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A Simple and Semi-Empirical Model to Predict THMs Generation in Water Facilities Including pH Effects

Abstract: This work presents a study focused on the development of a simple useful tool to predict the generation of trihalomethanes in drinking water purification systems, using two precursors and trichloromethane as model compounds through a simple chlorine decay model. This work proposed a semiempirical model without adjustable power parameters where fast and slow stages and the effect of pH were included. Despite that the model is not based in a complete kinetic scheme, using the proposed equations it is possible to predict the simultaneous evolution of chlorine and TCM with a set of linear kinetics parameters which characterize the system and will be obtained using simple routine laboratory measurements. The results show that both TCM formation and chlorine decay are strongly dependent on the chemical nature of the model precursor. Although resorcinol and phenol have different reactivity with chlorine and represent different functional groups which are present in natural compounds, the TCM generation appears to be properly described in both cases by the total chlorine consumption. Considering that during the potabilization processes the pH changes, the study of the effects of this variable is very important to achieve the minimization of THMs generation. The pH has a significant effect on the time evolution of chlorine-substituted hydroxybenzene intermediates and therefore on the TCM formation, since the properties of the reacting species are directly affected by the reaction medium for their participation in the different reaction paths. The study of the distribution and selectivity of the intermediate species allowed explaining the results obtained for the kinetics of formation of TCM. The results suggest that in order to understand the effect of pH, the nature of oxidation of HOCl and ClO^-, should be considered simultaneously with the electronegative nature of the precursor compounds. Finally, in terms of minimizing the generation of THM it is important to consider the potential impact of pH changes within the water treatment process and supply and the stages where chlorination may be carried out.

Keywords: chlorination, trihalomethane, potabilization

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Introduction

Since the publication of Rook's pioneering work [1], water chlorination has become associated with the occurrence of chloroform (trichloromethane, TCM). TCM, the main trihalomethane (THM) species is a suspected human carcinogen often detected at high concentration.

Numerous halogenated compounds have been identified and associated with water disinfection using chlorine. They are produced by the interaction of chlorine with natural compounds (Natural Organic Matter, NOM) present in water, known as precursors, mainly humic substances [1, 2]. Despite these recognized disadvantages, for different reasons chlorine is the most commonly disinfecting agent used in water facilities. Furthermore, it is difficult to decrease the dose of chlorine in water treatment processes taking into account the need for a disinfectant residual capacity in the supply system. Studies performed under controlled laboratory conditions, for example, to model the kinetics of THM formation or identify different types of precursors and intermediates of the chlorination reaction, raised the possibility of m-dihydroxybenzenes structures as the main THM precursor fragments in aquatic humic materials. Rook [2] proposed a mechanism of THM formation based on the chemistry of the reaction between chlorine

and resorcinol (R). This study was later extended by Rebenne et al. [3], Arnold et al. [4] and Cimetiere et al. [5]. However, even though resorcinols are quite common DBPs precursors, other functional groups can also participate. In experiments with humic acid, Rook [2] found non-uniform kinetics of THM formation, a fast start followed by a much slower secondary stage. This evidence suggests a dichotomy in the reaction mechanism of both stages. Korshin et al. [6] reported that the differential spectra of chlorinated NOM contain two kinetically and spectroscopically different components. One of these attributable to functional groups that react rapidly with chlorine, and a second one associated with slowly reacting chromophores that arise following the depletion of the fast chromophores. Gallard and von Gunten [7] showed that the rate of THM formation from R is too fast to involve all THM precursors contained in NOM and suggested that slowly reacting THM precursors may consist of monohydroxybenzenes as phenol (P).

Several studies have suggested different kinetic models in order to predict THM formation for specific natural water sources [7–9] and model precursors [10, 11] but the rates of the complex sequential and parallel reaction pathways of the consumption of chlorine are not completely known. Therefore, the development of robust analytical mechanistic kinetic models of THM formation in water supply systems is still a challenge, despite the efforts of various authors to achieve this goal. This has led to the use of empirical reaction kinetic models derived from linear and non-linear statistical regression analysis. However, most of them are heavily dependent on large, expensive to collect and analyze datasets which form the basis of regression analyses [12]. A recent review has established that even in the case of the successful empirical correlations, it is not clear which could be the most easily accessible parameters and, at the same time, the most representative ones to characterize the precursors reactivity, for example, TOC, UV, Color Index [12]. For the chlorination process of ionizable compounds, the pH is expected to affect THM formation. Considering that during the potabilization processes the pH changes, the study of the effects of this variable is very important to achieve the minimization of THMs generation [13].

A rational strategy for developing a semi-empirical model useful to predict the generation of THMs in drinking water purification systems should probably include two stages: (i) the derivation of the equations based on "simple precursors" where fast and slow stages and the effect of pH should be included and (ii) the model validation using analogous processes involving humic material and, finally, the work with natural waters [14].

This work presents a study focused on the development of a useful tool to the THM simulation using two precursors and TCM as model compounds. Through a simple chlorine decay model, a set of constants was obtained using simple laboratory measurements. The model can be considered as a first step to proceed with a validation in analogous processes involving humic materials and natural water.

Methods

Solutions were prepared using high purity compounds (R, Fluka; P, Carlo Erba) and ultra purified water (Osmoion). By further dilution in a buffer (KH_2PO_4/Na_2HPO_4), stock solutions for these compounds were obtained. A NaOCl commercial solution (85 g/L Cl_2, Crisol Lab) was directly diluted with the buffer solution to obtain a stock solution of 1,600 μM Cl^*, which represents the total concentration of chlorine oxidative species ($HOCl+OCl^-$).

Experiments for P (25°C, pH 5, 7, and 10) were conducted in a well-mixed batch reactor (2,000 ml). Special care was taken to ensure complete seal of the system in order to avoid leaks and losses of TCM. Chlorination experiments started when 1,000 ml of NaOCl solution were added to the same volume of stock solutions of P. At fixed time intervals, an aliquot was taken from the reactor in order to make the residual chlorine analysis. Simultaneously, using another aliquot, the reaction was quenched (sodium thiosulfate) to determine P, TCM and chlorinated intermediaries.

Chlorination experiments of R (25°C, pH 5, 7, and 10) were performed in amber glass well-mixed bottles (25 mL) sealed with Parafilm and screw caps. Three reactors were used to perform the determination of chlorine in triplicate. Other three reactors were used for intermediate, TCM and precursor monitoring. Two blank runs without buffer or precursors were made to discard interferences from water or chemical reagents.

The chlorine concentration was monitored by spectroscopic quantification of the triiodide ion (351 nm; Varian Cary 100 UV-Vis); analyses of R, P and Chloro-Phenol Intermediates (ClPs) were performed by HPLC (Waters 1525; LC-18 column; methanol/water/acetonitrile, 50/30/20; 1.0 ml min^{-1}; R: 272 nm and isocratic flow; P and ClPs: 276 and 294 nm, linear gradient flow program). Determination of TCM was performed by

GC-SPME (HP 5090 Series II, ^{63}Ni ECD; ZB50 phenomenex column) following the standard practice for the solid phase micro extraction (SPME) [15] using a 100-μm polydimethylsiloxane (PDMS) fiber; headspace mode was used for sampling. Nitrogen was used as carrier gas (flow 1.0 ml/min); column temperature: 40°C (5 min) and then increased to 160°C (15°C/min); temperature detector and injector: 300 and 250°C. Extractive derivatization coupled to GC-MS (Varian CP-3800 GC, Varian Saturn 2000 MS, VF-5MS column) was applied to the determination of chloro-resorcinol intermediates (ClRs). Using acetic anhydride, resorcinols were transformed into the corresponding esters, which were extracted with high recoveries from the aqueous phase using PDMS fiber. Helium was employed as carrier gas (flow 1.0 ml/min). The injector temperature was 280°C. The column temperature program was 40°C (3 min), heated to 70°C (10°C/min), and finally heated to 250°C (20°C/min) and held for 6 min.

Results and discussion

The chemical reactions chlorine-precursors

Considering that the goal of this paper is to obtain a semi empirical model to predict THM generation in water facilities, a previous experimental work was made to establish the conditions to simulate the real disinfection processes as pre–post chlorination, for example, the residual chlorine. Figure 1 shows an example of the previous assays of chlorination using R and P as precursors, at different experimental conditions.

Although the complete results will be presented and discussed later, several issues arise. Independently of the different time scale, the shape of the curve for the two precursors reflects a non-uniform reaction kinetic, two stages being distinguished in all cases. During the first minutes a rapid chlorine decay was observed followed by a slower secondary stage. This dichotomy in the curve is more marked for resorcinol. The results show that the chlorine decay was affected by the chemical nature and initial concentration of the precursor and the pH. It is interesting to note that the shape of the curves of the TCM generation is consistent with the chlorine decay curves since an initial rapid TCM formation was observed followed by a slower secondary stage. This would indicate an initial fast chlorine consumption for the formation of chlorine-substituted hydroxybenzene intermediates. In both cases, and taking into account the proposals already

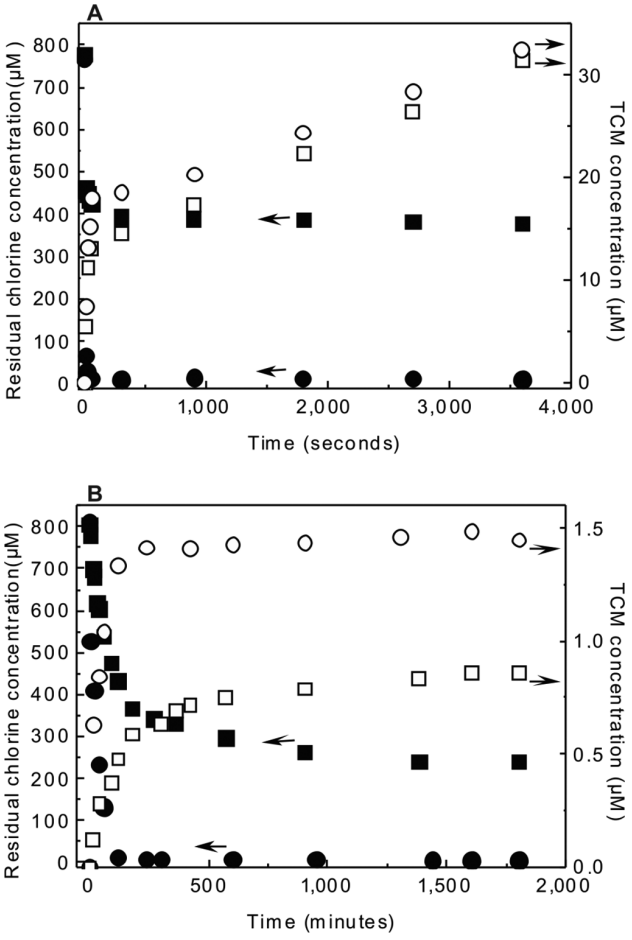

Figure 1 Time evolution of Cl (full symbol) and TCM (open symbol) from chlorination of resorcinol at pH = 10 (A) and phenol at pH = 5 (B), initial concentration of P or R= 53 μM (circle), 160 μM (square), $[Cl^{*,0}]$ = 800 μM.

made by Hua [16], Courtis et al. [17], and Brown et al [12], these results suggest that the evolution of TCM could be represented in terms of chlorine consumption.

Our experiments demonstrated that the decay of precursor and chlorine were faster by increasing the pH value. Moreover, the chlorine consumption per mole of precursor was affected by the pH and chemical nature of the precursor (at pH 5 and 7, a constant value around 9–10 was obtained for R and P, while at pH 10 it decreased to 8 for R and to 6 for P).

A semi empirical modeling of chlorine decay and THM formation

Several models have been proposed to represent the reaction kinetics of chlorine decay, but these mathematical models are unable to predict the short- and long-term

Table 1 Chlorine decay and TCM formation constants of resorcinol (R) and phenol (P).

pH	5		7		10	
Pr	**R**	**P**	**R**	**P**	**R**	**P**
			Cl			
f	0.642	0.715	0.632	0.693	0.475	0.284
$k_{Cl_r^*}$ ($M^{-1}s^{-1}$)	1.986×10^{2}	0.421	1.101×10^{3}	4.312	2.382×10^{3}	1.369×10^{1}
$k_{Cl_s^*}$ (s^{-1})	1.203×10^{-5}	4.527×10^{-7}	3.161×10^{-5}	3.053×10^{-6}	1.236×10^{-5}	3.373×10^{-6}
			TCM			
k_{TCM_r} ($M^{-1}s^{-1}$)	3.489	0.001	5.400×10^{1}	0.019	7.665×10^{1}	0.014
k_{TCM_s} (s^{-1})	2.339×10^{-14}	5.607×10^{-9}	2.255×10^{-14}	3.607×10^{-8}	1.377×10^{-5}	9.235×10^{-8}

Notes: We tested the statistical goodness-of-fit using the following tools: sum of squares due to error (SSE), *R*-square Adjusted, *R*-square, and Root mean squared error (RMSE). The maximum dispersion in all cases was less than 10%.

THM formation as a function of chlorine consumption. In this sense, it seems important to take into account that along the stages of water purification and distribution, rapid steps impact heavily on the plant itself (e.g., pre-chlorination) while the slow stages will become important in the supply systems.

In the first part of this work, we analyzed the model recently modified by Chang et al. [11] for the evolution of chlorine, which proposed the existence of two steps, one fast and one slow, that occur in parallel:

$$\text{reactive sites}_r + Cl^* \rightarrow \cdots \rightarrow \text{TCM (rapid reaction)} \quad [1]$$

$$\text{reactive sites}_s + Cl^* \rightarrow \cdots \rightarrow \text{TCM (slow reaction)} \quad [2]$$

Facing the complexity of obtaining kinetic expressions based on mechanisms and taking into account precedents and contributions from other authors [18, 19], Chang et al. [11] proposed to differentiate the rates of both stages based on global and semi-empirical approximations of orders one and two, respectively:

$$\frac{d[Cl_r^*]}{dt} = -k_{Cl_r^*}[Cl_r^*]^2 \quad \text{subscript r denotes rapid} \quad [3]$$

$$\frac{d[Cl_s^*]}{dt} = -k_{Cl_s^*}[Cl_s^*] \quad \text{subscript s denotes slow} \quad [4]$$

The following expression was obtained by Chang et al. [11]:

$$[Cl^*] = [Cl^{*,0}]\left[\frac{f}{f[Cl^{*,0}]1k_{Cl_r^*}t + 1} + (1-f)\exp[-k_{Cl_s^*}t]\right] \quad [5]$$

where $k_{Cl_r^*}$ and $k_{Cl_s^*}$ are the apparent rate constant of chlorine decay and f represents the fraction of the Cl^* attributed to the rapid reaction.

Using eq. [5], the fit of the set of kinetic constants with our experimental data shows an excellent adjustment (see Table 1 and Figure 2).

Taking into account the precise correspondence of eq. [5] with our experimental data and the qualitative similar trend observed for the time evolution of TCM

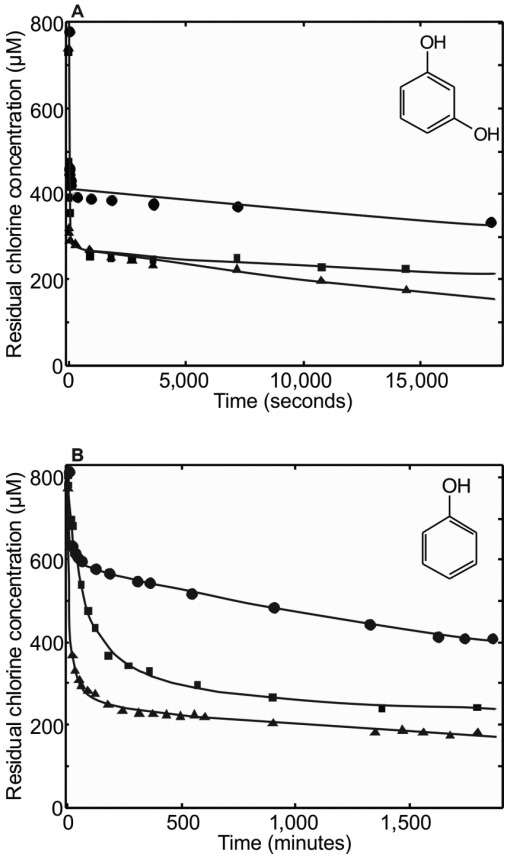

Figure 2 Chlorine decay data of (A) Resorcinol and (B) Phenol fitted to the parallel second- and first-order reaction model. Data points are experimental values: pH = 5 (square), pH = 7 (triangle), and pH = 10 (circle). The solid lines are the model fit data.

with respect to Cl^*, and considering the contributions of Hua [16], we propose equivalent expressions to represent TCM evolution:

$$\frac{d[TCM_r]}{dt} = k_{TCM_r}\left[Cl_r^*\right]^2 \quad [6]$$

$$\frac{d[TCM_s]}{dt} = k_{TCM_s}\left[Cl_s^*\right] \quad [7]$$

These equations should allow to link (see below) the potential generation of TCM with the evolution of the concentration of Cl^*. Combining eqs. [3–4] and [6–7] we can associate the generation of TCM with Cl^* consumption:

$$\frac{d[TCM_r]}{d\left[Cl_r^*\right]} = -\frac{k_{TCM_r}}{k_{Cl_r^*}} \quad [8]$$

$$\frac{d[TCM_s]}{d\left[Cl_s^*\right]} = -\frac{k_{TCM_s}}{k_{Cl_s^*}} \quad [9]$$

To separate the contributions of Cl^* to the fast and slow reactions, we can define the following parameters: $\eta_r = \frac{[TCM_r]}{[Cl_r^*]}$ and $\eta_s = \frac{[TCM_s]}{[Cl_s^*]}$ which represent a virtual "yield" of Cl^* to TCM formation for each of the reaction "paths". Then,

$$\left[Cl_r^*\right]\frac{d\eta_r}{d\left[Cl_r^*\right]} + \eta_r = -\frac{k_{TCM_r}}{k_{Cl_r^*}} \quad [10]$$

$$\left[Cl_s^*\right]\frac{d\eta_s}{d\left[Cl_s^*\right]} + \eta_s = -\frac{k_{TCM_s}}{k_{Cl_s^*}} \quad [11]$$

when $\eta_r = \eta_s = 0$, $\left[Cl_r^{*,0}\right] = f\left[Cl^{*,0}\right]$, and $\left[Cl_s^{*,0}\right] = (1-f)\left[Cl^{*,0}\right]$, where superscript (0) represents the initial condition.

Then, from eqs. [8–11]

$$[TCM_r] = \frac{k_{TCM_r}}{k_{Cl_r^*}}\left(f\left[Cl^{*,0}\right] - \left[Cl_r^*\right]\right) \quad [12]$$

$$[TCM_s] = \frac{k_{TCM_s}}{k_{Cl_s^*}}\left((1-f)\left[Cl^{*,0}\right] - \left[Cl_s^*\right]\right) \quad [13]$$

Finally, considering that $[TCM] = [TCM_r] + [TCM_s]$ we can obtain

$$[TCM] = \left\{\frac{k_{TCM_r}}{k_{Cl_r^*}} f\left[Cl^{*,0}\right]\left[1 - \frac{1}{f\left[Cl^{*,0}\right]k_{Cl_r^*}\,t + 1}\right]\right\} + \left\{\frac{k_{TCM_s}}{k_{Cl_s^*}}(1-f)\left[Cl^{*,0}\right]\left[1 - \exp(-k_{Cl_s^*}t)\right]\right\} \quad [14]$$

The simultaneous solution of eqs. [5] and [14] represents the time evolution of Cl^* and TCM, in terms of a simple and easily measurable variable as Cl^*, with a set of linear kinetic constants but without empirically adjustable power parameters.

Eqs. [5] and [14] are linked through parameters $k_{Cl_r^*}$, $k_{Cl_s^*}$, and f, which could be obtained experimentally. Despite the fact that eq. [14] does not arise from a complete "kinetic model," it is clear that it contains an implicit assumption that the "reactivity" of precursors can be modeled from the evolution of Cl^* concentration. This means that it represents a mathematical tool to model and predict the generation of THMs, using a set of linear parameters which characterize the "reactivity" of water. The numerical simulation of eqs. [5] and [14] will be compared with experimental data using a nonlinear regression optimization program (Statistics Toolbox function-nlinfit, Matlab) to obtain the optimal values of the kinetic parameters. The values of the kinetic constants are shown in Table 1, whereas Figures 2 and 3 present the

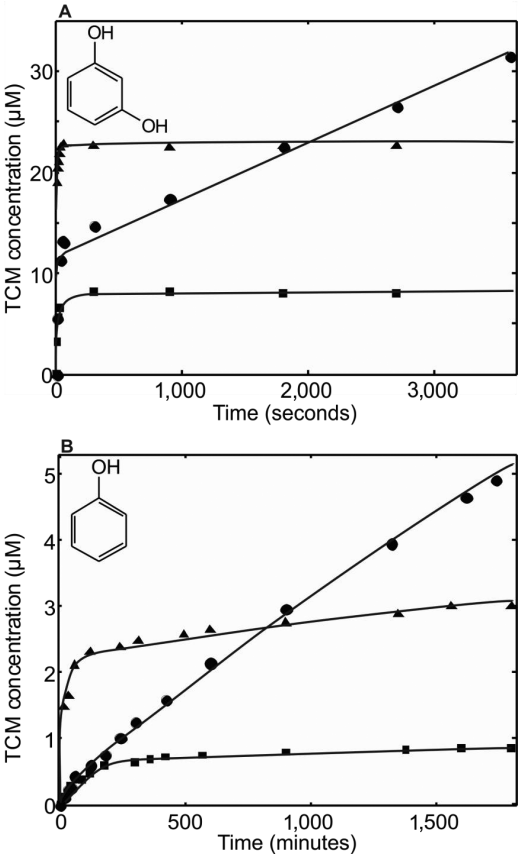

Figure 3 TCM formation data of (A) Resorcinol and (B) Phenol fitted to the parallel second- and first-order reaction model. Data points are experimental values: pH = 5 (square), pH = 7 (triangle), and pH=10 (circle). The solid lines are the model fit data.

comparison of the simulation and experimental data. This would seem to indicate that a semi-empirical model to predict THMs generation in water purification systems that simultaneously includes the fast and slow stages could be directly linked with a simple measured variable such as Cl^* concentration.

The pH effect and the distribution of the intermediate species

The strong dependence between the pH and the rates of chlorine decay and TCM generation is presented in Figure 4. The values of $k_{Cl_r^*}$ from both precursors rise linearly over the entire pH range studied (Figure 4A). The largest $k_{Cl_r^*}$ at high pH values is consistent with the progressive increase in the concentration of chlorine-substituted hydroxybenzene intermediates from pH 5 to 10 (see below). Unlike the preceding case, the slow constants $k_{Cl_s^*}$ show a maximum in the pH range 7–8 for R and 8–9.5 for P (Figure 4B). The shape of

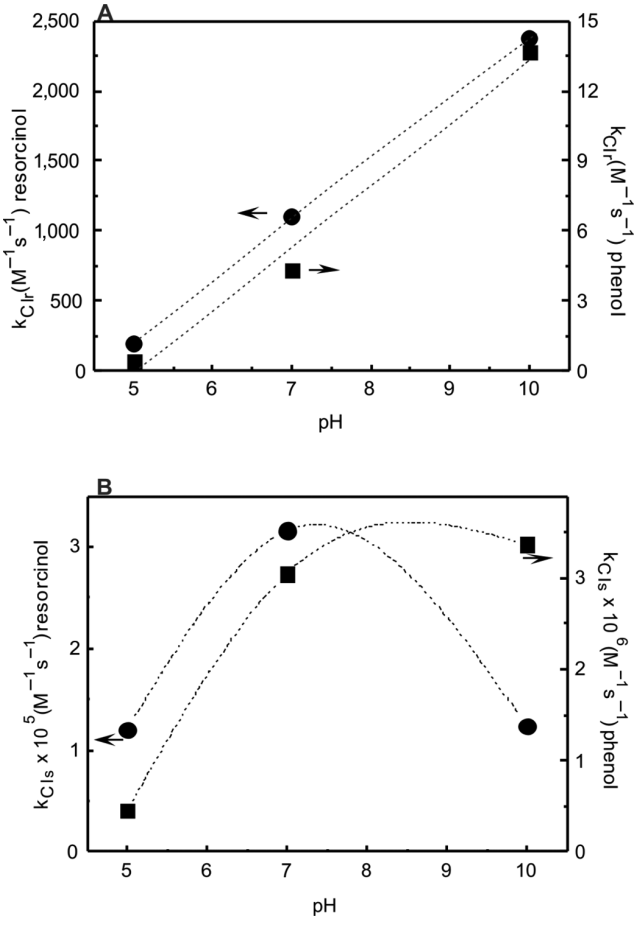

Figure 4 pH-dependence of the apparent rate constant for rapid (A) and slow (B) chlorine decay from resorcinol (circle+dash) and phenol (square+dash).

the rate profile can be explained by simultaneously considering the speciation of both chlorine and precursor species and the reaction of chlorine with ionized and un-ionized forms of the mentioned precursors. A greater reactivity of m-dihydroxybenzene R compared with mono-hydroxybenzene P is indicated by the highest values of $k_{Cl_{r,s}^*}$ in the two stages of the resorcinol chlorination.

From Table 1 it can be observed that approximately 60–70% of the chlorine consumption was attributed to the rapid reaction (f) at pH 5 and 7, while at pH 10 only 30–47% was responsible for its disappearance. The greatest f value may be due to the simultaneous existence of oxidation and substitution reactions only in the acidic and neutral media.

Moreover, the simultaneous analysis of pH-dependence of $k_{TCM_{r,s}}$ values and the time distribution of Chloro-Phenol Intermediates (ClPs) (Figure 5) allowed the following interpretations:

(i) The lower value of k_{TCM_r} at pH 5 could be due to the favored existence of the oxidation reaction in acidic medium over the chlorine substitution reaction [20]. The existence of parallel oxidation reactions competing with the formation of TCM reactions is demonstrated by the lack of agreement between the values of total phenols concentration TPs (P plus ClPs) and the initial concentration of P;

(ii) The higher 2,4,6-trichlorophenol (TCP) concentration in neutral medium for the first stage can be explained by an increase of chlorine substituted products with the pH value, while that of concentration of oxidation products decreases [20]. This results, coupled with the high value of the apparent rate constant for dichlorophenol initial chlorination at pH 7 [21], directly results in the highest value of k_{TCM_r};

(iii) The fundamental cause of the slow rate of TCM formation in the first stage at pH 10 is the slow rate of DCP chlorination in alkaline medium. The concentration of 2-monochlorophenol plus 4-monochlorophenol (MCP) was higher in acidic and neutral media than in alkaline medium, and has been almost completely converted to 2,6-dichlorophenol plus 2,4-dichlorophenol (DCP) at pH 10. This is consistent with the behavior of the apparent rate constant of initial chlorination of P and MCP reported by Gallard and von Gunten [10], which increased by increasing the pH from 5 to 10. The DCP concentration was higher in alkaline medium, apparently because the oxidation nature of ClO^- is limited, while

the electronegative nature of P and MCP increases with the increase of pH, which consequently favors the chlorine substitution reaction mainly. The accumulation in the first stage of DCP generated at pH 10, probably occurs because the rate of conversion to TCP and ring-opened products is slower in a strongly alkaline medium, as indicated by the lower amount of TCP and the higher TPs concentration at pH 10.

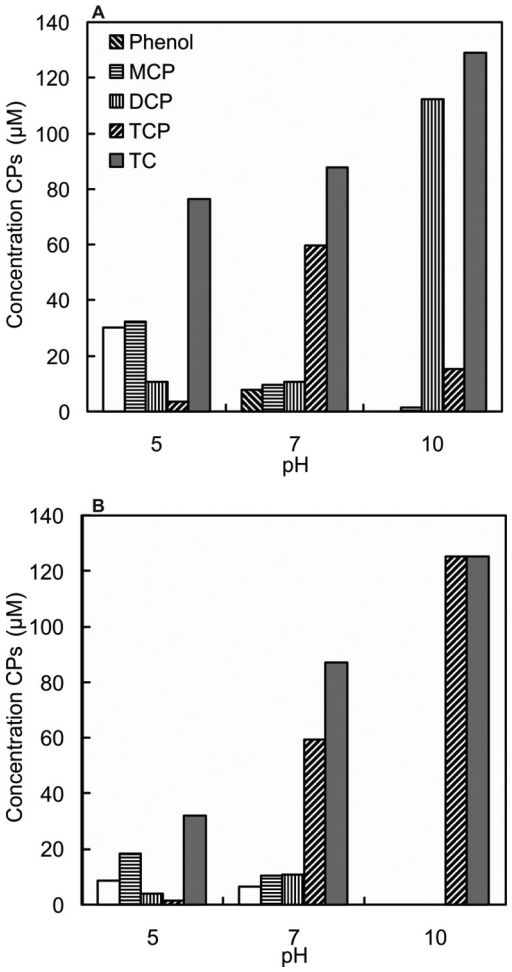

Figure 5 Distribution of the concentration of P and ClPs in acidic, neutral and alkaline media. Reaction time: (A) 15 minutes and (B) 600 minutes.

For the second stage of the phenol chlorination, k_{TCM_s} and TCP concentrations were higher at pH 10 compared with the other pH conditions studied. This indicates that although the rate of conversion of DCP to TCP and ring-opening products is slow at pH 10 for the first stage, the alkaline medium favors the evolution of the reaction of chlorinated intermediaries formation by increasing the stability of carbanions, leading to increase the rate and formation of long-term TCM.

The identified chloro-resorcinol intermediates (ClRs) were 2 and 4-chlororesorcinol, 4,6 and 2,4-dichlororesorcinol, 2,4,6-trichlororesorcinol, and 2,2,4,4,6-pentachloro-5-cyclohexene-1,3-dione. The behavior of the apparent rate constants for rapid TCM formation from the resorcinol chlorination (k_{TCM_r}) shows the higher reactivity of this precursor compared to that of phenol. The value of k_{TCM_r} increased significantly with increasing pH from 5 to 10, according to the progressive increase in the ClRs concentration (data not shown). In the second stage, small values of k_{TCM_s} indicate that the TCM formation is carried out mainly in the first stage of the resorcinol chlorination.

Conclusion

In order to develop a simple useful tool to predict the generation of THMs in potabilization processes, this work proposed a semiempirical model without adjustable power parameters. Despite the fact that the model is not based in a complete kinetic scheme, using the proposed equations it is possible to predict the simultaneous evolution of chlorine and TCM with a set of linear kinetic parameters which characterize the system.

The results show that both TCM formation and chlorine decay are strongly dependent on the chemical nature of the model precursor. Although resorcinol and phenol have different reactivity with chlorine, and represent different functional groups which are present in natural compounds, TCM generation appears to be properly described in both cases by the total chlorine consumption.

However, in addition to the observations made in agreement with other authors, it is interesting to note that the pH has a significant effect on the time evolution of chlorine-substituted hydroxybenzene intermediates and therefore on TCM formation, since the properties of the reacting species are directly affected by the reaction medium for their participation in the different reaction paths. The study of the distribution and selectivity of the intermediate species allowed explaining the results obtained for the kinetics of formation of TCM. The results suggest that in order to understand the effect of pH, the nature of oxidation of HOCl and ClO^- should be considered simultaneously with the electronegative nature of the precursor compounds.

Finally, in terms of minimizing the generation of THM, it is important to consider the potential impact of pH changes within the water treatment process and supply, and the stages where the chlorination can be made.

Acknowledgements: Thanks are given to Universidad Nacional del Litoral and CONICET for financial help and the doctoral fellowships of M.B.G. The technical assistance of Silvina Addona and Juan C. Andini is gratefully appreciated.

Notation

TCM	Trichloromethane
THM	Trihalomethane
NOM	Natural organic matter
R	Resorcinol
P	Phenol
Cl^*	Total concentration of chlorine oxidative species ($HOCl+OCl^-$)
ClPs	Chloro-phenol intermediates
ClRs	Chloro-resorcinol intermediates
f	Fraction of the Cl^* attributed to the rapid reaction
k	Apparent rate constant
MCP	2-monochlorophenol plus 4-monochlorophenol
DCP	2,6-dichlorophenol plus 2,4-dichlorophenol
TCP	2,4,6-trichlorophenol
TPs	Phenol plus Chloro-phenol intermediates

Greek Letters

η	virtual "yield" of Cl^* to TCM

Subscripts

TCM	Relative to trichloromethane
Cl^*	Relative to total concentration of chlorine oxidative species ($HOCl+OCl^-$)
r	Denotes rapid reaction
s	Denotes slow reaction

Superscripts

0	Represents initial condition

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