Effects of pH on the chlorination process of phenols in drinking water

Fei Ge [a,b], Lizhong Zhu [a,*], Hairong Chen [a]

[a] *Department of Environmental Science, Zhejiang University, Hangzhou, Zhejiang 310028, China*
[b] *Department of Environmental Engineering, Xiangtan University, Xiangtan, Hunan 411105, China*

Abstract

Toxic organic compounds detected generally in source water could combine with chlorine and contribute significantly to chlorination disinfection by-products (CDBPs). The effects of pH on species distribution of CDBPs and the kinetics of chlorination were investigated using phenol as a model of ionizable toxic organic compounds in the pH range of 6.0–9.0. It was found that five chlorination products including 2-monochlorophenol (2-MCP), 4-monochlorophenol (4-MCP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (TCP) were produced by successive chlorination substitution. MCP (2-MCP and 4-MCP) were the dominant products and phenol partly remained in acid media, while TCP and DCP (2,6-DCP and 2,4-DCP) were the main components in neutral and alkaline media. A steady equilibrium of phenol and its chlorination products was reached in 20–30 min in acid-, neutral- and slightly alkaline media, and was delayed to 60–180 min in alkaline media. The difference in properties between phenols and phenolates, and those between HOCl and ClO⁻ should be considered simultaneously in explaining the effects of pH on the chlorination process with the theory of electrophilic substitution. These results show that pH plays an important regulating role in the species distribution of CDBPs and the kinetics of chlorination for ionizable toxic organic compounds in chlorination.

Keywords: Phenols; Chlorination; Drinking water; Disinfection by-products; pH

1. Introduction

Chlorination disinfection has been widely used in drinking water treatment in developing countries. Since the pioneering work of Rook [1], many investigations have been conducted in the formation and the precursors of chlorination disinfection by-products (CDBPs). In a broad spectrum of compounds, natural organic matter (NOM) is generally regarded as the main precursor of CDBPs in source water [2–4]. Chlorine in water would combine with NOM and, thus, yield a large range of CDBPs, such as trihalomethanes (THMs), haloacetic acids (HAAs), chlorophenols, phenolic acids, chlorinated quinines, which exhibit potentially carcinogenic, teratogenic and mutagenic activities to human health [5]. Meanwhile, except NOM, there exist large quantities of toxic organic compounds in source water, which is generally in the level of ng–µg/L. The concentration of these toxic organics compounds is much lower than that of NOM, but their contribution to CDBPs is significant due to their high activities [6–8].

Phenols, which are significant toxic organic compounds, are broadly used as materials, such as production of pesticides, dyes, drugs, plastics, antioxidants, pulp processes, wood, textile, and leather preservation [9]. Phenols are frequently detected in source water with the highest average concentration of 10 µg/L and 11 kinds of them have been classified as priority pollutants in USEPA [10]. Moreover, it has been proved that phenols are the main configurations composing of humic substances, which are regarded as the important NOM in source water [11–13].

For the ionizable toxic organic compounds, pH would be an important factor affecting the formation of CDBPs in the chlorination process. Early kinetic studies of the chlorination of phenol and chlorine-substituted phenols by Lee [14] and later by Brittain et al. [15] have shown that the overall reaction is second-order and proportional to the concentration of aqueous chlorine and phenol. Similar results were also obtained by Rebenne et al. [16] in the pH range of 2–12 and by Gallard et al. [17] over the pH range of 1–11, both investigators observed that the rate was highly pH dependent and there was a maximum in neutral or slightly alkaline pH range.

* Corresponding author. Tel.: +86 571 88273733; fax: +86 571 88273733.
E-mail addresses: gefei@xtu.edu.cn (F. Ge), zlz@zju.edu.cn (L. Zhu), cers_dzb@zju.edu.cn (H. Chen).

Meanwhile, previous studies have shown that chlorination of phenols was a successive progress. The first step is the chlorination of aromatic ring, which led to the formation of mono-, di- and tri-chlorophenols [18,19]. With the next steps of enolization, hydrolysis and decarboxylation, phenols may gradually produce THMs and HAAs [4,20]. Phenolic structure in humic substances, especially, the resorcinol-type structure is confirmed to be the main active center to produce THMs and HAAs. With the further studies, it was found that THMs precursors could be divided into a fast and a slowly reacting fraction. Resorcinol-type structure could possibly be responsible for the fast reacting THMs precursors; Experiments with phenol showed that they were slowly reacting THMs precursors, which represent 70% of the THMs precursors of natural water [21]. From these results, it could be supposed that some phenols would not produce THMs as fast as resorcinol in drinking water treatment, but just convert to other intermediate CDBPs, such as chlorophenols.

Moreover, in the successive chlorination process, pH could affect not only the kinetics of chlorination of phenols, but also the formation and species distribution of CDBPs. Since the toxicity of chlorophenols has been proved to be enhanced with the increasing of substituted chlorine atom in phenolic ring [22], it is essential to investigate the process and factors in chlorination of phenols. And pH is more important than other factors in chlorination process for ionizable toxic organic compounds, so it would be possible to decrease the producing of CDBPs and, thus, to control the risk of them by regulating pH in drinking water treatment. But studies on the chlorination process of phenols and species distribution of intermediate CDBPs at different pH are limited. There are still uncertainty and not well description of the successive progress and the intermediate CDBPs in chlorination of phenols.

The objectives of this study are using phenol as a model of ionizable toxic organic matter: (1) to investigate the successive chlorination process, (2) to discuss the effects of pH on the species distribution of CDBPs and kinetics of chlorination in the pH range of drinking water, and (3) to describe a mechanism for the effects of pH on the chlorination process.

2. Materials and methods

2.1. Materials

Phenol, 2-monochlorophenol (2-MCP), 4-monochlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP) and 2,4,6-trichlorophenol (TCP) were obtained from Acros Organics and the purities of them are greater than 99%. The physico–chemial properties of them were listed in Table 1. Phenol stock solution with concentration of 10.64 mmol/L was prepared, which was based on the mass of raw material and diluted to target concentration with Milli-Q pure water (Mill-Q SP VOC, Millipore Co., Bedford, MA). Meanwhile, 7.84 mmol/L of 2-MCP and 4-MCP, 6.13 mmol/L of 2,4-DCP and 2,6-DCP, 1.26 mmol/L of TCP standard solution were also prepared with raw material and then diluted to target concentration with Milli-Q pure water, and 1–5 mL methanol in 100 mL aqueous solution (reagent for HPLC) was added

due to their low aqueous solubility, respectively. A stock of free chlorine solution was prepared from commercial sodium hypochlorite (NaOCl, 5% active chlorine) and then diluted with Milli-Q pure water. The acute concentration of sodium hypochlorite solution was standardized by sodium thiosulfate titration.

2.2. Chlorination procedure

Sodium hypochlorite was added with the concentration of 0.4233 mmol/L in 500 mL aqueous solution, and the pH of solution were adjusted to 6.0, 6.5, 7.0, 7.5, 8.0, 8.5 and 9.0 by 50 mL phosphoric acid buffer solution and measured with a pH-meter (Mettler-Toledo, Switzerland). And, then, the standard phenol solution was quickly added to the glass reactors with concentration of 0.1064 mmol/L and placed in air bath with temperature maintained at $25 \pm 1\,°C$ and reciprocating rate at 120 rpm. Samples of 10 mL were taken out at 5, 10, 20, 30, 60, 120, 180, and 240 min. The residual sodium hypochlorite in samples was decomposed by adding excess sodium thiosulfate and, then, 2 mL samples at different reaction time were analyzed by HPLC.
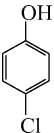
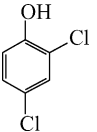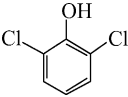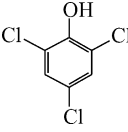### 2.3. Analysis conditions

The concentration of phenol and its chlorination products were determined by HPLC with UV-spectrophotometer at wavelength 272 nm with flow rate of 1.0 mL/min. HPLC analyses were performed on a Hitachi Instruments (L-7000 Series, Japan) with C18 reverse phase column (Wakosoil, $250 \times \Phi 4.6\,mm$, Japan). The initial mobile phase composition was methanol/water of 70/30 (v/v), which decreased linearly to 60/40 (v/v) from 3 to 12 min, and then increased linearly to 70/30 (v/v) from 12 to 18 min.

3. Results and discussion

3.1. Chlorination process of phenol

The chromatograms of phenol and its chlorination products at pH 7.0 were shown in Fig. 1. Five chlorophenols were formed in the experiment, which included 2-MCP, 4-MCP, 2,6-DCP, 2,4-DCP and TCP. After contacting 5 min, these chlorination products were detected and the chromatogram peak of each component was separated completely with the analysis conditions in the experiment. Fig. 2 showed the concentration changes of phenol and its chlorination products with time at pH 7.0. It was clear that the concentration of phenol decreased from 0.1064 to 0.0118 mmol/L, while that of TCP increased to 0.0725 mmol/L at the initial 20 min, and then the concentration of them almost maintained steady. Contrast with TCP, the concentration of MCP (2-MCP and 4-MCP) was much lower, which increased to 0.0169 mmol/L (2-MCP, 0.0087 mmol/L; 4-MCP, 0.0082 mmol/L) at initial 5 min and then decreased quickly to 0.0110 mmol/L (2-MCP, 0.0039 mmol/L; 4-MCP, 0.0071 mmol/L) at 20 min. The concentration of DCP (2,6-MCP and 2,4-DCP) was as low as that of MCP, which

Table 1
Selected physico–chemial properties of phenolic compounds

Compound	Molecular formula	MW (g/mol)	log K_{ow} [23]	S_w [24] (g/L, H_2O, 25 °C)	pK_a [24]
Phenol		94.1	1.51	80.23	9.95
2-Monochlorophenol		128.5	2.15	21.02	8.44
4-Monochlorophenol		128.5	2.39	18.32	9.29
2,4-Dichlorophenol		163.0	3.25	5.03	7.77
2,6-Dichlorophenol		163.0	2.84	2.65	6.79
2,4,6-Trichlorophenol		197.5	3.75	0.42	6.19

increased to 0.0134 mmol/L (2,6-DCP, 0.0070 mmol/L; 2,4-DCP, 0.0064 mmol/L) at initial 5 min and then decreased quickly to 0.0096 mmol/L (2,6-DCP, 0.0037 mmol/L; 2,4-DCP, 0.0059 mmol/L) at 20 min.
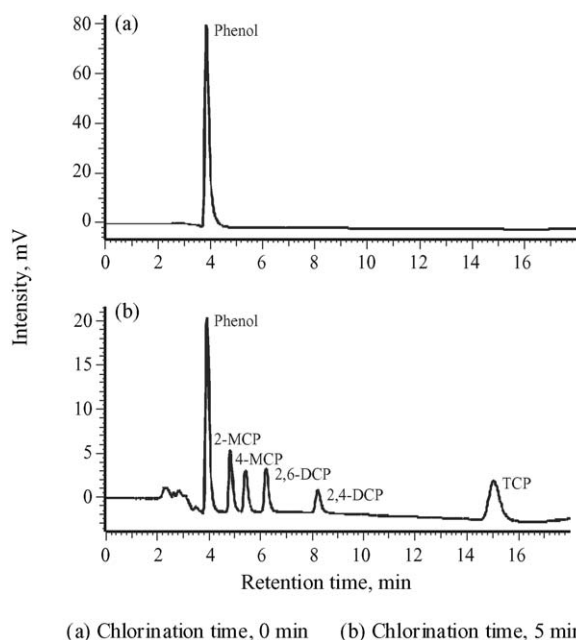
These observations suggested that phenol could convert to 2-MCP, 4-MCP, 2,6-DCP, 2,4-DCP and TCP by successive chlorination process and the pathway of this process was described in Fig. 3, which was similar to the results of previous studies [25]. Meanwhile, TCP was found to be the final chlorine-substituent phenol and no tetrachlorophenol or pentachlorophe-

(a) Chlorination time, 0 min   (b) Chlorination time, 5 min

Fig. 1. Chromatograms of phenol and its chlorination products at pH 7.0.
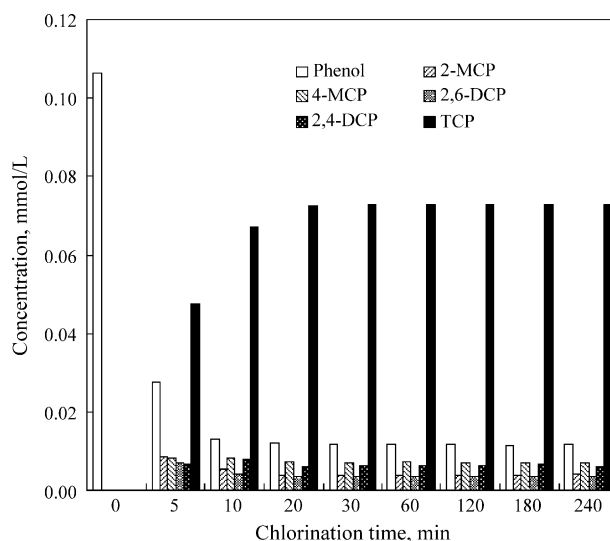

Fig. 2. Concentration of phenol and its chlorination products with time products at pH 7.0.
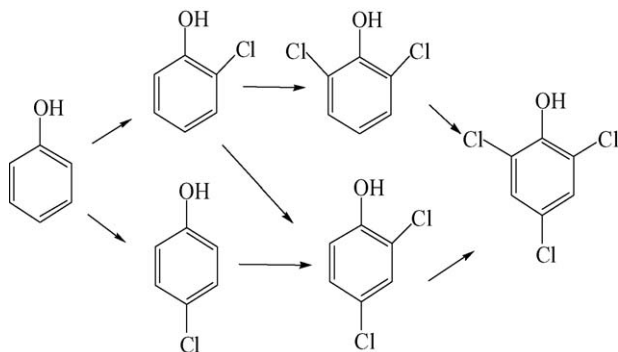
Fig. 3. Pathway of successive chlorination of phenol.

nol was detected in the experimental conditions. Equilibrium of phenol and its chlorination products was reached in 20–30 min, then the ratio of each component kept steady till 240 min. The findings are in accord with the reported results [19], which investigated the phenol–chlorine reaction in environmental water and obtained the chlorination products of phenol were essentially a mixture of mono-, di-, and tri-chlorophenols at ambient temperature.

3.2. Effects of pH on the chlorination process of phenol

Effects of pH on species distribution and kinetics of phenol and its chlorination products were investigated in the experiment. The concentration changes of phenol, MCP (2-MCP and 4-MCP), DCP (2,6-DCP and 2,4-DCP) and TCP with time in the pH range of 6.0–9.0 were shown in Fig. 4.

In Fig. 4(a), it was noted that phenol could partly remain in slightly acidic and neutral media but disappeared quickly in slightly alkaline and alkaline media. Phenol could not be detected just after 10–20 min at pH 8.0–9.0, but still remained 0.0021 mmol/L at pH 7.5, 0.0116 mmol/L at pH 7.0, 0.0271 mmol/L at pH 6.5 and 0.0334 mmol/L at pH 6.0 after 240 min. The initial reaction rate of phenol increased with the increase of pH from 6.0 to 9.0. Similar results were reported by Rebenne et al. [16], who studied aqueous chlorination kinetics and the mechanism of substituted dihydroxy-benzenes and found that the apparent chlorination rate constants (k_{app}) were a minimum in the pH range of 3–6 and a maximum over the pH range of 8–11. For example, the $\log k_{app}$ of resorcinol was about $2.4\,M^{-1}\,s^{-1}$ at pH 6, and then increased continuously to $4.3\,M^{-1}\,s^{-1}$ till pH reached 11. Gallard et al. [17] also observed that the rate constants of chlorination of phenols varied from 0.02 to $2.71 \times 10^4\,M^{-1}\,s^{-1}$ using mono- and di-hydrobenzenes as model compounds in aqueous media over the pH range of 1–11.

The concentration variation of MCP with time at different pH was shown in Fig. 4(b). It was found that the concentration of MCP increased in the first 5–10 min and then quickly decreased till reached steady. The maximal concentration of MCP was 0.0209 (pH 6.0), 0.0196 (pH 6.5), 0.0169 (pH 7.0), 0.0086 (pH 7.5), 0.0069 (pH 8.0), 0.0093 (pH 8.5) and 0.0185 (pH 9.0) mmol/L, but the variation of MCP with time was much different at each pH. MCP could not be detected just after 30 min at pH 9.0

and after 60 min at pH 8.5, while it still remained 0.0039 mmol/L at pH 7.0, 0.0108 to 0.0118 mmol/L at pH 6.0–7.0 after 240 min. These data indicated that MCP were the main components in slightly acidic media, but almost converted to DCP and TCP in slightly alkaline and alkaline media.

The variation of DCP was similar to that of MCP in Fig. 4(c) with maximal concentration of 0.0045 (pH 6.0), 0.00121 (pH 6.5), 0.0134 (pH 7.0), 0.0121 (pH 7.5), 0.0413 (pH 8.0), 0.0581 (pH 8.5) and 0.0755 (pH 9.0) mmol/L. At 240 min, the concentration of DCP was as high as 0.0310 mmol/L at pH 9.0, 0.0264 mmol/L at pH 8.5, 0.0125 mmol/L at pH 8.0, but was only 0.0032 mmol/L at pH 6.0, 0.0071 mmol/L at pH 6.5, 0.0097 mmol/L at pH 7.0 and 0.0050 mmol/L at pH 7.5. Thus, it was confirmed that more phenol and MCP converted to DCP at slightly alkaline and alkaline media.

As the final chlorine-substituent phenol in the experiment, TCP increased sequentially with time till reached steady at different pH in Fig. 4(d). The maximum concentration of TCP was 0.0038 (pH 6.0), 0.0177 (pH 6.5), 0.0728 (pH 7.0), 0.0949 (pH 7.5), 0.0912 (pH 8.0), 0.0793 (pH 8.5) and 0.0746 (pH 9.0) mmol/L. Contrast to in slightly acidic media, TCP was the dominant product in neutral and alkaline media. Furthermore, the initial production rate of TCP increased with pH increasing from 6.0 to 7.5, but then decreased with pH increasing from 8.0 to 9.0.

These results suggested that pH could play an important role in the chlorination process of phenol. Phenol was easier to be substituted by chlorine in neutral and alkaline media at pH values between 6.0 and 9.0, and DCP and TCP were the main components. However, phenol could still partly remain and MCP were the dominant products in slightly acidic media. A steady equilibrium of phenol and its chlorination products was reached at 20–30 min in slightly acidic and neutral media, but it was delayed to 60–180 min in slightly alkaline and alkaline media.

3.3. The mechanism for effects of pH on phenol chlorination

Chlorination of phenols is a typical electrophilic substitution and there are generally three main steps in the reaction process. First, electrophile (E) attacks phenolic ring to form a π-complexes and still keeps the structure of phenolic ring. Second, the electrophile in the π-complexes attaches one of carbon atom of phenolic ring and changes to σ-complexes. Third, hydrogen atom linked with phenolic ring leaves away and produces H^+. This process could be described as Eqs. (1)–(3).
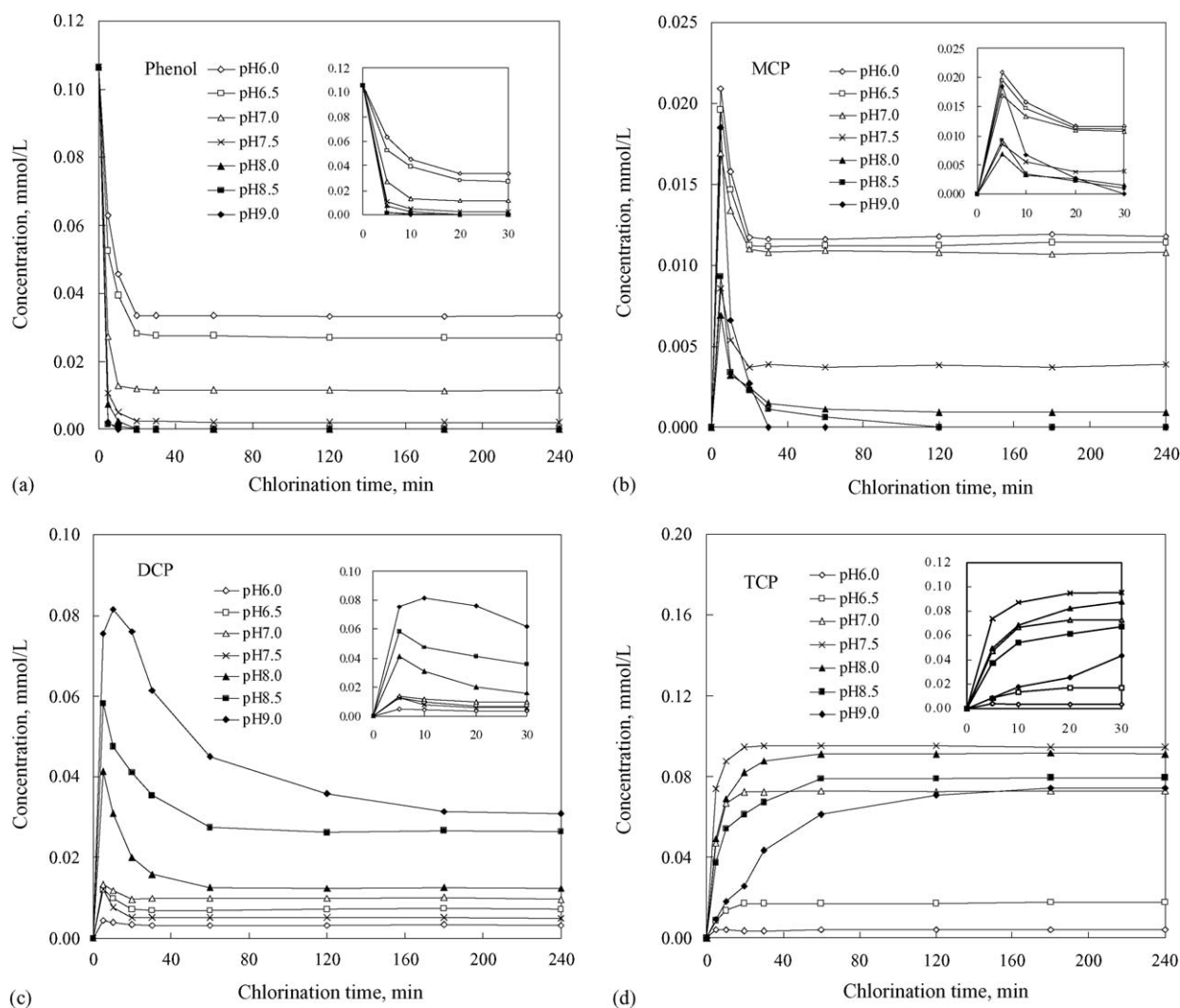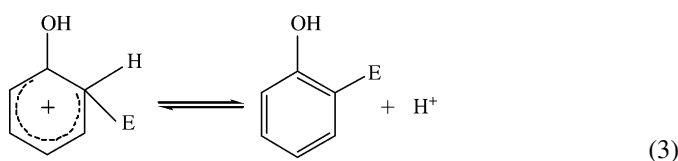

$$(1)$$

$$(2)$$
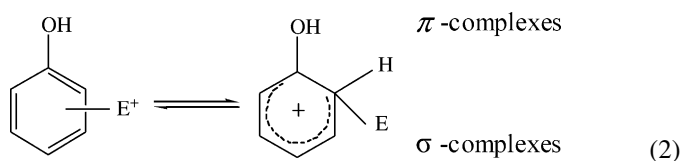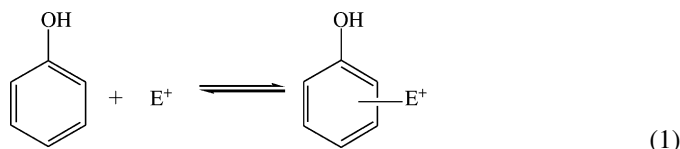
Fig. 4. Concentration of phenol and its chlorination products with time at different pH: (a) Phenol; (b) MCP; (c) DCP; (d) TCP.

(3)

From Eq. (3), it is clear that when the σ-complexes convert to substituted phenols, H^+ is released from phenolic ring to the solution. Thus, pH would affect the equilibrium of the reaction. Contrast to in neutral and alkaline media, it is difficult to release H^+ and the reaction would be blocked in acid media.

Meanwhile, the configurations of initial reactants were also affected by pH. In previous studies, more emphases were put on the effects of pH on ionizable phenol, just as Eqs. (4)–(8).

$$HOCl \rightleftharpoons ClO^- + H^+ \tag{4}$$

$$Phenol \rightleftharpoons Phenolate + H^+ \tag{5}$$

$$Phenol + HOCl \rightleftharpoons Products \tag{6}$$

$$Phenolate + HOCl \rightleftharpoons Products \tag{7}$$

$$Phenol + HOCl + H^+ \rightleftharpoons Products \tag{8}$$

The reaction of HOCl with phenolate was considered to control the overall reaction when pH ≥ 5 (Eq. (7)). The k_{app} for the reaction of HOCl with phenolate were observed 10^3–10^5 folds greater than that with phenol [17], which was due to the higher activating effects of phenolate than that of phenol upon electrophilic substitution. When pH changed from 6.0 to 9.0, more phenol converted to phenolate in solution. And in the successive chlorination, the producing rate of TCP was also related to MCP and DCP in the solution. In Table 1, the pK_a of phenols decreases from 9.99 to 6.79 with the number of chlorine atom increasing, so the effects of pH on the distribution coefficient of ionizable MCP and DCP was more sensitive than that of phenol at pH 6.0–9.0. When pH increases, the electronegative nature of phenol, MCP and DCP also increases, thus, more TCP would be produced and the production rate of TCP would increase with the increase of pH.

However, in the experiment, the production rate of TCP just reached a peak value at pH 7.5 and a steady equilibrium of phenol and its chlorination products was delayed to 60–180 min at pH 8.0–9.0. These phenomena suggested that the effects of pH on HOCl would be considered simultaneously as that on phe-
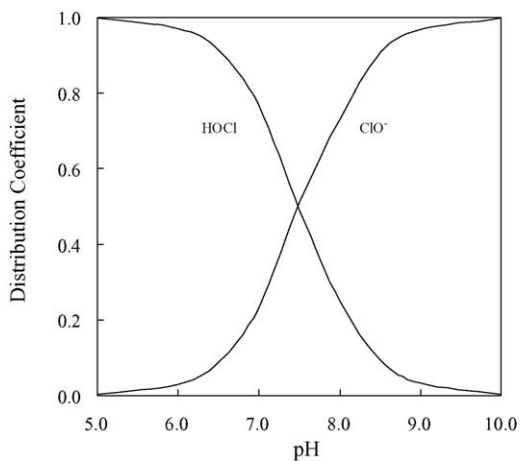
Fig. 5. Relationship between pH and distribution coefficient of HOCl, ClO⁻.

nol in the chlorination process. But in previous study, HOCl was regarded as the only electrophile and the difference in reaction activities between HOCl and ClO⁻ were usually neglected [19,20].

When hypochlorite is dissolved in water, it hydrolyzes rapidly according to Eq. (9) and combined with H⁺ according to Eq. (10).

$$NaOCl \rightleftharpoons Na^+ + ClO^- \tag{9}$$

$$ClO^- + H^+ \rightleftharpoons HOCl \tag{10}$$

Hypochlorous acid is a slightly acid, which means that it tends to undergo partial dissociation and could be described in Eq. (11):

$$K_a = \frac{[H^+][ClO^-]}{[HOCl]} \tag{11}$$

where K_a is the ionization constant, [H⁺], [ClO⁻] and [HOCl] is the concentration of H⁺, ClO⁻ and HOCl in aqueous solution, respectively. K_a varies in magnitude with temperature and pK_a could be computed by the formula as Eq. (12) [26].

$$pK_a = \frac{3000}{T} - 10.06 + 0.0253T \tag{12}$$

The pK_a of HOCl is 7.52 at 25 °C, thus, the distribution coefficient of HOCl could be calculated from Eq. (11) and showed in Fig. 5. It is clear that the distribution coefficient of HOCl decreases from 0.97 to 0.03 when pH increases from 6.0 to 9.0, while that of ClO⁻ increases from 0.03 to 0.97 in the same pH range. In electrophilic substitution, reaction rate is related to electropositive nature of the electrophile. In the experiments, it was observed that ClO⁻ could attack the phenolic ring as electrophile in alkaline media. And ClO⁻ is an electronegative active group, while HOCl is an electron neutral molecule, so it could be considered that ClO⁻ was more difficult to attack phenolic ring than that of HOCl. With the increase of pH, the electronegative nature of phenol, MCP and DCP increases, while electropositive nature of HOCl decreases. Thus, the effects of pH on activities of phenols and HOCl would be considered simultaneously in the chlorination process.

4. Conclusions

In drinking water treatment, toxic organic compounds could combine with chlorine and contribute significantly to CDBPs. For ionizable toxic organic compounds, pH was an important factor affecting the chlorination process and the species distribution of CDBPs. In chlorination of phenol over the pH range of 6.0–9.0, TCP and DCP were the main components in neutral and alkaline media, but MCP were the dominant products in acid media. A steady equilibrium of phenol and its chlorination products was obtained and the equilibrium time was highly related with pH. The difference in properties between phenols and phenolates, and those between HOCl and ClO⁻ should be considered simultaneously in explaining the effects of pH on chlorination process with the theory of electrophilic substitution. These results show that pH plays a regulating role in species distribution and kinetics of chlorination of phenols and the risk of chlorophenols is possible to be controlled under slightly acidic media.

References

[1] J.J. Rook, Formation of haloforms during chlorination of nature water, J. Water Treat. Exam. 23 (1974) 234–243.
[2] D.L. Norwood, D.J. Johnson, R.F. Christman, Reaction of chlorine with selected aromatic models of aquatic humic material, Environ. Sci. Technol. 14 (1980) 187–190.
[3] D.A. Reckhow, P.C. Singer, R.L. Malcolm, Chlorination of humic materials: by-product formation and chemical interpretations, Environ. Sci. Technol. 24 (1990) 1655–1664.
[4] E.R. Blatchley III, D. Margetasb, R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res. 37 (2003) 4385–4394.
[5] X. Yang, C. Shang, Chlorination by-product formation in the presence of humic acid, model nitrogenous organic compounds, ammonia, and bromide, Environ. Sci. Technol. 38 (2004) 4995–5001.
[6] V.L. Heasley, A.M. Fisher, E.E. Herman, F.E. Jacobsen, E.W. Miller, A.M. Ramirez, N.R. Royer, J.M. Whisenand, D.L. Zoetewey, D.F. Shell-hamer, Investigations of the reactions of monochloramine and dichloramine with selected phenols: examination of humic acid models and water contaminants, Environ. Sci. Technol. 38 (2004) 5022–5029.
[7] J. Hu, T. Aizawa, S. Ookubo, Products of aqueous chlorination of bisphenol A and their estrogenic activities, Environ. Sci. Technol. 36 (2002) 1980–1987.
[8] M.C. Dodd, C. Huang, Transformation of the antibacterial agent sulfamethoxazole in reactions with chlorine: kinetics, mechanisms, and pathways, Environ. Sci. Technol. 38 (2004) 5607–5615.
[9] A. Vermeulen, K. Welvaert, J. Vercammen, Evaluation of a dedicated gas chromatography–mass spectrometry method for the analysis of phenols in water, J. Chromatogr. A 1071 (2005) 41–46.
[10] D. Mattinez, E. Pocurull, R.M. Marce, F. Borrull, M. Calull, Separation of eleven priority phenols by capillary zone electrophoresis with ultraviolet detection, J. Chromatogr. A 734 (1996) 367–373.
[11] R.A. Larson, A.L. Rockwell, Chloroform and chlorophenol production by decarboxylation of natural acids during aqueous chlorination, Environ. Sci. Technol. 13 (1979) 325–329.

[12] B.E. Watt, R.L. Malcolm, H.M.B. Hayes, N.W.E. Clark, J.K. Chipman, Chemistry and potential mutagenicity of humic substances in waters from different watersheds in Britain and Ireland, Water Res. 30 (1996) 1502–1516.

[13] J.V. Hanna, W.D. Johnson, R.A. Quezada, M.A. Wilson, X. Lu, Characterization of aqueous humic substances before and after chlorination, Environ. Sci. Technol. 25 (1991) 1160–1164.

[14] F.C. Lee, In Principles and Applications of Water Chemistry, Wiley, New York, 1967.

[15] J.M. Brittain, P.C.B. De la Mare, In the Chemistry of Halides, Pseudo-halides, and Azides. Part I, Wiley, New York, 1983.

[16] L.M. Rebenne, A.C. Gonzalez, T.M. Olson, Aqueous chlorination kinetics and mechanism of substituted dihydroxybenzenes, Environ. Sci. Technol. 30 (1996) 2235–2242.

[17] H. Gallard, U.V. Gunten, Chlorination of phenols: kinetics and formation of chloroform, Environ. Sci. Technol. 36 (2002) 884–890.

[18] V.L. Heasley, M.E. Anderson, D.S. Combes, D.S. Elias, J.T. Gardner, M.L. Hernandez, R.J. Moreland, D.F. Shellhamer, Investigations of the structure and reactions of the intermediate in the chlorination of resorcinol, Environ. Toxicol. Chem. 12 (1993) 1653–1659.

[19] P. Patnaik, M. Yang, E. Powers, Phenol-chlorine reaction in environmental water: formation of toxic chlorophenol derivatives, Am. Lab. New 32 (2000) 16.

[20] S.D. Boyce, J.F. Hornig, Reaction pathway of trihalomethane formation from the halogenation of dihydroxyaromatic model compounds for humic acids, Environ. Sci. Technol. 17 (1983) 202–211.

[21] H. Gallard, U.V. Gunten, Chlorination of natural organic matter: kinetics of chlorination and of THM formation, Water Res. 36 (2002) 65–74.

[22] T. Kishino, K. Kobayashi, Relation between toxicity and accumulation of chlorophenols at various pH, and their absorption mechanism in fish, Water Res. 29 (1995) 431–442.

[23] E. Argese, C. Bettiol, G. Giurin, P. Miana, Quantitative structure–activity relationships for the toxicity of chlorophenols to mammalian submitochondrial particles, Chemosphere 38 (1999) 2281–2292.

[24] K. Wagner, S. Schulz, Adsorption of phenol, chlorophenols, and dihydroxy-benzenes onto unfunctionalized polymeric resin at temperatures from 294.15 to 318.15 K, J. Chem. Eng. Data 46 (2001) 322–330.

[25] J.M. Gnaim, R.A. Sheldon, Highly regioslective *ortho*-chlorination of phenol with sulfuryl chloride in the presence of amines, Tetrahedron Lett. 36 (1995) 3893–3896.

[26] C.G. White, Handbook of Chlorination and Alternative Disinfections, Fourth ed., John Wiley & Sons, New York, 1998.