Iron corrosion as a factor contributing to haloacetic acids formation in the distribution system: experimental assessment and model development

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ABSTRACT

In this paper, the results of an experimental investigation into four potential explanatory factors (i.e. Fe(II) ions, pH, phosphate and reaction time) with different levels, and their influence in the formation of haloacetic acids (HAAs) in water samples are presented. This study revealed that Fe(II) ions ($p = 0.0001$), phosphate based corrosion inhibitor ($p = 0.01$) and pH ($p = 0.003$) were the main significant factors for HAAs formation. A change in Fe(II) ions concentration from 0 to 3 mg/L, and PO_4 dosage from 0 to 1.5 mg/L, decreased HAAs formation by more than 50 and 14% respectively. In contrast, HAAs formation was observed to increase 7.92% with the increase in pH values from 6.5 to 8.5 in the same reaction systems. Considering all of the significant factors, a predictive model for HAAs formation was developed using 40 experiments. The adequacy of the developed model was checked statistically using numerical and graphical diagnostics. The model was found to be statistically significant, and the lack of fit test was found to be insignificant. An independent data set, obtained from HAAs formation study using the natural water samples collected from three main water treatment plants in Nova Scotia, Canada, was used to validate the model.

Key words | corrosion inhibitors, Fe(II) ion, haloacetic acids, model, pH, phosphate

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INTRODUCTION

According to an American Water Works Association (AWWA) survey in 1996, it has been reported that the majority of distribution system pipes are composed of iron materials: cast iron (38%), ductile iron (22%), and steel (5%) (AWWA 1996). The interior surface of an unlined cast iron water distribution pipe is typically exposed to an oxidizing environment that causes corrosion. Hozalski *et al.* (2008) have reported the reduction of pipe wall as a zero-valent iron (Fe°); and correspondingly when (Fe°) ions come in contact with water, Fe^{2+} ions start to appear in water through iron corrosion releasing electrons ($Fe^o \rightarrow Fe^{2+} + 2e^-$) (Lin *et al.* 2001). Oxidants such as oxygen and free chlorine (HOCl and OCl⁻) or monochloramine (NH_2Cl) are available in drinking water to accept these released electrons ($O_2 + 4H^+ + 2e^- \rightarrow 2H_2O$; $HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$; $NH_2Cl + 2H^+ + 2e^- \rightarrow Cl^- + NH_4^+$) (Folkes *et al.* 1995;

Vikesland & Valentine 2002; Sarin *et al.* 2004a). Consequently, the concentration of Fe^{2+} ions in drinking water distribution systems increases under these corrosion conditions (Kirmeyer *et al.* 2000). Therefore, it has been suggested that Fe(II) ions are being added continuously in drinking water distribution systems (Sarin *et al.* 2004b). Previously, a laboratory study revealed that the release rate of Fe(II) ions ranges from $0.003 \, mg \, m^{-1} \, h^{-1}$ in iron pipe loops with flowing oxygenated water to $0.01 \, mg \, m^{-1} \, h^{-1}$ under stagnant anoxic conditions (Sarin *et al.* 2004b). However, corroded iron pipes are the main source of aqueous Fe(II) ions in distribution systems. The concentration of Fe(II) ions was found to be 7.2 mg/L, dry weight basis in a center sample; and 17.1 mg/L, dry weight basis in a side sample of 40–50-year-old iron pipe collected from the

distribution system in Melbourne, Australia (Lin *et al.* 2001).

Several laboratory studies have reported that Fe^o is a robust reductant that reduces different types of halogenated solvents including chlorinated by-products: haloacetic acids (Zhang *et al.* 2004; Hozalski *et al.* 2008), carbon tetrachloride (Matheson & Tratnyek 1994), trichloro(nitro)methane (chloropicrin) (Pearson *et al.* 2005), 1,1,1-trichloroethane (Fennelly & Roberts 1998), and pentachlorophenol (Kim & Carraway 2000). Consequently, Chun *et al.* (2005) have discovered the susceptible reduction of some halogenated disinfection by-products (DBPs) (trichloro-nitromethane, trichloroacetonitrile, 1,1,1-trichloropropanone, and trichloroacetaldedyde hydrate) by Fe(II) ions associated with the synthetic main iron corrosion scales (i.e. magnetite and goethite). Fe(II) ions can also be a cause of unpleasant metallic taste and rusty color in water, when dissolved iron is found to be greater than the United States Environmental Protection Agency (USEPA) recommended level 0.3 mg/L (Cham *et al.* 2010).

Chlorine has been used most widely and effectively as a secondary disinfectant since 1913, and has helped to eliminate most waterborne diseases (i.e. typhoid and cholera) in developed countries. Approximately 90% of the water supply systems in Canada use chlorine for disinfection purposes (Health Canada 2009). However, increased concentration of chlorine would be expected to increase corrosion (Eisnor & Gagnon 2004), and DBP formation in drinking water distribution systems (Sadiq & Rodriguez 2004a). Therefore, it has been hypothesized that these corrosion scales and Fe(II) ions react with free chlorine and disinfectant by-products in drinking water distribution systems. On the other hand, phosphate based corrosion inhibitors are an alternative additive in drinking water for mitigating metal corrosion protection, red water control, and turbidity reduction (Maddison *et al.* 2001; Rahman & Gagnon 2014). Unfortunately, published research concerning the reactivity of phosphate based corrosion inhibitors in the formation or reduction of HAAs in presence and absence of soluble Fe(II) ions is not well established yet.

The formation of HAAs and their species distribution is a complex phenomenon, and depends on several factors including the characteristics of water, treatment procedures, and water distribution pipe materials and their associated corrosion by-products (Rahman & Gagnon 2013). Previous studies have mostly reported on both the formation of HAAs and their reduction in full scale distribution systems (Singer *et al.* 1995; Arora *et al.* 1997; Williams *et al.* 1997; Pecher *et al.* 2002; Hozalski *et al.* 2008; Arnold *et al.* 2010). In addition to the reported data on HAAs formation study, some models considering the most significant factors (i.e. pH, reaction time, temperature, and different concentration of chlorine, bromine and dissolved organic matter (DOM)) for predicting the formation of HAAs in real distribution systems have been proposed (Sung *et al.* 2000; Clark *et al.* 2001; Shimazu *et al.* 2005; Uyak *et al.* 2007; Zhang *et al.* 2011). Previously excellent reviews of the various models for DBP prediction were reported in the literature (Amy *et al.* 1987; Sadiq & Rodriguez 2004b). Nevertheless, the development of HAAs formation models in the presence of soluble Fe(II) ions in water, and their relationship with phosphate based corrosion inhibitors for the different pH values and different stagnation times are very limited in the existing literature.

In this present study, the effect of four potential explanatory factors including pH, Fe(II) ions, phosphate based corrosion inhibitor and reaction time in the formation of HAAs were investigated in synthetic water under the laboratory conditions. The goal of this study was to investigate the most significant factors as well as their rank influencing HAAs formation for a range of water quality parameters. This was accomplished using a 2^4 full factorial design approach at a 95% confidence level, which was used to seed the development of a mathematical model. Graphical and numerical diagnostic methods were used to evaluate the model's adequacy. To validate the developed model, an independent set of data was used to assess the effectiveness of the fitted model equation.

EXPERIMENTAL SECTION

Batch experiments

Bench scale experiments were conducted for HAAs formation analysis in $NaHCO_3$ (assay: 100%, Fisher Scientific, USA) buffered synthetic water samples consisting of differing characteristics. Humic acid (HA) (Technical

grade, Sigma Aldrich, USA) was used as a source of DOM in synthetic water. The detailed method for preparation of purified HA stock solution is described elsewhere (Yang & Shang 2004; Li & Zhao 2006). However, a required amount of purified HA stock solution was employed as the surrogate for DOM (2.85 mg/L as dissolved organic carbon (DOC)) in synthetic water samples. The required pH values in the buffered water samples were adjusted using 0.5N HCl (assay: 36.5–38%, Fisher Scientific, Canada) and 0.5 N NaOH (assay: 100%, Fisher Scientific, Canada) solution. Zinc ortho-polyphosphate (Virchem 937, Carus Chemical Corporation, USA) was used as a source of phosphate considering corrosion inhibitor. The water samples were chlorinated (chlorine to carbon mole ratio of 0.79), and $FeSO_4.7H_2O$ (assay: 100%, Fisher Scientific, USA) was added to get the required amount of Fe(II) ions in the solutions. A comprehensive study was conducted in presence of different dosages of Fe(II) ions (0.35, 0.7, 1.5,

2.0 and 3 mg/L), phosphate ions (0 and 1.5 mg/L), different pH values (6.5 and 8.5), and at different reaction times (3.5, 24, 48, 84 and 130 h).

However, the solutions were mixed properly, and transferred into headspace-free 250 mL chlorine demand free serum bottles (reactor). The bottles were capped immediately using a PTFE (polytetrafluoroethylene) screw cap with teflon-lined septa. Finally the serum bottles (reactors) were wrapped with aluminum foil to prevent photochemical reaction, and kept in the dark for the designated reaction times. After each designated reaction period, the water samples were collected into headspace-free 25 mL glass vials with ammonium chloride. All samples were refrigerated at 4 °C not more than 2 weeks prior to extraction. In addition to the comprehensive study, a 2^4 full factorial design study was conducted for HAAs formation study with the typical water quality parameters (Table 1). Consequently, all HAA samples were extracted following liquid-liquid extraction

Table 1 | Matrix of the experimental study for a 2^4 full factorial design with center point approach for HAAs formation in synthetic water samples

Exp. No.	Factors				Response, HAAs formation (μg/L)			
	Fe(II) (A), (mg/L)	pH (B)	PO₄ (C), (mg/L)	Time (D), (h)	Response 1	Response 2	Average	St dev.
1	0	6.5	0	3.5	78.87	83.75	81.31	3.45
2	3	6.5	0	3.5	27.76	28.43	28.095	0.47
3	0	8.5	0	3.5	75.56	74.95	75.255	0.43
4	3	8.5	0	3.5	86.67	73.51	80.09	9.31
5	0	6.5	1.5	3.5	64.12	74.74	69.43	7.51
6	3	6.5	1.5	3.5	15.13	16.93	16.03	1.27
7	0	8.5	1.5	3.5	61.12	50.48	55.8	7.52
8	3	8.5	1.5	3.5	26.51	31.91	29.21	3.82
9	0	6.5	0	24	75.51	81.49	78.5	4.23
10	3	6.5	0	24	29.13	29.39	29.26	0.18
11	0	8.5	0	24	80.16	83.18	81.67	2.14
12	3	8.5	0	24	80.07	71.16	75.615	6.30
13	0	6.5	1.5	24	75.83	78.55	77.19	1.92
14	3	6.5	1.5	24	17.25	17.35	17.3	0.00
15	0	8.5	1.5	24	84.74	66.15	75.445	13.15
16	3	8.5	1.5	24	33.85	37.72	35.785	2.74
I	1.5	7.5	0.75	10.5	61.12	52.12	56.62	6.36
II	1.5	7.5	0.75	10.5	50.48	45.78	48.13	3.32
III	1.5	7.5	0.75	10.5	37.72	40.3	39.01	1.82
IV	1.5	7.5	0.75	10.5	67.57	64.23	65.9	2.36

procedure, and HAA concentrations were quantified by gas chromatography (Varian, CP 3800 Gas Chromatography) with an electron capture detector (GC/ECD) according to USEPA Method 552.2 (USEPA 1995).

Subsequently, post filtered water samples collected from three major water treatment plants in Halifax, Nova Scotia: (1) JD Kline Water Supply Plant, (2) Lake Major Water Supply Plant and (3) Bennery Lake Water Supply Plant were used for HAAs formation study in presence of different dosages of Fe(II) ions and phosphate, at different pH values and reaction times. The results of this study were followed to validate the developed HAA prediction model equation. The water quality parameters for the three water supply plants are presented in Table 2.

Experimental design and data analysis

A 2^4 full factorial design approach was followed to evaluate the importance and interaction of the Fe(II) ions, pH values, phosphate dosages and reaction times in the formation of HAAs. Four experiments were carried out at the center point level, for estimation of experimental error. The range and levels of the studied variables for this study are presented in Table 1. The statistical analysis of the experimental data was performed by a windows version program Minitab® 16 (MINITAB Inc., State College, Pennsylvania, USA). The analysis provided relevant statistical parameters including

the F-test associated with probability $p(F)$, and determination of the coefficient, r^2. The statistical significance of the regression coefficient was determined by the Student t-test associated with probability $p(t)$. The Fisher's test was followed for determining the model equation and the proportion of the variance explained by the model. It was given by the multiple coefficient of determination, r^2. The predicted values of HAAs were compared with the measured values in accordance with the following equation (Equation (1)). It should be noted that the criterion of model fitness is met if a predicted value falls within ±20 percent (%) of the measured values

$$\text{Absolute model deviation} = \left[\frac{\text{Predicted value} - \text{Observed value}}{\text{Observed value}}\right] * 100 \qquad (1)$$

RESULTS AND DISCUSSION

A methodical investigation was conducted to determine the effects of Fe(II) ions and other factors in the formation of HAAs, and their speciation in different reaction systems. Bromine was not present significantly in the studied water samples. As a result, the formation of major brominated species was found to be below the detection limit in most

Table 2 │ Raw and treated water quality for J. Douglas Kline (JDK), Lake Major (LM) and Bennery Lake (BL) water supply plant (WSP)

Parameter[a]	JDK-WSP[b] (Pockwock)		LM-WSP[a] (Lake Major)		BL-WSP[a] (Bennery Lake)	
	Raw Water	Treated Water	Raw Water	Treated Water	Raw Water	Treated Water
pH (unit)	5.6	7.4	5.4	7.3	6.1	7.3
Alkalinity (as $CaCO_3$)	< 1.0	19.0	< 1.0	14.5	< 5.0	45.0
TOC[c]	2.7	1.9	4.0	1.5	4.2	2.0
Iron (Total)	< 0.063	< 0.05	0.16	< 0.02	0.23	< 0.05
Chloride	6.5	9.0	6.0	8.0	8.0	11.5
Chlorate	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.70
Chlorite	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
HAA_5 (avg.)	< 0.005	0.062	< 0.005	0.061	–	0.072
THMs[d] (avg.)	–	0.073	–	0.089	< 0.001	0.080

[a]Unit: milligrams per liter unless shown otherwise.
[b]Source: Halifax Regional Water Commission (2011).
[c]Total organic carbon (TOC).
[d]Trihalomethanes (THMs).

of the cases throughout the study. Therefore, major brominated species were not included in the 'Results and discussion' section. Nevertheless, the effects of different factors studied are presented below.

Effect of Fe(II) ions and reaction time

To understand the effect of Fe(II) ions in the formation of HAAs, different dosages of ferrous iron were added into the buffered synthetic water samples having pH 6.5, DOC 2.85 mg/L and chlorine to carbon mole ratio of 0.79. This bench scale study was conducted for the different reaction periods ranging from 3.5 to 130 h. This study revealed that in the presence of 0.35 mg/L Fe(II) ions, the formation of HAAs was significantly reduced (41.1 to 51.9%) compared with the control water system for the studied reaction periods ranging from 3.5 to 130 h respectively (Figure 1). This study also illustrated that the reduction in HAAs formation increased gradually, from 41.5 to 73.1% reduction, with the increase in Fe(II) ions concentrations (0.3 to 3 mg/L) in solution. This finding is consistent with the reported results by numerous studies (Amonette *et al*. 2000; Pecher *et al*. 2002; Chun *et al*. 2005; Lee *et al*. 2008), which have mentioned that Fe(II) ions bound with iron oxide surface (i.e. magnetite, goethite) accelerate the reduction rates of various organic compounds and halogenated by-products. Lee *et al*. (2008) have reported that the degradation rate for TCNM (trichloronitromethane), a non-regulated DBP, depends on water-

soluble iron in water systems. Recall that Fe(II) is a strong reductant (Arnold *et al*. 2010); and when the Fe(II) ions concentration is increased, it increases the reactive surface area, via oxidation of Fe(II) to Fe(III) by residual disinfectants along with other oxidants. Numerous studies have reported that free chlorine is used up preliminarily by iron oxides; therefore, it has been suggested that less free chlorine is available to react with DBP precursors to form DBPs (Zhang & Andrews 2012). Consequently, the bench scale experiments showed that the formation of HAAs was lower in the presence of Fe(II) ions compared with the control water systems. Thus, HAAs formation was decreased gradually with the increase in Fe(II) ions concentration in the water samples (Figure 1).

The major portion of HAAs formation in all samples was observed at the initial 3.5 h of the reaction period (Figure 1). However, the formation of HAAs was monitored up to 130 h (5.5 days) of the reaction periods. It was found that HAAs concentrations in control water systems were gradually and slightly increased with the increase in reaction times. Conversely, HAAs formation appeared relatively constant for the different reaction periods in the presence of different dosages of Fe(II) ions in solutions. This finding was in agreement with the results reported by Zhang & Andrews (2012), who conducted batch tests in control water systems, and in the presence of iron coupons. They observed that HAAs formation stayed constant after the reaction period of 24 h in the presence of iron coupons. Statistical analysis (two-way analysis of variance (ANOVA) test) for this study in the formation of HAAs data revealed that Fe(II) ions significantly ($p < 0.001$) reduced HAAs formation at a 95% confidence level. The results of this study suggested that the presence of ferrous iron in solution changed the reactivity between chlorine and DOM, which led to a net decrease in HAAs formation. Conversely, the ANOVA test revealed that the reaction time was not statistically significant ($\alpha = 0.05$, $p > 0.05$) for the change in HAAs formation at the different dosages of Fe(II) ions presented in solution.
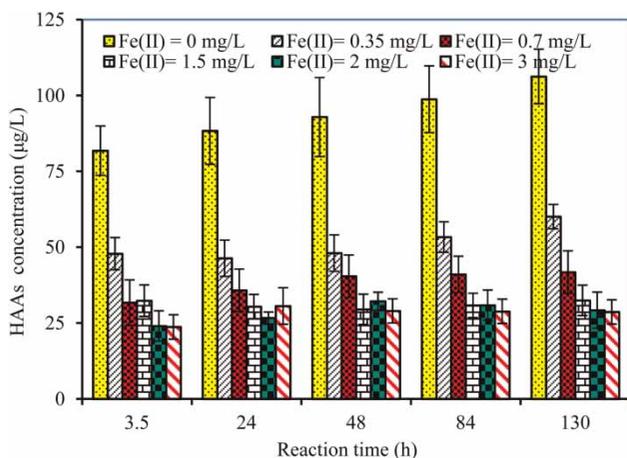
Effect of pH

Typical pH value in drinking water distribution systems has been reported to be 6.5 to 9 (Chun *et al*. 2005). Therefore, this study was conducted at pH 6.5 and 8.5, for chlorine

Figure 1 │ Effect of Fe(II) ions concentration and reaction time on HAAs formation in synthetic water at pH 6.5, chlorine to carbon mole ratio of 0.79 and 21 ± 1 °C temp.

to carbon mole ratio of 0.79 and reaction period of 24 h in four different reaction systems. This study revealed that in the control water systems (in absence of Fe(II) ions and PO_4), with the changes in pH values from 6.5 to 8.5, the average formation of HAAs was not changed significantly (Figure 2). Conversely, this study revealed that in the presence of 3 mg/L Fe(II) ions in solution, the changes in pH values from 6.5 to 8.5, led to a 2.5-fold increment for HAAs formation in water samples following the same reaction conditions. The results of this study were in agreement with the research by Liu et al. (2011), who indicated that in the presence of ferric iron during chlorination, solution pH had an obvious impact on the formation and distribution of DBPs. Nevertheless, this study revealed a similar trend to increase HAAs formation significantly for the changes in pH values from 6.5 to 8.5 in the presence of a phosphate based corrosion inhibitor (1.5 mg-PO_4/L) associated with Fe(II) ions (3 mg/L) in solution (Figure 2). The influence of pH on the formation and distribution of HAAs in the iron water system could be affected by the following possible reasons: (1) at a higher pH level, the dissolved metal ions could directly enhance chloride ions ($OCl^- \rightarrow O_2 + Cl^-$, Gray et al. 1977), (2) with the increase in pH value from 6.5 to 8.5, Fe(II) oxidation significantly increases to generate Fe(III) oxides (Davidson & Seed 1983), (3) Fe(III) oxides adsorb DOM profoundly compared to Fe(II) oxides

(Rahman et al. 2013), and (4) Fe(III) oxides interaction with DOM increases the number of DOM reactive sites for chlorine attack as well as modifying the DOM characteristics (Hassan et al. 2006). Therefore, the results of this study might have implications for understanding the fact that pH change in drinking water distribution systems not only affects the Fe(II) ions oxidation but also has an impact on the formation of HAAs as well as affecting the reactivity between DOM and chlorine (Liu et al. 2011). However, HAAs formation was observed to be similar in control water, and phosphate (1.5 mg/L) water systems for the pH values of 6.5 and 8.5.

This study revealed that in control water systems, dichloroacetic acid (DCAA) formation was favored for a high pH value of 8.5 but the adverse trend was observed for the formation of trichloroacetic acid (TCAA). Figure 2 demonstrates that TCAA formation exceeds DCAA formation at pH 6.5. Conversely, in the presence of Fe(II) ions alone, and along with a phosphate based corrosion inhibitor an increment for DCAA, TCAA and bromochloroacetic acid (BCAA) formation was observed for the change in pH values from 6.5 to 8.5 (Figure 2). These findings are consistent with the reported results in the literature (Liang & Singer 2003). However, it is noted that the impact of pH on the formation of HAAs is complicated, because the rate of HAAs formation and hydrolysis varies for each individual species in different reaction systems (Uyak et al. 2007).
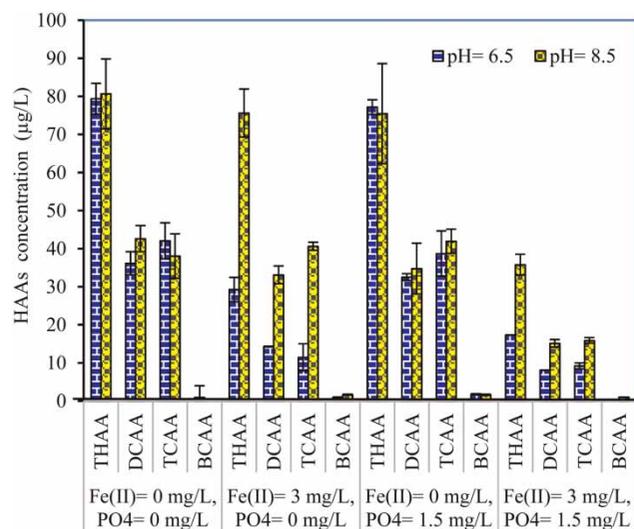
Effect of PO_4 dosage and reaction time

Phosphate based corrosion inhibitors are typically dosed into their treated water at a dosage of 0.5 to 3 mg-PO_4/L (Kirmeyer et al. 2000; Maddison et al. 2001). Therefore, a 1.5 mg/L, phosphate dosage was selected for this bench scale study. This study was conducted in the presence of different dosages of Fe(II) ions in synthetic water samples at different reaction times (3.5, 24, 48, 84, 130 h) for a fixed pH value of 6.5. This comprehensive study revealed the interaction effects of a phosphate based corrosion inhibitor for the different dosages of Fe(II) ions in the formation of HAAs. The paired Student t-test illustrated that HAAs formation was significantly ($\alpha = 0.05$) lower for the presence of phosphate (1.5 mg-PO_4/L) in iron water systems

Figure 2 | Effect of pH on HAAs formation and speciation in different reaction systems (for a chlorine to carbon mole ratio of 0.79, reaction period of 24 h at 21 ± 1 °C temp).

compared with the iron water systems only (no phosphate) for the reaction periods of 24 h ($p = 0.008$), 48 h ($p = 0.042$), 84 h ($p = 0.036$) and 130 h ($p = 0.005$) respectively (Figures 3(b)–(e)). This finding was in agreement with the research by Zhang & Andrews (2012), who indicated that HAAs formation was decreased significantly in the presence of phosphate associated with iron coupon compared with the presence of iron coupon only. However, for the reaction period of 3.5 h, the phosphate based corrosion inhibitor (1.5 mg-PO$_4$/L) did not show a statistically ($\alpha = 0.05$, $p = 0.878$) significant effect to reduce HAAs formation in the same reaction systems (Figure 3(a)). The finding of this study was in agreement with the research by Zhang & Andrews (2012), who conducted batch tests using three metal coupons (Fe, Cu and Pb) in the presence of 1 mg/L phosphate, and in the absence of phosphate. They reported that during a short reaction period (<12 h), phosphate did not considerably affect the formation of HAAs. The analysis of the results illustrated that in the presence of a phosphate based corrosion inhibitor (1.5 mg-PO$_4$/L) in the iron water systems, the statistical variation ($\alpha = 0.05$, $p \leq 0.005$) for

HAAs formation was higher for the reaction period of 130 h (Figure 3(e)), compared with the reaction periods of 84, 48, 24 and 3.5 h respectively (Figures 3(a)–(d)).

The speciation of HAAs in the presence of a phosphate based corrosion inhibitor alone; and along with Fe(II) ions for the different pH values illustrated that less formation of DCAA, TCAA and BCAA occurred in the presence of 1.5 mg/L phosphate in the iron water systems compared with the absence of phosphate in the same reaction systems (Figure 2). This result was similar to the published results in the literature (Zhang & Andrews 2012), which acknowledged less formation of DCAA, TCAA, monochloroacetic acid (MCAA) and BCAA in water samples having 1 mg/L ortho-phosphate along with iron coupon compared with the iron coupon only.

Overall correlation

The Pearson's correlation matrix between all the variables (i.e. Fe(II) ions, pH, phosphate dosage, reaction time, total HAAs and HAA species) in synthetic water samples
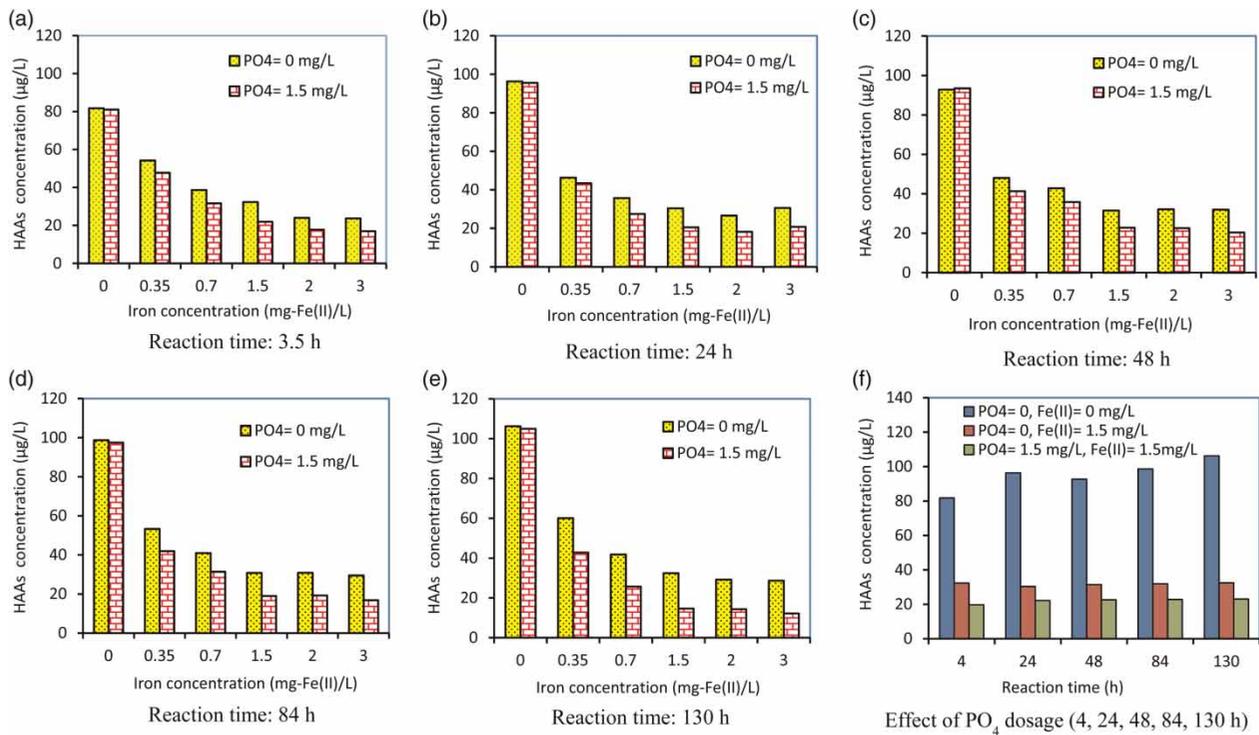

Figure 3 | Effect of phosphate (1.5 mg-PO$_4$/L) on HAAs formation in synthetic water at pH 6.5, chlorine to carbon mole ratio of 0.79, reaction periods of (a) 3.5 h, (b) 24 h, (c) 48 h, (d) 84 h, (e) 130 h and (f) all reaction periods together.

(number of observations 79) was performed using a windows version software 'IBM SPSS Statistics 20' (IBM, USA); and the results are presented in Table 3. This study revealed a significant positive correlation between the pH values and the formation of both total HAAs ($r = 0.45$, $p < 0.0001$); and individual HAA species, i.e. DCAA ($r = 0.42$, $p < 0.0001$), TCAA ($r = 0.49$, $p < 0.0001$) and BCAA ($r = 0.74$, $p < 0.0001$). Conversely, a negative and moderate correlation was observed between the phosphate based corrosion inhibitor and the formation of total HAAs ($r = 0.48$, $p < 0.0001$), DCAA ($r = 0.51$, $p < 0.0001$), and TCAA ($r = 0.46$, $p < 0.0001$) in the same reaction systems. The Pearson's correlation analysis showed a moderate and negative relationship between Fe(II) ions and the formation of total HAAs ($r = 0.47$, $p < 0.0001$), DCAA ($r = 0.43$, $p < 0.0001$), and TCAA ($r = 0.48$, $p < 0.0001$). The correlation coefficients values between total HAAs and individual HAA species were positively higher ranging from 0.62 to 0.98 ($p < 0.0001$), showing that each HAA species was strongly related to the other HAA. The most significant positive correlation was observed between pH and BCAA ($r = 0.74$, $p < 0.0001$). A moderate correlation between Fe(II) ions and pH ($p = 0.023$) was observed indicating that an interaction may exist between the two independent variables. Therefore, the affiliation between one of the independent variables (pH or Fe(II) ions), and the dependent variable (HAAs) was dependent upon the value of the other independent variables. The correlation among the other factors can also be found in Table 3.

MODEL DEVELOPMENT

A mathematical model for HAAs formation was developed based on a 2^4 full factorial design with center points approach including four potential explanatory variables, i.e. Fe(II) ions, pH, phosphate and reaction time (Table 1). All experiments for the factorial design were conducted in duplicate, and the repeatability was checked by the paired Student t-test at a 95% confidence level. The average values for each test were used for 2^4 full factorial design analyses. Statistical analysis of the experimental data was conducted using the Minitab 16 statistical package (MINITAB Inc., State College, Pennsylvania, USA), and the results of the analysis are summarized in Table 4, which presents the estimated parameter values, their standard errors, and summarizes the hypothesis results for the significance of each parameter. The statistical significance is represented in terms of Prob $> |t|$ in Table 4.

In this study, the negative value of the coefficient indicated that a high level setting of the factor provided lower content of HAAs formation than the low level setting, and vice versa for the positive value of the coefficient. Statistical analysis for the HAA formation results revealed that the Fe(II) ions concentration (factor A) was the most significant factor ($p < 0.0001$, contribution 50.85%) in the formation of HAAs followed by the phosphate based corrosion inhibitor ($p = 0.003$, contribution 14.96%) and pH ($p = 0.01$, contribution 7.92%) respectively at a 95% confidence level (Table 4). Several interaction factors including AB (Fe(II) ions and pH, contribution 13.94%, $p = 0.003$), AC (Fe(II)

Table 3 | Pearson correlation coefficients between HAAs, DCAA, TCAA, BCAA, pH, PO$_4$ dosages, Fe(II) ion concentration and reaction times

	HAAs	DCAA	TCAA	BCAA	pH	PO$_4$	Fe(II)	Time
HAAs	1							
DCAA	0.96[b]	1						
TCAA	0.98[b]	0.88[b]	1					
BCAA	0.69[b]	0.62[b]	0.68[b]	1				
pH values	0.45[b]	0.42[b]	0.40[b]	0.74[b]	1			
PO$_4$ Conc. (mg/L)	− 0.48[b]	− 0.51[b]	− 0.45[b]	− 0.12	− 0.04	1		
Fe(II) ion (mg/L)	− 0.47[b]	− 0.43[b]	− 0.48[b]	− 0.07	0.26[a]	0.17	1	
Reaction time (h)	0.09	− 0.22	0.01	0.19	− 0.36[b]	− 0.04	0.16	1

[a]Correlation is significant at the 0.05 level (2-tailed).
[b]Correlation is significant at the 0.01 level (2-tailed).

Table 4 │ Estimated parameters and their significance for HAAs formation study in synthetic water samples

Term	Effect	Coef SE	Coef	t-value	p-value	Impact (%)
Constant		56.6	1.725	32.82	0.000	
Fe(II) ions (mg/L)	− 35.4	− 17.7	1.725	− 10.26	0.000	50.85
pH Unit	13.97	6.98	1.725	4.05	0.010	7.92
Phosphate (mg-PO$_4$/L)	− 19.2	− 9.6	1.725	− 5.56	0.003	14.96
Reaction Time (h)	4.44	2.22	1.725	1.29	0.254	0.80
Fe(II)*pH	18.53	9.27	1.725	5.37	0.003	13.94
Fe(II)*Phosphate	− 9.48	− 4.74	1.725	− 2.75	0.040	3.65
Fe(II)*Time	− 3.31	− 1.65	1.725	− 0.96	0.382	0.44
pH*Phosphate	− 9.9	− 4.95	1.725	− 2.87	0.035	3.97
pH*Time	2.6	1.3	1.725	0.75	0.486	0.27
Phosphate*Time	4.37	2.18	1.725	1.27	0.261	0.77

$r^2 = 0.99$, r^2 (pred) $= 0.89$, r^2 (adj) $= 0.99$.

ions and phosphate dosage, contribution 3.65%, $p = 0.04$) and BC (pH and phosphate dosage, contribution 3.97%, $p = 0.035$) were also shown to be statistically significant ($\alpha = 0.05$). A half-normal probability plot is used to evaluate graphically the statistical significance of the parameters in the formation of HAAs (Figure 4). The statistically significant effects in the formation of HAAs are indicated by the solid square signs showing a large deviation from the normal distribution line. The data presented in Figure 4 were consistent with the analysis performed for the significant results presented in Table 4.

The effects of the simultaneous variability of the factors on HAAs formation study are shown in the contour
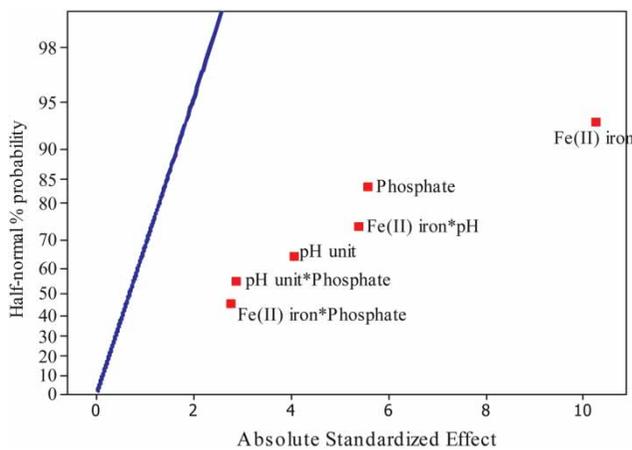
Figure 4 │ Half-normal plot showing the effect of studied factors and their interaction on HAAs formation study.

plots (Figure 5). Curvature in the contour plots indicates the presence of two factor interactions (Montgomery 2009; Chowdhury et al. 2010). In this study, the contour plots for AB depict the interaction effect of Fe(II) ions concentration (A) and pH on HAAs reduction showing curvature in the contour plots (Figure 5(a)). These two factors: A (Fe(II) ions) and B (pH) are also interacted strongly with the factor C (phosphate dosage) showing curvature in Figures 5(b) and (d). However, the contour plots show that there are no significant ($\alpha = 0.05$) interactions effect for DA (time and Fe(II) ions), DB (time and pH) and DC (time and phosphate) on HAAs formation study (Figures 5(c), (e) and (f)), which are consistent with the results presented in Table 4.

The main effects of the significant variables in this study are plotted in Figure 6(a) to assess visually their impact on the formation of HAAs. The signs of the effect indicate the direction of the effect. It has been observed in Figure 6(a), that the main effects of Fe(II) ions concentration (factor A) and phosphate dosage (factor C) are negative having slopes −35.4 and −19.2 respectively. This indicates that when Fe(II) ions concentration and phosphate dosage are changed from a lower to a higher level, it reduces the formation of HAAs. However, a reverse trend is observed for the main effect of pH value (factor B) (Figure 6(a)) having slope +13.9. One of the major benefits of a factorial design approach is that it gives more insight about the interaction between the input parameters and the responses (Montgomery 2009). The
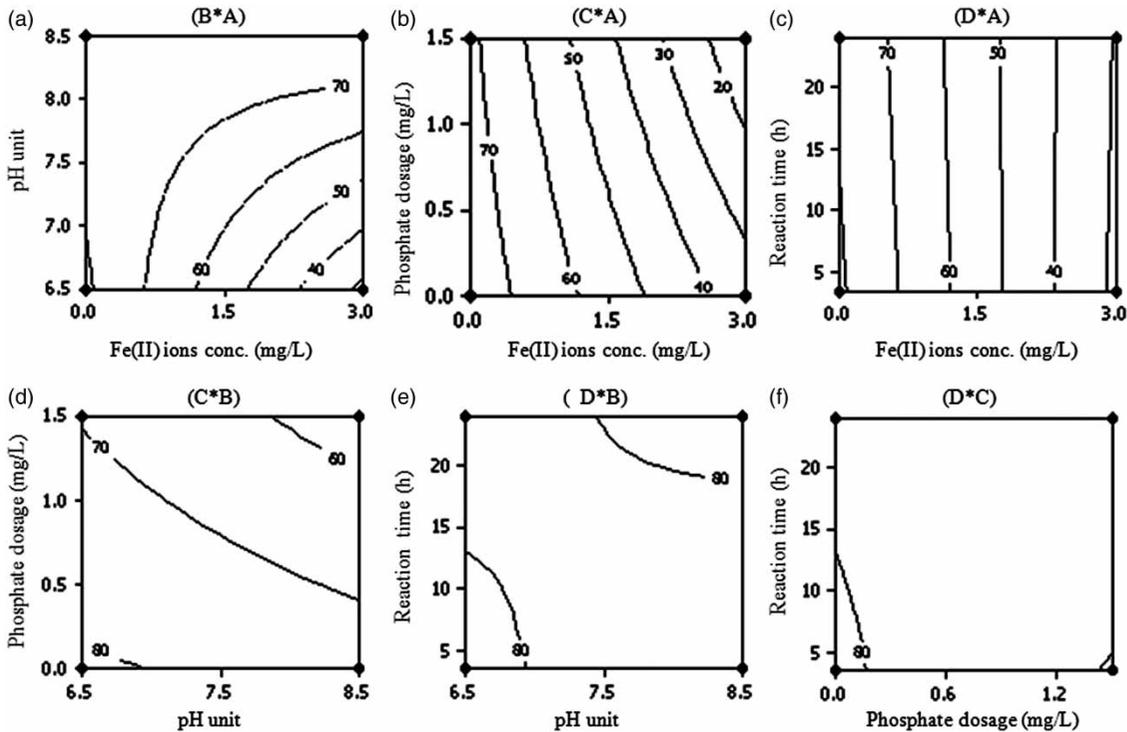
Figure 5 | Contour plots for interaction effects on HAAs formation in synthetic water following a factorial design approach.

interaction effects of the studied factors (i.e. *AB, AC, BC, AD, BD* and *CD*) in the formation of HAAs are plotted in Figure 6(b). The non-parallel lines in these figures are indication of interaction between the two factors. The interaction plots for the factors of Fe(II) ions and pH demonstrate that the effect of Fe(II) ions concentration in reducing HAAs formation is very large when the pH value is at a low level (pH 6.5); but small when the pH value is at a high level (pH 8.5). However, the Fe(II) ions and PO_4 ions interaction plots show the opposite trend indicating that Fe(II) ions have more impact to reduce HAAs formation at a high level of phosphate (1.5 mg/L) compared with a low level of phosphate dosage (0 mg/L) (Figure 6(b)). On the other hand, the interaction plots for pH and phosphate dosage indicate that a high level of phosphate (1.5 mg/L) has a lower interaction effect but a reverse trend is observed for the lower phosphate dosage in solution. Conversely, the interaction plots between Fe(II) ions and reaction time (*AD*); pH and reaction time (*BD*); and phosphate and reaction time (*CD*) show parallel lines indicating that there is no interaction effect in the formation of HAAs. Therefore, this study

illustrated that the lowest content of HAAs formation would appear to be obtained, when the pH value was at a low level (6.5) and the phosphate dosage was at the high level (1.65 mg/L) in iron water systems.

According to the Student *t*-test, *F*-test and graphical analysis of the HAA formation data, the effect of reaction time (single factor: *D*) and several interaction effects (*AD, BD* and *CD*), which were statistically insignificant at a 95% confidence level compared with the other effects were discarded. Therefore, the parameter estimated for the final model is summarized in Table 5. The regression model for prediction of HAAs can be presented as follows.

HAA predicted model

$$\hat{y}_{HAAs} = \hat{\beta}_0 + \hat{\beta}_1 A + \hat{\beta}_2 B + \hat{\beta}_3 C + \hat{\beta}_{12} AB + \hat{\beta}_{13} AC$$
$$+ \hat{\beta}_{23} BC \qquad (2)$$

$$\hat{y}_{HAAs} = 56.62 - 17.7(Fe^{2+}) + 6.98(pH) - 9.6(PO_4)$$
$$+ 9.27(Fe^{2+}.pH) - 4.74(Fe^{2+}.PO_4)$$
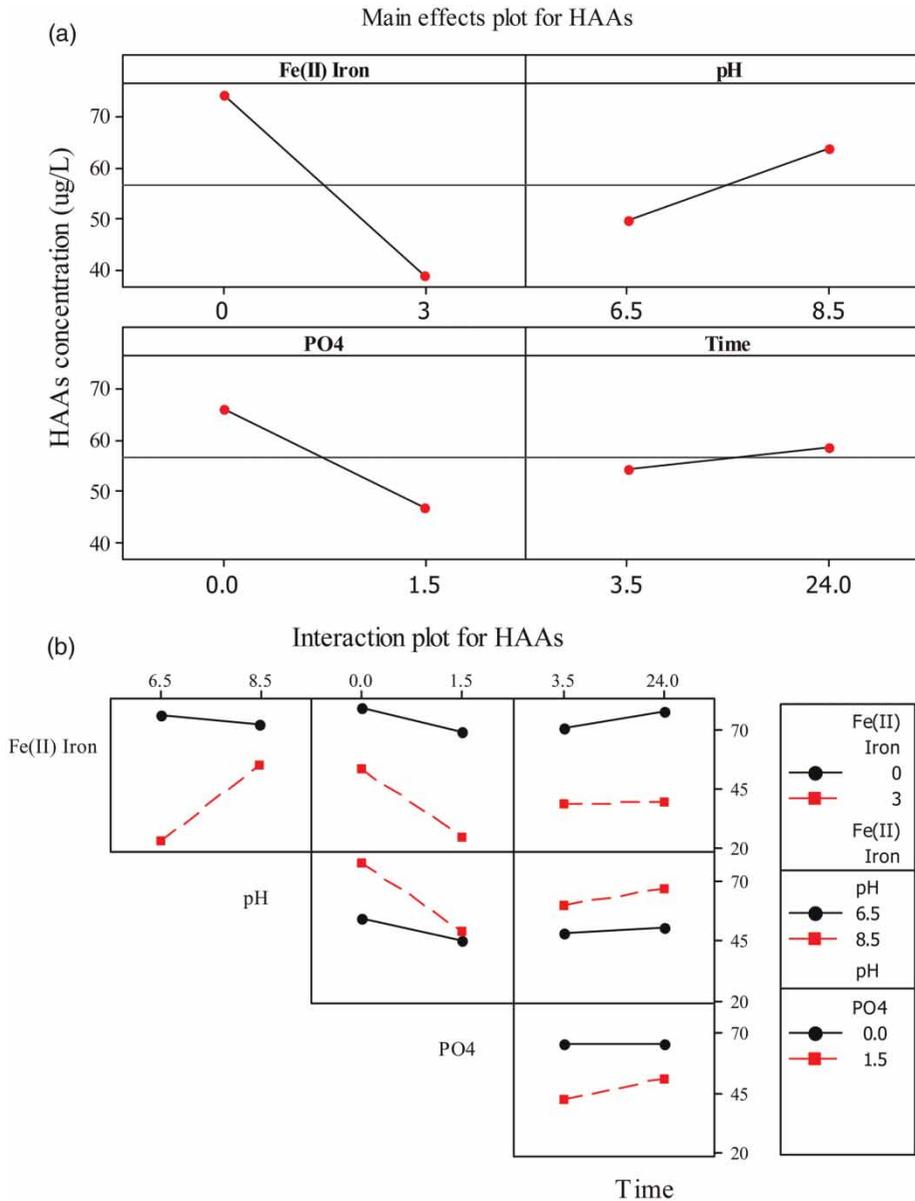$$- 4.95(pH.PO_4) \qquad (3)$$

Figure 6 | Plots for HAAs formation in synthetic water for (a) main effects and (b) interaction effects following a factorial design approach.

where $\hat{y}_{HAAs}$ is the predicted total haloacetic acids concentrations in water (μg/L), pH is the studied pH value, and PO_4 is phosphate based corrosion inhibitor dosage (mg-PO_4/L).

The ANOVA test for the fitting linear model and model lack of fit (LOF) test for the formation of HAAs are shown in Table 6. In this study, the F_{model} value for HAAs (21.8) was greater than the critical value ($F_{0.05,6,11} = 3.09$); and the p-value for the model was very low ($p < 0.0001$)

demonstrating a high significance for the regression model (Montgomery 2009). The goodness of fit of the model was checked by the determination coefficient (r^2). In this case, the coefficient of determination for the model was found to be 91.64%, which indicated that only 8.36% of the total variations were not explained by the proposed model for HAAs formation. The value of the adjusted determination coefficient (adj r^2) was also high advocating a high significance of the model. The F-value of the LOF test associated

Table 5 | Parameter estimates for the development of HAAs formation model

| Term	Parameter	Effect	Coef SE	Coef	t- value	P-value	Remark
Constant	β_0		56.62	1.796	31.54	0.000	
Fe(II) ions (mg/L)	β_1	− 35.4	− 17.7	1.796	− 9.86	0.000	Decrease
pH Unit	β_2	13.97	6.98	1.796	3.89	0.004	Increase
Phosphate (mg-PO$_4$/L)	β_3	− 19.2	− 9.6	1.796	− 5.35	0.000	Decrease
Fe(II)*pH	β_4	18.53	9.27	1.796	5.16	0.001	Increase
Fe(II)*Phosphate	β_5	− 9.48	− 4.74	1.796	− 2.64	0.027	Decrease
pH*Phosphate	β_6	− 9.9	− 4.95	1.796	− 2.76	0.020	Decrease

$r^2 = 0.95$, r^2 (pred) $= 0.85$, r^2 (adj) $= 0.92$.

Table 6 | Quantitative diagnosis for final model of HAAs formation

Source	DF	Seq SS	SS (Adj)	MS	F	P
Model	6	9,361.7	7,249.32	1,560.28	21.801	0.000
Residual Error	12	858.9	858.86	71.57		
LOF	1	179.2	179.16	179.16	2.899	0.117
Pure Error	11	679.7	679.71	61.79		
Total	19	10,278.5				

with the elimination of a few insignificant factors was 2.89 for the linear model which can be compared with the tabulated value at a 95% confidence level for the appropriate number of degrees of freedom. The mean sum square ratio (F-value) for the LOF test was smaller than the tabulated value ($F_{0.05,1,11} = 4.48$), and the p value for the LOF test was larger (Table 6); therefore, it could be concluded that these eliminated factors did not have statistical significance on the linear model for HAAs formation. However, the LOF test (Table 6) provides additional evidence that the models adequately fit the data for HAAs formation study.

In this study, the residuals also had to be examined for normal distribution, and were used to assess model adequacy (Montgomery 2009). The values of the residuals for the response factors are plotted in a normal probability plot (Figure 7). It has been observed in Figure 7 that all data points for the response factors lay close to a straight line and within the 95% confidence intervals line with mean value near to zero. Since the residuals lay approximately along a straight line, the data were considered to be normally distributed. The model prediction was
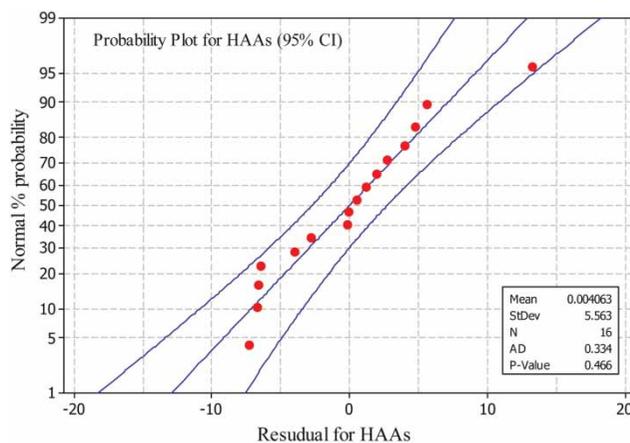
Figure 7 | Normal probability plot of the residuals at 95% confidence interval for the response factor, HAAs formation.

compared with the experimental data, and it was observed (figure not shown here) that there was a strong linear correlation having a strong coefficient ($r^2 = 0.93$). According to the systematic statistical and graphical diagnostics, it could be concluded that the proposed model adequately fits the data.

Model validation

To validate the model against an independent data set, a number of water quality and operation parameters (e.g. Fe(II) ions, phosphate, pH and stagnation time) in real iron pipe water distribution systems, are needed. pH, phosphate based corrosion inhibitor dosage and stagnation time in the water treatment plants and in distribution systems can be obtained easily. On the other hand it is a challenge to obtain the actual Fe(II) ions concentration in distribution systems especially for the different stagnation times (Benjamin & Miller 1990). The variability of Fe(II) ions can be attributed to the inorganic compounds, bio-geochemical processes, leaching due to the iron pipe corrosion and environmental conditions. However, there are no reported data for the concentration of Fe(II) ions, PO_4 ions, HAAs, pH, or water stagnation time in distribution systems in Nova Scotia, Canada. Therefore, the post-filtered natural water samples collected from three major water treatment plants in Halifax, Nova Scotia (Table 2) were spiked with the different dosages of Fe(II) ions (0.5 to 3 mg/L) for different pH values (5.5 to 8.5) and for different reaction times (3.5 to 24 h) in the absence and presence of a phosphate based corrosion inhibitor (1.5 mg-PO_4/L) in the formation of HAAs. The data for HAAs concentration in natural water were used to validate the developed model equation (Equation (2)). The results of the validation analysis for the HAA formation model show in Figure 8 that the correlation coefficient (r^2)
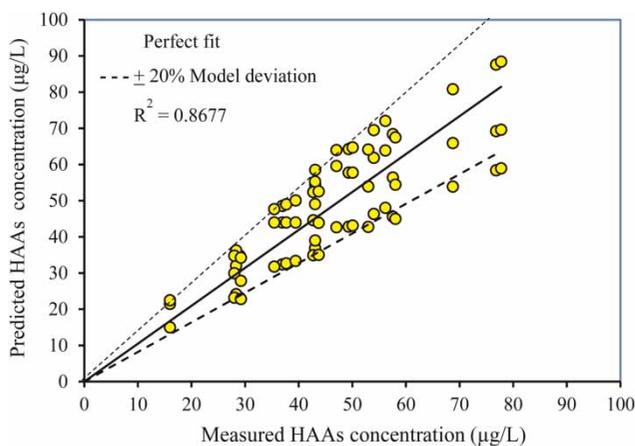

Figure 8 | Model predictions and measured concentrations of HAAs in natural water sample collected from three water supply plants in Nova Scotia, Canada.

for the predicted and measured values of HAAs formation in the natural water samples was found to be 0.87, which indicated the goodness of fit of the model. The result for the percentage of absolute model deviation revealed that 83.33% of the total observed HAA formation data lay within ±20% of the predicted values. The validation results seem to be at a satisfactory level for the explanation of the observed variability under these experimental conditions which indicate the variation of Fe(II) ions concentrations, pH values, phosphate dosages and reaction times.

SUMMARY AND CONCLUSIONS

This study revealed that the formation of HAAs in the presence of Fe(II) ions was lower in the iron water systems compared with the control water systems for the different reaction systems. In the iron water systems, phosphate significantly reduced the formation of HAAs for the different reaction periods. The effect of pH in the formation of HAAs and their speciation in the iron water systems was complicated compared with the control water systems, because the rate of HAAs formation and hydrolysis varies for each individual species in the presence of dissolved metal ions. Therefore, the results of this study might have implications for understanding the fact that pH change in drinking water not only affects the Fe(II) ions oxidation process but also has an impact on the formation of HAAs, and their speciation as well as affecting reactivity between DOM and chlorine.

The 2^4 full factorial design approach revealed that Fe(II) ions, pH and phosphate based corrosion inhibitor were the main significant factors in the formation of HAAs. However, this study revealed that the main effect of Fe(II) ions concentration really dominated this process, accounting for over 50.85% of total variability, whereas the main effect of pH and phosphate dosage, accounted for about 7.92 and 14.96% of total variability, respectively. Several interaction factors were also shown to affect HAAs formation significantly at a 95% confidence level. However, this study conclusively demonstrated that the lowest content of HAAs formation would appear to be obtained in the presence of a phosphate based corrosion inhibitor (1.65 mg-PO_4/L) at a pH value of 6.5 compared with a pH value of 8.5 in the iron water systems.

The adequacy of the developed model was tested statistically using numerical and graphical diagnostics. The model was found to be statistically significant and the LOF test was found to be insignificant. No visible trend was observed in the residuals plot. The predicted and the experimental HAA concentration data demonstrated no systematic deviation with a correlation coefficient (r^2) of 0.93. It has been indicated that the model functioned well during the course of the entire range of experiment conditions. The validation of the model using three different sources of natural waters collected from the main water treatment plants in Halifax, Canada, illustrated that 83.33% of the total observed HAA formation data lay within ±20% of the predicted values. The model performance was found to be excellent under a wide range of Fe(II) ions and HAAs concentrations. There was no systematic under or over prediction observed throughout the whole range of HAAs concentrations. Modeling results demonstrated that there was a good agreement between the experimental and model values. Therefore, it could be possible to estimate the HAA level in iron pipe water distribution systems with the use of the developed model. Conversely, the models can also be very useful in verifying key operational and water quality parameters, which may help to explain the HAA formation potential. Therefore, the model may be used as a decision-making tool by the drinking water industries. However, it should be said that it is difficult to develop a universally applicable HAA formation model due to the complexity of HAAs formation reaction depending on different factors.

ACKNOWLEDGEMENTS

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