified (Huang et al., 2001) to Equations 4 and 5:

$$d[\text{CP}]/dt = -k_1 [\text{CP}] \quad (4)$$

$$k_1 = k_2 [\text{KMnO}_4]_0 \quad (5)$$

Where k_1 is the (observed) pseudo-first-order rate constant (s^{-1}) for CP, $[\text{KMnO}_4]_0$ is the initial permanganate concentration (M). k_2 the second-order rate constant ($\text{M}^{-1} \text{s}^{-1}$) calculated from Equation 5 (Yan and Schwartz, 1999; Huang et al., 2002; Zhai et al., 2006). The above hypotheses are verified through the experimental data. k_1 are obtained by integrating Equation 4 (from 0 to t), to get Equation 6:

$$\ln [\text{CP}]_t = -k_1 t + \ln [\text{CP}]_0 \quad (6)$$

Where $[\text{CP}]_0$ and $[\text{CP}]_t$ are the concentrations of CP at beginning and at time t , respectively.

RESULTS AND DISCUSSION

Analysis of CP during oxidation

The absorbance measurements for the determination of CP concentration were made at pH 12 for 294 nm (2-CP), 292 nm (3-CP), 298 nm (4-CP), 305 nm (2, 4-DCP), 299 nm (2, 6-DCP) and 312 nm (2,4,6-TCP) in order to obtain higher sensitivity during permanganate oxidation and to avoid interference from the absorption of quenching agent. Further details of the analysis method are elsewhere (Hossain and McLaughlan, 2012). Therefore, CP degradation during oxidation could be determined by measuring the decrease in absorbance at wavelength range 292 to 312 nm as a function of time. For example, in order to measure the 4-CP concentration during permanganate oxidation, it was necessary to quench the reaction at a specific time. A quenching agent (Na_2SO_3) was added to eliminate interference caused by residual permanganate to the measurement of UV absorbance. It reacts with residual permanganate only and therefore the target residual analyte (4-CP) remains unchanged. The filtrate was analysed for residual 4-CP at pH 12. The disappearance of peaks at 244 and 298 nm indicates degradation of 4-CP after reaction with permanganate (Figure 1). At pH 12 measurements were carried out at 298 nm to avoid the interferences.

Reaction order

The kinetics of oxidation of chlorophenols by KMnO_4 were studied in un-buffered solution with ionic strength ~0.02 M under pseudo-first-order conditions. Batch

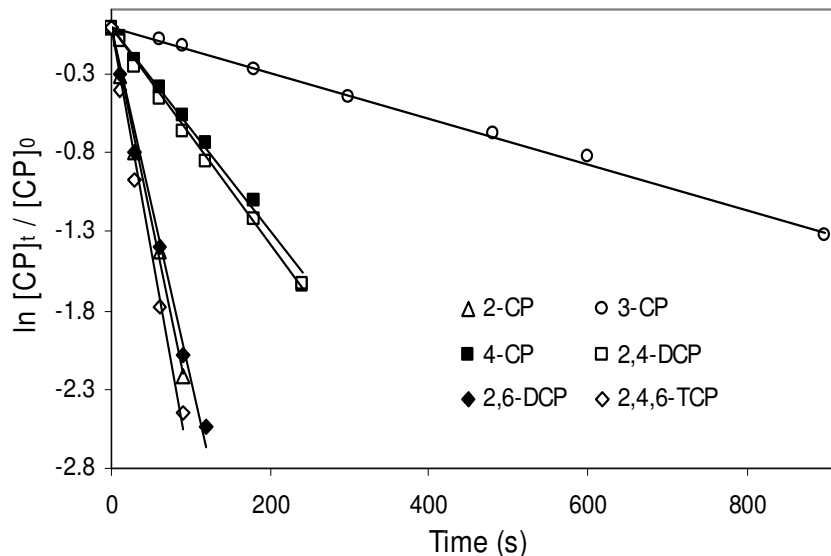


Figure 2. Degradation of 2-CP, 3-CP, 4-CP, 2,4-DCP, 2,6-DCP (~ 0.16 mM) and 2,4,6-TCP (~ 0.08 mM) by KMnO_4 (1.5 mM): I ~ 0.02 M, Initial pH 7.0 (22°C).

Table 1. Rate constants for CP oxidation by KMnO_4 (1.5 mM): I to 0.02 M, Initial pH 7.0 (22°C) [#]Czaplicka, 2004.

Chlorophenols	^a k_1 ($\times 10^{-3} \text{ s}^{-1}$)	r^2	Half-life (min)	[#] pK _a
2-CP (~ 0.16 mM)	24.6 ± 0.244	0.996	0.47	8.3 - 8.6
3-CP (~ 0.16 mM)	1.4 ± 0.003	0.998	8.25	8.8 - 9.1
4-CP (~ 0.16 mM)	6.6 ± 0.141	0.998	1.75	9.1 - 9.4
2,4-DCP (~ 0.16 mM)	6.9 ± 0.054	0.996	1.67	7.5 - 8.1
2,6-DCP (~ 0.16 mM)	22.3 ± 0.108	0.989	0.52	6.7 - 7.8
2,4,6-TCP (~ 0.08 mM)	28.5 ± 0.229	0.989	0.41	6.0 - 7.4

^a k_1 (pseudo-first-order rate constant) = the mean value \pm 95% confidence interval.

experiments were performed to verify the oxidation of CP by KMnO_4 is second-order overall, and first-order with respect to either CP or KMnO_4 . For all these experiments rate constants were determined by evaluating the CP degradation. The data of CP degradation for all chlorophenols are well fit with a first-order decay model ($r^2 = 0.98 - 0.99$). The plot $\ln [\text{CP}]_t / [\text{CP}]_0$ versus time for all chlorophenols lie around straight lines (Figure 2). Therefore, the results indicate that the reaction is first-order with respect to CP. The observed pseudo-first-order rate constants (k_1) and half-lives are listed in Table 1.

The reaction order is 2,4,6-TCP > 2-CP \sim 2,6-DCP > 2,4-DCP \sim 4-CP > 3-CP. It reflects that the number and position of chlorine atoms in the aromatic ring influences significantly on the CP degradation by KMnO_4 . The degradation is rapid for most of the compounds with half-lives less than 2 min while 3-CP is the exception with a half-life of 8 min.

Equation 5 can be used to investigate the reaction order with respect to KMnO_4 . Equation 5 shows that k_1 is proportional to $[\text{KMnO}_4]_0$ and almost constant when used

in excess during each reaction. Therefore, the degradation rate of CP at various initial excess KMnO_4 concentrations (0.8 to 3.2 mM) was determined to investigate the influence of oxidant concentration on the first-order rate constants and to verify the reaction order with respect to KMnO_4 . So, the different experimental values of k_1 for CP degradation from various initial excess concentration of $[\text{KMnO}_4]_0$ can be obtained using Equation 6.

If the reaction is first-order with respect to KMnO_4 then the slope of the straight line from the plot of $\ln k_1$ versus $\ln [\text{KMnO}_4]_0$ will be close to one. Experimentally the initial excess permanganate concentration was varied for 2-CP, 2,6-DCP from 0.8 to 2 mM, for 3-CP, 4-CP and 2,4-DCP from 1.2 to 3.2 mM and for 2,4,6-TCP from 0.97 to 2.0 mM while the initial concentration of CP was fixed for 2-CP, 3-CP, 4-CP, 2,4-DCP, 2,6-DCP at ~ 0.16 mM and for 2,4,6-TCP at ~ 0.08 mM. Figure 3 shows a plot of $\ln k_1$ against $\ln [\text{KMnO}_4]_0$ gives a linear curve ($r^2 > 0.98$) with slopes in the range from 0.91 to 0.98 that is, close to one indicating that the reaction order is first-order for all

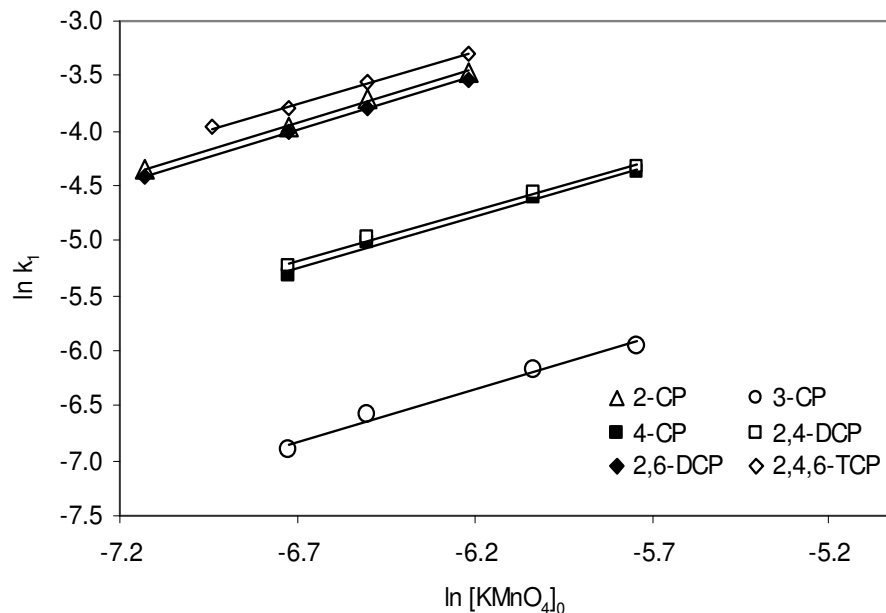


Figure 3. Plot of pseudo-first-order rate constant $\ln k_1$ versus initial concentration of permanganate $\ln[\text{KMnO}_4]_0$. $[\text{CP}]_0 \sim 0.16$ mM, except 2,4,6-TCP ~ 0.08 mM, $[\text{KMnO}_4]_0$ 0.8–3.2 mM, $I \sim 0.02$ M, Initial pH 7.0 (22°C).

chlorophenols with respect to KMnO_4 when reacting with fixed CP. The rate law for the CP oxidation can be expressed as Equation 3. Thus, the reaction between CP and KMnO_4 was of second-order overall, and first-order with respect to each reactant. The second-order rate constants (k_2) for all chlorophenols can be determined using Equation 5 are shown in Table 2. As shown in Table 2, the pseudo-first-order rate constants were increased for individual CP with oxidant concentration which indicated that the rate of reaction has a relationship with the concentration of potassium permanganate. An increase in oxidation rate with oxidant concentration was also reported in the literature (Huang et al., 1999). For example, Figure 4 shows a typical graph for the degradation of 4-CP curves by excess various initial KMnO_4 concentrations (1.2, 1.5, 2.4 and 3.2 mM) with a constant initial 4-CP concentration of ~ 0.16 mM during the experiments. The oxidation of 4-CP by KMnO_4 in all runs shows linear relationship reveals a pseudo-first-order kinetic model where $r^2 > 0.99$. Pseudo-first-order rate constants were calculated from the results in Figure 5.

The pseudo-first-order reaction rate was increased from $4.9 \times 10^{-3} \text{ s}^{-1}$ to $12.7 \times 10^{-3} \text{ s}^{-1}$ for 4-CP, with the increasing permanganate dosage (1.2 to 3.2 mM). Similarly, the pseudo-first-order reaction rate where $r^2 = 0.98 - 99$ was increased for 2-CP, 3-CP, 2,4-DCP, 2,6-DCP and 2,4,6-TCP under different excess initial permanganate concentration is shown in Table 2.

The second-order rate constants (k_2) (Table 2) for the oxidation of CP and KMnO_4 at 22°C and initial pH 7 are

comparable to ~ 8 to $20 \text{ M}^{-1} \text{ s}^{-1}$ obtained by He et al. (2010) at much lower concentrations of KMnO_4 and CP than those used in this study. The second-order rate constant for 2,4,6-TCP (17 to $21 \text{ M}^{-1} \text{ s}^{-1}$) at pH 7.6 with permanganate was found by Bastos et al. (2008) is also comparable to this study. It is noted that our second-order rate constant was lower for 2-CP, 3-CP, 2,4-DCP and 2,4,6-TCP than the rate constant of 2-CP ($74 \text{ M}^{-1} \text{ s}^{-1}$), 3-CP ($13.4 \text{ M}^{-1} \text{ s}^{-1}$), 2,4-DCP ($142 \text{ M}^{-1} \text{ s}^{-1}$) and 2,4,6-TCP ($120 \text{ M}^{-1} \text{ s}^{-1}$) determined by Waldemer and Tratnyek (2006). However, Waldemer and Tratnyek (2006) obtained second-order rate constant (k_2) from pseudo-first-order conditions by measuring decreasing concentration of permanganate in a continuous system with excess chlorophenols in phosphate buffered system. But this study obtained second-order rate constant (k_2) by measuring decreasing concentrations of chlorophenols with excess permanganate in un-buffered system. Jiang et al. (2009) also found that the second-order rate constant for 2,4-dichlorophenol ($45 \text{ M}^{-1} \text{ s}^{-1}$) at pH 7 in 50 mM phosphate buffer was much higher than without phosphate buffer ($19 \text{ M}^{-1} \text{ s}^{-1}$). The second-order rate constant values for 2-CP ($10.8 \text{ M}^{-1} \text{ s}^{-1}$) and 2,4-DCP ($2.44 \text{ M}^{-1} \text{ s}^{-1}$) was determined by Lee and Sebastian (1981) in alkaline conditions are close to this study. Our second-order reaction sequences are 2,4,6-TCP > 2-CP \sim 2,6-DCP > 2,4-DCP \sim 4-CP > 3-CP and are similar to those of He et al. (2010) and Waldemer and Tratnyek (2006) but differ from Zhang et al. (2003).

It was proposed that the position of chlorine atoms may induce significant steric and electronic effects in the

Table 2. Rate constants for the oxidation of 2-CP, 3-CP, 4-CP, 2,4-DCP, 2,6-DCP and 2,4,6-TCP with various concentrations of KMnO_4 : I ~ 0.02 M, Initial pH 7.0 (22°C).

[CP] ₀ ($\times 10^{-3}$ M)	[KMnO ₄] ₀ ($\times 10^{-3}$ M)	r ²	^a k ₁ ($\times 10^{-3}$ s ⁻¹)	^b k ₂ (M ⁻¹ s ⁻¹)	^c k ₂ (M ⁻¹ s ⁻¹)
2-CP (~0.16)	0.8	0.996	13.4 ± 0.010	16.8	
2-CP (~0.16)	1.2	0.997	18.8 ± 0.215	15.7	
2-CP (~0.16)	1.5	0.996	24.6 ± 0.244	16.4	16.2 ± 0.502
2-CP (~0.16)	2.0	0.995	31.4 ± 0.258	15.7	
3-CP (~0.16)	1.2	0.996	1.0 ± 0.019	0.83	
3-CP (~0.16)	1.5	0.998	1.4 ± 0.003	0.93	
3-CP (~0.16)	2.4	0.994	2.1 ± 0.036	0.88	0.86 ± 0.050
3-CP (~0.16)	3.2	0.998	2.6 ± 0.066	0.81	
4-CP (~0.16)	1.2	0.999	4.9 ± 0.079	4.1	
4-CP (~0.16)	1.5	0.998	6.6 ± 0.141	4.4	
4-CP (~0.16)	2.4	0.993	9.9 ± 0.069	4.1	4.2 ± 0.160
4-CP (~0.16)	3.2	0.994	12.7 ± 0.165	4.0	
2,4-DCP (~0.16)	1.2	0.998	5.4 ± 0.074	4.5	
2,4-DCP (~0.16)	1.5	0.996	6.9 ± 0.054	4.6	
2,4-DCP (~0.16)	2.4	0.996	10.4 ± 0.128	4.3	4.4 ± 0.168
2,4-DCP (~0.16)	3.2	0.994	13.3 ± 0.153	4.2	
2,6-DCP (~0.16)	0.8	0.999	12.0 ± 0.011	15.0	
2,6-DCP (~0.16)	1.2	0.998	18.1 ± 0.360	15.1	
2,6-DCP (~0.16)	1.5	0.989	22.3 ± 0.108	14.9	14.9 ± 0.158
2,6-DCP (~0.16)	2.0	0.995	29.3 ± 0.291	14.7	
2,4,6-TCP (~0.08)	0.97	0.998	18.8 ± 0.141	19.4	
2,4,6-TCP (~0.08)	1.2	0.993	22.7 ± 0.157	18.9	
2,4,6-TCP (~0.08)	1.5	0.989	28.5 ± 0.229	19.0	19.0 ± 0.305
2,4,6-TCP (~0.08)	2.0	0.985	37.1 ± 0.329	18.6	

^ak₁ (pseudo-first-order rate constant) = the mean value ± 95% confidence interval, ^bk₂ (second-order rate constant) is determined from $k_2 = k_1 / [\text{KMnO}_4]_0$ using the mean of k₁ values, ^ck₂ (second-order rate constant) = the mean value ± 95% confidence interval.

phenolic ring (Han et al., 2004). The 3-CP is shown to be most resistant to oxidation (Table 2). The deficiency of electrons in the carbon-carbon double bond, induced by meta-chloro substituent in 3-CP reduces the oxidation rate. The fact that the meta-chloro substitution are unable to participate in π -resonance interactions and their effect on reactivity is dominated by their σ -electron-acceptor only (Ulrich and Stone, 1989). On the other hand the 4-CP and 2,4-DCP was found higher in reactivity than 3-CP this may be due to the π -resonance interaction through electron donating conjugative effect which is partially counteracted with the σ -electron withdrawing effect (Stone, 1987). A higher reactivity of mono ortho (2-CP) and di-ortho (2,6-DCP) degradation compared to other chlorophenol (for example, 4-CP and 2,4-DCP) was also found (Table 2). It indicates that a significant steric effect was evident in the reaction by the interaction of

electron-withdrawing chlorine and hydroxyl group. Previous studies reported that permanganate first attacked on phenolate anion during the oxidation of potassium permanganate and chlorophenols (Lee and Sebastian, 1981). So formation of phenolate ion accelerates the oxidation process. Han et al. (2004) suggested that acidities of all ortho chlorophenol are stronger than other chlorophenols. It means available of PhO^- anion from all ortho chlorophenol is quicker than other chlorophenol (4-CP and 2,4-DCP). Consequently, higher oxidation rates for all ortho chlorophenol with permanganate may be applicable. The pK_a also effects the rate of reaction as the initial pH 7.0 used in this study is the closer value of ionization constant that is, pK_a (Table 1) for 2,6-dichlorophenol and 2,4,6-trichlorophenol which is plausible reason for the rapid rate of reaction. However, more kinetic data are needed to be able to

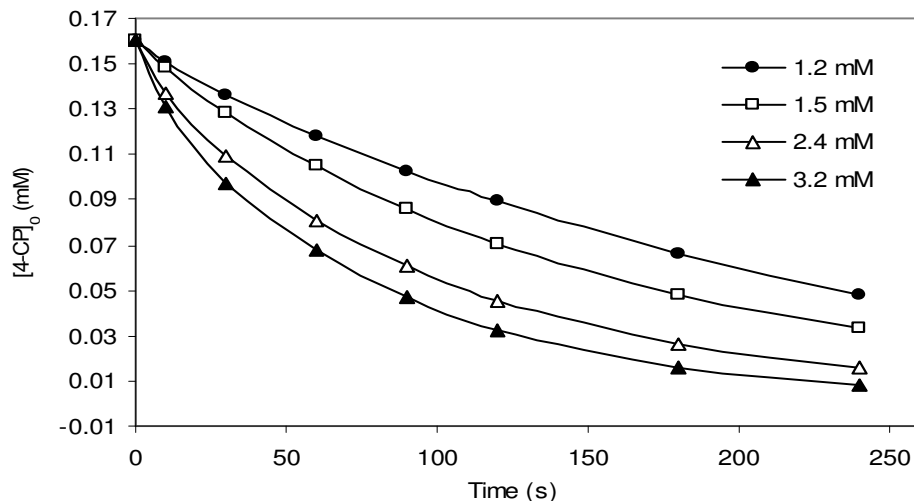


Figure 4. Degradation of 4-CP under various concentration of KMnO_4 . $[\text{4-CP}]_0 \sim 0.16$ mM, $[\text{KMnO}_4] \sim (1.2\text{--}3.2$ mM), $I \sim 0.02$ M, Initial pH 7.0 (22°C).

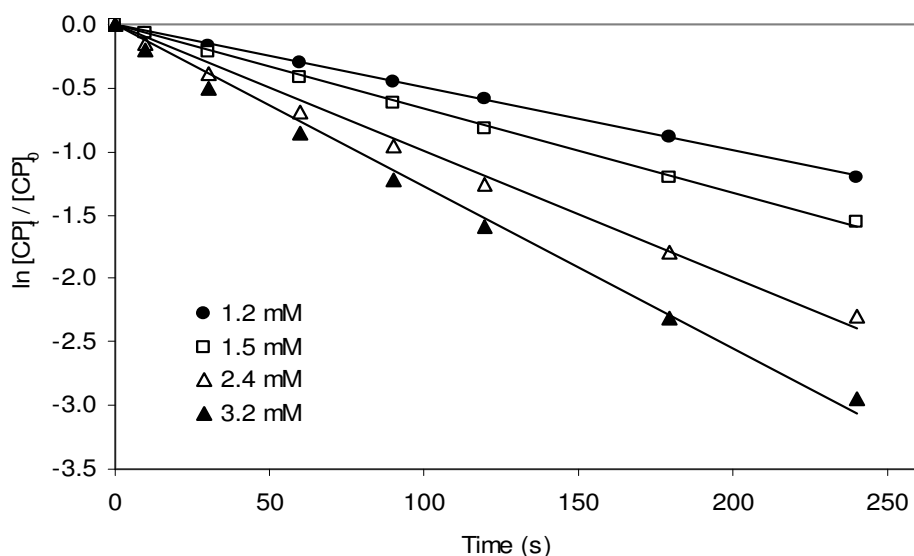


Figure 5. Oxidation fit curves of 4-CP at various concentration of KMnO_4 . $[\text{4-CP}]_0 \sim 0.16$ mM, $[\text{KMnO}_4] \sim (1.2$ to 3.2 mM), $I \sim 0.02$ M, Initial pH 7.0 (22°C).

explain for these reaction sequences.

Effect of ionic strength and pH

Few published studies on the effect of water quality on CP degradation by KMnO_4 were found. The effect of ionic strength (0 to 0.2M KCl) and pH (5.5 to 8.5) on the oxidation of 4-CP by permanganate was investigated. These ionic strengths cover most of the natural subsurface groundwater (Huang et al., 2002). The chosen pH ranges was below the $\text{pK}_a = 9.1 - 9.4$ (Table 1) for 4-CP. The results fit with a pseudo-first-order model

($r^2 = 0.98 - 0.99$) and showed little effect due to variations in the ionic strength and pH. The observed pseudo-first-order rate and calculated second-order-rate constants are shown in Table 3. Therefore, 4-CP oxidation with permanganate is relatively insensitive to pH within the range 5.5 to 8.5. Xiao et al. (2010) found little impact on the rate of 2,4-DCP degradation during permanganate assisted ozonation over an initial pH range of 5.5 to 8.5.

The experimental results are based on a simplified set of environmental conditions. In practice, other factors may influence the reaction processes outlined here. For example, MnO_4^- may also react with non-targeted organic matter and inorganic elements in the soil (USEPA, 2006).

Table 3. Rate constants for 4-CP (~0.16 mM) oxidation by KMnO₄ (1.5 mM) at ionic strength (0.02 to 0.2 M) and initial pH 5.5–8.5 (22 °C).

Ionic strength (M)	Initial pH	^a k ₁ (×10 ⁻³ s ⁻¹)	r ²	^b k ₂ (M ⁻¹ s ⁻¹)
0.0 ^c	7.0	6.3 ± 0.031	0.996	4.2
0.02	7.0	6.6 ± 0.141	0.998	4.4
0.05	7.0	6.6 ± 0.021	0.998	4.4
0.15	7.0	6.5 ± 0.041	0.997	4.3
0.20	7.0	6.2 ± 0.010	0.999	4.1
0.02	5.5	6.4 ± 0.062	0.999	4.3
0.02	8.5	7.2 ± 0.083	0.989	4.8

^ak₁ (Pseudo-first-order rate constant) = the mean value ± 95% confidence interval, ^bk₂ (second-order rate constant) is determined from k₂ = k₁ / [KMnO₄]₀ using the mean of k₁ values, ^cOxidation of CP by KMnO₄ in Milli-Q water.

Therefore, a larger amount of permanganate is required in excess of the amount needed to treat the organic contaminants. In addition oxidant access to the contaminants may be restricted as a result of the reactions. MnO₂ is produced as a result of the oxidation (Crimi and Siegrist, 2004) which may cause a reduction of soil permeability due to precipitation. Although, we found that pH and ionic strength within the studied range had little effect of 4-CP reactions it may affect the reactivity of other chlorophenol compounds.

Conclusion

This work shows that chlorophenols can be rapidly degraded by permanganate in aqueous solution. The reaction of CP with permanganate is second-order in total and first-order individually with respect to CP and KMnO₄. The half-life of 3-CP is longer compare to other chlorophenols which indicates resistance to degradation. The rate of reaction increases with the concentration of permanganate within this investigation range, confirming the independence of the second-order rate constant from the concentration of permanganate. Consequently, the CP degradation rates can be enhanced by increasing oxidant concentration. Further work on the effect of water quality (ionic strength, pH) should be undertaken across a range of CP. Also, the degradation by-product of CPs with permanganate should be quantified. The findings of this study can be valuable in designing *in situ* treatment of chlorophenol-contaminated soil and groundwater.

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