Research article

Haloacetic acids degradation by an efficient Ferrate/UV process: Byproduct analysis, kinetic study, and application of response surface methodology for modeling and optimization

Hassan Aslani a, b, Simin Nasseri c, d, Ramin Nabizadeh c, e, *, Alireza Mesdaghinia c, Mahmood Alimohammadi c, Shahrokh Nazmara d

a Health and Environment Research Center, Tabriz University of Medical Sciences, Tabriz, Iran
b Department of Environmental Health Engineering, Faculty of Health, Tabriz University of Medical Sciences, Tabriz, Iran
c Department of Environmental Health Engineering, Faculty of Public Health, Tehran University of Medical Sciences, Tehran, Iran
d Center for Water Quality Research, Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran
e Center for Air Quality Research, Institute for Environmental Research (IER), Tehran University of Medical Sciences, Tehran, Iran

Abstract

Haloacetic acids (HAAs) after trihalomethanes are the second main group of chlorination byproducts. In this study, decomposition of the two most common HAAs in drinking water was studied by an advanced oxidation process using a combination of Ferrate [Fe(VI)] and UV irradiation. The decomposition rate was measured, and the byproducts formed during the process and the mass balances were also analyzed. HAAs were quantified by GC-ECD, and the final products including acetate and chloride ions were measured by ion chromatography (IC). A central composite design was used for the experimental design, and the effect of four variables including the initial HAA concentration, pH, Fe(VI) dosage, and contact time were investigated by response surface methodology (RSM). Dichloroacetic acid decomposed more easily than TCAA. Results show that when TCAA and DCAA were studied individually, the degradation rates were 0.0179 and 0.0632 min⁻¹, respectively. When the HAAs were simultaneously placed in the reactor, the decomposition rates of both TCAA and DCAA decreased dramatically. In this case their decomposition rate constants decreased by 67% and 49%, respectively. In the mixture, the decomposition rate of DCAA was 2.5 times higher than that of TCAA. In summary, Fe(VI)/UV process can be used as a promising treatment option for the decomposition of recalcitrant organic pollutants such as HAAs, and RSM can be used for modeling and optimizing the process.

1. Introduction

Disinfection byproducts (DBPs), which can be formed by water and wastewater disinfection, are one of the major environmental and health issues; they have received the attention of researchers and legislators worldwide (Esclapez et al., 2012). Among the various harmful byproducts, haloacetic acids (HAAs), the second most important DBPs after trihalomethanes, are highly stable and nonvolatile compounds; they are produced by the chlorination of surface waters containing natural organic matters (Rodriguez et al., 2007; Tang et al., 2013; Wang et al., 2009). The US EPA drinking water regulations have set a maximum contaminant level of 60 μg L⁻¹ for five HAAs, viz. trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA) (US EPA, 1998). In addition, Japan’s drinking water standards for MCAA, DCAA, and TCAA are 20, 40, and 200 μg L⁻¹, respectively (Sakai et al., 2013). Among these HAAs, TCAA and DCAA occur in higher concentrations in potable water. Tri-HAA constituted 61–67% of the total HAAs, followed by 30–36% of di-HAA species (Zhang et al., 2010). TCAA and DCAA,
the two main fractions of HAAs, are important because of their potential risks to human, aquatic, and plant life (Chu et al., 2009). Zhao et al. reported that the carcinogenic risks of TCAA and DCAA are 100 and 50 times higher than other THMs, respectively (Xingfang, 2011). Several studies have attempted to degrade TCAA and DCAA using either advanced oxidation processes or electrochemical methods (Kosobutskii, 2001; Lei et al., 2014; Tang et al., 2015; Zhao et al., 2015, 2016); however, all the methods have disadvantages. Wang et al. (Lei et al., 2014) used glow discharge plasma for TCAA degradation. They reported that the complete dechlorination of TCAA was achieved after 7 h contact time, which is practically not feasible. According to Scildone et al. (Scildone et al., 2014) TCAA could not be degraded by the electrochemical method. A recent study focused on the sonoelectrochemical method for TCAA degradation (Esclapez et al., 2015). Although the results reported were promising, the method is very complex, and more difficulties may be faced during practical implementation. Our previous study showed that when [Fe(VI)] was used alone, it could not degrade TCAA (Aslani et al., 2016). In addition, Wang et al. (2009) reported that a single UV light and O₃ were not able to degrade HAAs after 30-min contact time. Therefore, it is crucial to find an effective, practical, and environmentally friendly technique for HAA degradation.

The common oxidation states of iron are +2 and + 3; however, higher oxidation states such as +4, +5, and +6 can be obtained under special environmental circumstances (Berry et al., 2006; Kozlak and Pach, 2011; Sharma, 2013). Because of very strong oxidation/disinfection potential, iron in the +6 oxidation state, commonly called Fe(VI), has recently received much attention in water and wastewater treatment processes (Han et al., 2015; Jiang et al., 2006, 2012; Sharma, 2002; Sharma et al., 2006; Taliaiekhozani et al., 2016; Wang et al., 2016). Moreover, its degradation byproduct, i.e., Fe(OH)₃ is a coagulant and adsorbent; therefore, no environmentally harmful byproduct is generated. Several combined Fe(VI)-based processes were studied recently. Chen et al. (2015), used Fe(VI)/UV process for the oxidation of an organophosphorus pesticide. The results showed that when they were combined, almost 20% more removal efficiency was achieved; this can be attributed to the synergistic effect of UV. On the other hand, Fe(VI)-UV-TiO₂ process has been studied extensively for the degradation of recalcitrant organic and inorganic contaminants (Ma et al., 2015; Sharma et al., 2010; Sharma et al., 2003). More recently Feng et al. were evaluated synergistic effect of aqueous removal of fluoroquinolones by the combination of peroxymonosulfate and ferrate (Feng et al., 2017). Moreover, Fe(VI) based processes have been widely studied for disinfection (Li et al., 2017; Yang et al., 2015), degradation of antibiotics (Feng et al., 2016; Karlesa et al., 2014), and emerging contaminants; however, no research has been conducted to date on the degradation of HAAs.

In this study, TCAA and DCAA were selected as the target compounds as they are the most widely detected HAAs in drinking water. The potential of Fe(VI)/UV process for TCAA and DCAA degradation (separately and combined) was investigated for the first time. Moreover, response surface methodology (RSM) was used for modeling and optimizing the process. This study was conducted in two phases: (i) A preliminary study of Fe(VI)/UV process was carried out to determine the process performance and effect of different variables, and (ii) it was followed by the main study designed based on the results obtained in the first phase of the study. Finally, the trend of byproduct formation was determined, and mass balance between the initial HAA and final byproducts was analyzed.

2. Materials and methods

2.1. Materials

All the materials used in this study were of analytical grade except noted. Potassium Ferrate, K₂FeO₄, with a purity of >92% was purchased from BOC Science (NY, USA) and used as received without further purification. TCAA, DCAA, MCAA, methyl tert-butyl ether (MTBE), 1,2,3-trichloropropene, and 2-bromobutanoic acid were obtained from Sigma-Aldrich. Analytical-grade pure methanol, sodium sulfate, sodium bicarbonate, sulfuric acid, hydrochloric acid, and sodium hydroxide were obtained from Merck (Germany).

2.2. Analytical methods

The HAAs were determined by liquid–liquid microextraction, methylation, and derivatization following the EPA method 552.3. In brief, 40 mL of water samples were transferred to a special 60-mL glass container and spiked with 20 μL of 20 μg mL⁻¹ 2-bromobutanoic acid as the surrogate standard. The sample pH was adjusted to below 1 using concentrated sulfuric acid, and a predetermined amount of sodium sulfate (10–15 g) was added immediately to increase the ionic strength of the sample. MTBE containing the internal standard (1,2,3-trichloropropene) was added as the extraction solvent. After the completion of methylation conducted for at least 2 h in a sand bath maintained at 55 ± 2 °C, the HAA esters were analyzed by GC. A gas chromatograph (Varian CP 3800, USA) equipped with an ECD detector and DB-1701 capillary column (30 m × 0.25 m × 0.25 m, Optima, Germany) was used for quantitative analysis. The GC programming has been reported elsewhere (Aslani et al., 2016). To determine Cl⁻ and acetate ions as the other products of the process, an IC 850 professional instrument (Metrohm, Switzerland) equipped with a Metrosep A Supp 1-250/4.6 anionic column and conductivity detector was used. Sodium carbonate (3.2 mM L⁻¹) was used as the background eluent.

2.3. Ferrate characterization

The Fe(VI) concentration was quantitatively determined by UV–visible spectroscopy. Fig. S1 shows the characteristic UV–vis spectrum of Fe(VI). The maximum absorbance was in the range 505–510 nm, consistent with other studies (Luo et al., 2011; Noorhasan et al., 2010). The molar absorptivity at 510 nm has been reported as 1150 M⁻¹ cm⁻¹, which was used for the quantitative determination in this study. To minimize the ferric oxide colloidal interferences, baseline correction was conducted at 385 nm (Jiang, 2014; Li et al., 2005).

2.4. Experimental

2.4.1. Laboratory experiments

All reactions were carried out in a self-made photoreactor with an effective volume of 0.5 L and equipped with a cooling system (water circulation); the photoreactor was placed on a magnetic stirrer for complete mixing in the entire reaction period (Fig. 1). To evaluate the performance of HAA degradation, a maximum concentration of 1000 μg L⁻¹ was selected; 2–3 times higher than its reported concentration in distribution systems. An HAA stock solution of a determined concentration was prepared using ultrapure water, generated using a Human water purification system (Human Corporation, Korea), in a 2-L glass container, and 0.5 L of this
solution was transferred to the reactor after dosing with a determined Fe(VI) concentration and adjusting pH with 0.1 M NaOH or HCl. Quartz-protected UV light was turned on 15 min earlier to achieve a constant irradiation intensity. A 75-W low-pressure mercury UV lamp ($\lambda_{max} = 365, 310$, and 254 nm, respectively) with 0.225 mW cm$^{-2}$ intensity was used as the UV light source and placed in the center of the reactor (see Fig. S2). To minimize the colloidal Fe disturbance effect on UV-light performance, phosphate in the PO$_4$ form was added to the reactor, because Fe-PO$_4$ complex is soluble and does not interfere with UV light (Jiang, 2014; Noorhasan et al., 2010).

2.4.2. Experimental design

Design of the experiments was divided into two steps. To study all the factors, a full factor preliminary design including four variables, namely, the initial TCAA concentration (TCAA$_0$), pH, Fe(VI) concentration, and contact time, was implemented in the first step, and the effective range of each variable was determined (data not shown). In the second step and based on the results obtained in the first step, a new design was developed. A total of 44 runs, for TCAA and DCAA each, in two orthogonal blocks using a central composite design (CCD) including 16 design points, 8 axial points, and 20 center points were designed and carried out in the laboratory. The range of variables and design parameters are shown in Table 1. The selected variables were coded using Eq. (1).

$$X_i = \frac{(X_i - X_0)}{\Delta X_i}$$ (1)

Table 1

<table>
<thead>
<tr>
<th>Variables</th>
<th>Symbol</th>
<th>Coded values</th>
<th>Real values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$-2$</td>
<td>$-1$</td>
</tr>
<tr>
<td>HAA (µg L$^{-1}$)</td>
<td>$X_1$</td>
<td>100</td>
<td>339</td>
</tr>
<tr>
<td>pH</td>
<td>$X_2$</td>
<td>3</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe(VI) (mg/L)</td>
<td>$X_3$</td>
<td>10</td>
<td>18</td>
</tr>
<tr>
<td>Time (min)</td>
<td>$X_4$</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

where $X_i$ is the dimensionless coded value of the independent variable, $x_0$ is the independent variable real value in the center point, $X_i$ is the independent variable real value, and $\Delta X_i$ is the step change value. As a simple linear model cannot determine the interactions between variables; therefore, a full quadratic second-order model shown in Eq. (2) was used to determine the critical points and interactions.

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{i} X_i^2 + \sum_{i=1}^{k} \sum_{j=2}^{k} b_{ij} X_i X_j + c$$ (2)

where $Y$ represents the response variable; $b_0$ is a constant value; $b_i$, $b_{ij}$, and $b_{ijk}$ refer to the regression coefficient for linear, second order, and interactive effects, respectively; $X_i$ and $X_j$ are the independent variables; $c$ denotes the residual term. RSM analysis and the related statistical analyses, i.e., ANOVA, F-test, and t-test, were conducted using the R software for windows (version 3.0.3: 2014-03-06). Process optimization for TCAA and DCAA removal was carried out using Solver Add INS in Microsoft Excel.

2.4.3. Kinetic study and mass balance error (MBE)

Kinetic experiments were carried out under the optimized conditions. Notably, the kinetic studies for TCAA and DCAA were conducted individually and in combination. The first-order model shown in Eq. (3) was used to interpret the HAA removal in the reaction system.

$$C = C_0 e^{-kt}$$ (3)

where $C$ is the HAA concentration (µg L$^{-1}$) at any reaction time, $C_0$ is the initial HAA initial concentration (µg L$^{-1}$), $k$ is the first-order constant (min$^{-1}$), and $t$ is the reaction time (min). The observed first-order rate constants were obtained from the slope of linear regression line achieved by plotting ln($C/C_0$) vs. reaction time.

Mass balance of the compounds was analyzed based on the TCAA or DCAA basis of the byproducts. All of the byproducts were converted to the initial organic compound using Eqs. (4) and (5), and the error was calculated by subtracting the sum of the byproducts from the initial HAA concentration.

$$\text{byproducts as TCAA} = \frac{163.5 \times x_i}{M_{x_i}}$$ (4)
$$\text{byproducts as DCAA} = \frac{129 \times x_i}{M_{x_i}}$$ (5)

where $x_i$ is the concentration of any byproduct in µg L$^{-1}$, $M_{x_i}$ is the molecular weight of the byproduct, 163.5 and 129 are the molecular weights of TCAA and DCAA, respectively.

Dechlorination efficiency (DE) of the process for HAA was calculated using (Esclapez et al., 2012):

$$DE\% = \frac{[\text{Cl}^-]_{t=t_0} - [\text{Cl}^-]_{t=t_0}}{3 \times [\text{HAA}]}_{t=t_0} \times 100$$ (6)

4. Results and discussion

4.1. TCAA and DCAA degradation

Table 2 shows the 44 experiments designed in the second step of the study for TCAA and DCAA degradation and their relative removal percentage in the Fe(VI)/UV process. The predicted results
produced by the corresponding model of each compound are also shown in this Table. The highest removal efficiencies for TCAA and DCAA were 93.82% and 97%, respectively; they were achieved under the experimental conditions shown in run 23. On the other hand, a minimum removal of 72.7% and 27.27% for TCAA and DCAA, respectively, was observed when the reaction was stopped after 5-min contact time, while other factors were in the middle of their respective ranges (see run 29). Figs. S3 a and b show the predicted results versus the results obtained in laboratory for TCAA and DCAA, respectively. Clearly, the predicted results are in good agreement with those obtained experimentally, and the R2 value of 0.98 for both TCAA and DCAA confirms that RSF can be successfully used for modeling HAA removal by Fe(VI)/UV system. It should be noted that as the degradation was not completed, some byproducts were produced during the process, which will be discussed in the following sections.

4.2 Model development and analysis

As all of the model terms in TCAA removal did not significantly affect the model formula, the reduced quadratic model with only the significant terms and variance analysis of this model are shown in Tables 3 and 4, respectively. The entire model including all of the parameters is shown in Table S1. The model terms shown in Table 3 are divided into three parts, namely, first order or linear terms (FO), two-way interactions (TWI), and pure quadratic (PQ) terms. Table 3 clearly shows that the interactions among X2 (pH) and X4 (Time) play the most important role in model development and positively affected TCAA degradation by Fe(VI)/UV system. pH (X2) and Time (X4) were placed in the second and third places, respectively, showing that these two variables are very crucial for process operation and control. On the other hand, the initial TCAA concentration and contact time PQ terms with coefficient estimates of −10.88 and −16.7, respectively, negatively affected the process performance.

Model adequacy can be checked from the P-value as well as R2 and adjusted R2 (R2 adj). A P-value of 2.2 × 10−16 showed that the model is statistically significant with a very promising R2 value of 0.98. Moreover, a very good agreement was observed between R2 and R2 adj (the difference between these two parameters was 0.01), ensuring a satisfactory adjustment of the quadratic model to the experimental data (Lambropoulou et al., 2017). ANOVA analysis of the model with Fisher F-test showed that the FO and PQ terms are significant at the level of 0.001, whereas the TWI terms are mostly significant at the level of 0.05, except pH and time which are significant at the 0.001 level (see Table 4). The other most important factor of model validation is F-test lack-of-fit, which shows that the data variation around the developed model should be significant (Aslani et al., 2016). The value of lack-of-fit in our study was calculated as 0.294, indicating a significant correlation between factors and TCAA removal as the response. The reduced quadratic model of DCAA removal is shown in Table 4. The variance analysis (ANOVA) of the TCAA reduced model.

<table>
<thead>
<tr>
<th>Model term</th>
<th>Coefficient estimate</th>
<th>Std. Error</th>
<th>t value</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>48.93</td>
<td>0.51</td>
<td>95.2</td>
<td>2.2 × 10−16</td>
</tr>
<tr>
<td>X1</td>
<td>−10.88</td>
<td>1.136</td>
<td>−9.58</td>
<td>3.45 × 10−11</td>
</tr>
<tr>
<td>X2</td>
<td>31.65</td>
<td>1.137</td>
<td>27.82</td>
<td>2.2 × 10−16</td>
</tr>
<tr>
<td>X3</td>
<td>31.41</td>
<td>1.135</td>
<td>27.05</td>
<td>1.02 × 10−11</td>
</tr>
<tr>
<td>X4</td>
<td>24.33</td>
<td>1.136</td>
<td>21.41</td>
<td>2.2 × 10−16</td>
</tr>
<tr>
<td>X1×X2</td>
<td>−7.38</td>
<td>3.05</td>
<td>−2.42</td>
<td>0.02</td>
</tr>
<tr>
<td>X2×X3</td>
<td>6.87</td>
<td>3.04</td>
<td>2.25</td>
<td>0.03</td>
</tr>
<tr>
<td>X2×X4</td>
<td>33.43</td>
<td>3.05</td>
<td>10.95</td>
<td>1.07 × 10−12</td>
</tr>
<tr>
<td>X1×X2×X3</td>
<td>3.78</td>
<td>1.84</td>
<td>2.04</td>
<td>0.048</td>
</tr>
<tr>
<td>X1×X2×X4</td>
<td>−16.7</td>
<td>1.85</td>
<td>−9.02</td>
<td>1.51 × 10−10</td>
</tr>
</tbody>
</table>

R2 = 0.98, Adj R2 = 0.97, Pvalue = 2.2 × 10−16.
Table 5; the full model terms and parameters are shown in Table S2. This table clearly shows that all the variables in the FO and PQ terms significantly affect the model formula at the 0.001 level. Moreover, three interactions were found to be significant in the model shown in Table 5. All the factors positively affect DCAA removal except X1 (the initial concentration of DCAA); in other words, a higher DCAA removal efficiency was achieved by Fe(VI)/UV process when [DCAA0] was the lowest. The interactions between [DCAA0] and time, pH and Fe(VI), and pH and time are also highly significant terms affecting the model formula. Notably, the interactions between [DCAA0] and time negatively affect the model formula, indicating that the higher [DCAA0] and lower contact times were unfavorable conditions for the system. The \( R^2 \) and \( R_{adj}^2 \) of the model were 0.979 and 0.972, respectively. The \( R^2 \) value is very close to 1 and \( R_{adj}^2 \) necessary for a reliable model. Also, based on the p-value shown in the Table (P-value = 2.2 \times 10^{-10}) the model is highly significant. A higher \( R^2 \) coefficient, close to 1, ensures a satisfactory adjustment between the experimental data and quadratic model. The ANOVA analysis of the model is shown in Table 6. Clearly, FO, PQ, and TWI terms are significant at the 0.001 level, except the interactions of X1:X4 affecting the model at the 0.05 level. LOF of the model shown in Table S5 is 0.56, indicating that the model fitted the experimental data well.

4.3. Analysis of operational parameters by response surface and contour plotting

The three significant interactions observed in the model developed for TCAA removal in Table 3 are graphically shown in Fig. 2 for further consideration of operational parameters. Clearly, pH plays an important role and shows interaction with the other three operational parameters, i.e., [TCAA0], Fe(VI) dosage, and contact time. Fig. 2(a) shows that when the Fe(VI) dosage and contact time were fixed in their center points (25 mg L\(^{-1}\) and 32.5 min, respectively) in the entire TCAA range, the reduction efficiencies increased with increasing pH, and this is noticeable in the low TCAA concentration. In the case of pH and Fe(VI) interactions [see Fig. 2(b)], notably the highest removal efficiencies were obtained when the pH was in the alkaline range. The findings are in contrast with Fe(VI) reduction potential, which is the highest in the acidic range (eV = 2.7); therefore, a possible explanation for this phenomenon is that Fe(VI) is more stable at a higher pH range than in the acidic region where Fe(VI) permanently underwent self-decomposition. Hereafter, the role of UV illumination was considered using Eq. (7). UV light converts Fe(VI) to Fe(V) that is more reactive than the former and attacks the C–Cl and C–C bonds in the TCAA structure (Chen et al., 2015). The interaction between pH and time is shown in Fig. 2(c). Two distinct parts appeared in this Fig.; one is contact times <20 min, and the other is higher contact times. In the former, the reduction efficiencies are clearly not affected by pH variation, and fixed removal efficiencies were observed in the entire pH range. However, in the latter part, the process performance increased with the increase in pH from 3 to 9, and a maximum removal of –100% was achieved after almost 45-min contact time.

\[
{\text{FeO}_4}^2- + e_{cb}^{-} \rightarrow {\text{FeO}_4}^{3-}
\]

The contour plots of significant operational parameters in DCAA removal are shown in Fig. 3. Three main interactions were observed between time and [DCAA0], Fe(VI) and pH, and time and pH, affecting model development. Unlike the TCAA removal in which pH was the one side of all significant interactions explained, in this case, pH was replaced with time in Fig. 3(a). Fig. 3(a) clearly shows that the DCAA removal efficiency increased with time and maximized to 70%, occurred at 50-min contact time. In addition, the removal efficiency is inversely related to the initial DCAA concentration, and the Fe(VI)/UV process was found to be more efficient in low DCAA concentrations as low as 200–400 μg L\(^{-1}\). A possible explanation for this phenomenon is that higher concentrations of DCAA might need a higher Fe(VI) dosage to attack the Cl and C bonds in the DCAA structure. In the case of Fe(VI) and pH interaction, the TCAA removal efficiency was more affected by pH, and the highest removal efficiency was obtained in the alkaline pH range, i.e., pH = 9 where Fe(VI) is more stable and gradually activated by UV light. Fig. 3(c) shows the interaction between time and pH. The DCAA degradation efficiency clearly increased with pH and time. As mentioned previously, Fe(VI), among the other oxidants used in water treatment, showed the highest oxidation potential in the acidic condition; however, the self-decomposition rate is very fast in this pH range. Thus, a negligible removal of DCAA, 20–30%, observed at lower contact times (<15 min) and acidic conditions, can be attributed to only Fe(VI) oxidation potential. Notably, the highest removal efficiency of 100% was achieved when both the contact time and pH were the maximum, i.e., 50 min and pH = 8–9.

### 4.4. Degradation pathway, byproduct analysis, and modeling

#### 4.4.1. TCAA byproducts

As mentioned in previous studies, C–Cl and C–C bond cleavage, i.e., dechlorination, decarboxylation, and oxidation in aqueous solution are the known mechanisms for HAAs degradation in oxidation processes (Esclapez et al., 2012; Wang et al., 2008; Zhao et al., 2016). Fig. 4(a) shows that dechlorination of TCAA can occur in a stepwise manner, and the major byproducts were DCAA, MCAA, acetic acid (AA), and formic acid (was not quantitatively monitored in this study). In the first 40 min of the reaction, DCAA and MCAA concentrations first increased and then decreased gradually with as reaction proceeded. In contrast, AA concentration was low throughout the process. Ultraviolet (UV) light forms -OH and -H radicals through the reactions 8 and 9 (Attri et al., 2015);
Fe(VI) reduction to Fe(V) is also possible under UV illumination (Ma et al., 2015). In our experiments, TCAA degradation proceeded well by the UV/Fe(VI) process under higher-pH conditions (alkaline and near alkaline). Since \( \cdot \mathrm{H} \) radicals quickly disappear in alkaline environments, it seems that DCAA was mainly formed due to TCAA dechlorination by Fe(V) and OH\(^+\) species. (see reaction 10). The suggested pathway for TCAA and subsequently DCAA degradation is shown in Scheme 1.

\[
\begin{align*}
\text{CCl}_2\text{COOH} + \text{UV}/\text{Fe(VI)} & \rightarrow \text{CCl}_2\text{COOH} + \text{HCl} \\
\text{CHCl}_2\text{COOH} + \text{UV}/\text{Fe(VI)} & \rightarrow \text{CH}_2\text{ClCOOH} + \text{HCl} \\
\text{CH}_2\text{ClCOOH} + \text{UV}/\text{Fe(VI)} & \rightarrow \text{CH}_3\text{COOH} + \text{HCl} \\
\text{CCl}_2\text{COOH}^{\text{heat}} & \rightarrow \text{HCOOH} + \text{CO}_2
\end{align*}
\]

Similarly, MCAA and AA were produced by successive DCAA reduction steps. Formic acid may also be formed in this process as the result of the thermal reaction of DCAA radicals (Lei et al., 2014) or C-C bond cleavage by \( \cdot \mathrm{OH} \) radicals (Zhao et al., 2016).

\[
\begin{align*}
\text{UV} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^{\cdot} \\
\text{UV} + \text{H}_2\text{O}^{\cdot} & \rightarrow \text{OH}^{\cdot} + \text{H}^{+}
\end{align*}
\]

**Fig. 2.** Contour plots for the effects of (a) pH and TCAA\(_0\); (b) Fe(VI) dosage and solution pH; (c) contact time (min) and solution pH on TCAA removal.
Each of the byproducts was monitored as a response for the 44 experiments shown in Table 2 (data not shown) and analyzed by RSM. Table S3 shows the reduced quadratic model coefficients for DCAA production obtained from TCAA degradation. It can be inferred from this table that in the linear part of the model, all the variables except Fe(VI) showed significant positive effects on DCAA production. Notably, the effects of three variables, i.e., TCAA0, pH, and time were almost equal. TWI showed that the interactions between TCAA0 and time, and TCAA0 and Fe(VI) were the most effective terms in DCAA production. All the quadratic terms showed significant effect on model development; among them, pH2 showed the highest positive effect. Moreover, this term showed superior influence on DCAA production among all the model terms. $R^2$ and $R^2_{adj}$ for this model were 0.9 and 0.86, respectively, a good indication of model reliability. ANOVA analysis (not shown) of this model showed that the model LOF was 0.16 (higher than 0.05), certifying the model adequacy.

Graphical analysis of the interactions between the variables is shown in Fig. S4. Clearly, DCAA, up to 70 μg L$^{-1}$, was produced in the upper extreme pH range than the lower extreme [see Fig. S4 (a)]. This is because Fe(VI) is more stable in pH 9, and UV illumination forms Fe(V), which is more powerful than Fe(VI) to degrade TCAA. DCAA formation in the pH range 3–8 decreased from 50 μg L$^{-1}$ to 10 μg L$^{-1}$, especially because Fe(VI) has the highest reduction potential in the acidic range. The interactions between TCAA0 and Fe(VI) show that more DCAA was produced in either lower TCAA0

![Graphical analysis of the interactions between the variables](image-url)
or higher Fe(VI) concentration [Fig. S4 (b)]. The explanation for TCAA0 and time interaction is the same as previous, except in this case, more DCAA was produced when both TCAA0 and time were in their upper limits [Fig. S4 (c)]. The pH vs. time and pH vs. Fe(VI) relationships have produced similar contour lines. In both the cases, high pH values, i.e., ~9, in line with either longer contact times or higher Fe(VI) dosage resulted in more DCAA production as well as TCAA degradation [Fig. S4 (d and e)].

MCAA, the second TCAA byproduct, is directly produced from DCAA dechlorination. The reduced quadratic model of MCAA production is shown in Table S4. This table clearly shows that all the operating variables except Fe(VI) dosage significantly affected MCAA formation and influenced the model. $R^2$ and $R_{adj}^2$ of the MCAA production model were 0.67 and 0.6, respectively. MCAA was the second byproduct in TCAA degradation; therefore, the model reliability is almost acceptable. On the other hand, analysis of the variance table of the model showed that the LOF is lower than 0.05, indicating that the model did not fit well to the experimental data; therefore, it cannot be confidently used for practical purposes. The model coefficients clearly show that the interaction of time with both TCAA0 and pH is significant (P-value <0.05), and the latter (time vs. pH) showed the most significant impression among all the other terms of the model.

Acetate ion was the other product of TCAA degradation detected during the experiments. The quadratic model developed for acetate (not shown) showed that time, TCAA0, and Fe(VI) were the three significant parameters for acetate production, whereas the other terms showed no meaningful effect. The models $R^2$ and $R_{adj}^2$ were 0.52 and 0.44, respectively, indicating that the model is not as reliable as stated in the case of DCAA and MCAA production. However, the LOF of the model was 0.34, indicating that the model fitted well to the experimental data.

Chloride ion was the final product of TCAA degradation. According to the results shown in the CCD table (data not shown) and also RSM analysis, Fe(VI) was the only significant variable in the chloride release to the solution, whereas the other three variables did not show any considerable effect. In addition, based on the quadratic model, TCAA0 was the only significant term among others and showed hindering role in chloride formation.

4.4.2. DCAA byproducts

As noted previously, HAA degradation can occur in stepwise or parallel manners. During DCAA degradation, MCAA and acetate anion were detected as the main byproducts, and similar to the case of TCAA, chloride ion was obtained as the final degradation product. As shown in Scheme 1 and inferred from Fig. 4(b), acetate was detected early in the reactions, assuming that stepwise and parallel dechlorination reactions were the two main degradation pathways in the UV/Fe(VI) process. Decarboxylation is another possible channel for DCAA degradation, in which -OH radicals probably react with carboxylic group, generating $\text{CO}_2$ and $\text{HCl}_2\text{C}$ radicals, which are unstable and swiftly transform to $\text{CO}_2$ and HCOOH, respectively (Zhao et al., 2016). The reduced quadratic model of MCAA production is shown in Table S5. It can be inferred from this table that in the linear model, the terms of all the variables significantly influenced MCAA production; among them, pH showed the highest effect followed by DCAA0, time, and Fe(VI). Considering all the model terms (not just linear), clearly the interaction between pH and Fe(VI) dosage was placed in the second rank after pH. This is expected because pH plays a very important role in Fe(VI) stability and controls its self-decomposition. The model adequacy and reliability were checked with $R^2$ and LOF tests. $R^2$ and $R_{adj}^2$ of the MCAA production model were 0.95 and 0.93, respectively. On the other hand, LOF of the model was 0.056, indicating that the model fitted well to the experimental data. Graphical interpretation of the interactions between variables is shown in Fig. S5. Notably, in the case of DCAA0 interaction with both pH and Fe(VI) dosage, either alkaline pH (pH = 9) or a higher Fe(VI) dosage in combination with a higher DCAA0 led to the maximum MCAA production [Fig. S5 (a and b)]. The interaction of pH with both Fe(VI) dosage and time shows the same pattern in which a higher MCAA was obtained.
when alkaline pH was combined with either a longer contact time or higher Fe(VI) dosage [see Fig. S5 (c and d)].

The second byproduct of DCAA degradation was acetate ion, as detected in all the 44 experiments shown in Table 2. As noted for TCAA, in this case also, DCAA was first degraded to MCAA, followed by acetate formation in the reactor. The time of byproduct detection in the reactor, which will be discussed later in this paper, proved the majority of this degradation pathway. The reduced quadratic model of acetate formation is shown in Table S6. According to the model, in the linear terms, all the variables except Fe(VI) dosage significantly influenced acetate formation. Longer reaction times positively affected acetate production, whereas DCAA0 showed hindering effect. Variance analysis of the data indicates that the model is highly significant (p-value = 5 × 10⁻⁵), as well as very reliable (R² and R²_adj were 0.84 and 0.76, respectively).

4.5. pH analysis and modeling

As the pH played an important role in HAA degradation by Fe(VI)/UV process, the final pH of the solution was recorded as another response for the CCD Table and analyzed by RSM. Our findings show that in most of the experiments, the final pH of the solution was lower than the initial pH, and the variation was affected by other variables. The reduced quadratic regression models of the final pH for TCAA and DCAA degradation are shown in Tables S7 and S8, respectively. In the case of TCAA, clearly in the linear terms, all the variables except Fe(VI) dosage significantly influenced pH variation. Among the three effective variables, pH showed the highest impact, whereas Fe(VI) showed the minimum effect. R² and R²_adj were 0.80 and 0.77, respectively, indicating that the model is reliable. LOF of the model was 0.8, indicating that the model fitted well to the experimental data. Variation of pH in DCAA degradation was almost the same as TCAA with a slight difference observed in the significant terms of the model. Table S8 shows that the DCAAs_pH and Fe(VI)_time relationships were the other significant terms of the model. The R² and R²_adj of the model were 0.82 and 0.78, respectively.

As noted previously, the maximum HAA reduction occurred when the solution pH was in the highest range. During the experiments, it is well understood that for both TCAA and DCAA degradation, as the pH decreased significantly mainly due to HCl formation, a higher degradation efficiency was achieved.

4.6. Kinetic study

To determine the degradation rate of HAAs in Fe(VI)/UV process, three separate experiments including the separate consideration of TCAA and DCAA and also the combination of these two HAAs were conducted under the optimum conditions. The optimum conditions of each variable for TCAA and DCAA degradation, obtained from the CCD table, are shown in Table 7.

Fig. 4 shows the variation in HAA concentration under the optimum conditions shown in Table 7 and prolonged reaction time. Fig. 4(a) clearly shows that DCAA and MCAA were detected as the major byproducts in the early reaction times after the TCAA degradation started. The concentrations of both DCAA and MCAA increased in the first 40 min and then decreased till the end of the oxidation time. Clearly, after 100-min reaction time, the TCAA concentration decreased by more than 82%, additionally, other organic byproducts were present in the solution. This indicates incomplete TCAA degradation. Acetate and chloride ions were detected after ~10-min reaction time, indicating the stepwise degradation of TCAA.

DCAA degradation and the resulting byproducts are shown in Fig. 4(b). Unlike TCAA, DCAA degraded more efficiently, and at the end of the process, the DCAA concentration decreased by almost 97%. As noted for TCAA, the concentration of MCAA, the major byproduct of DCAA degradation, increased in the first 40 min and then decreased gradually. At the end of the process, the chloride and acetate ions had 120 and 10 μg L⁻¹ concentrations, respectively, indicating that Fe(VI)/UV process is more efficient for DCAA degradation than TCAA.

As both TCAA and DCAA are present in the natural environments, it would be useful to consider a mixture of these two HAAs in one reactor. The concentration of each HAA in the mixture solution was 250 μg L⁻¹, and the results are shown in Fig. 4. As shown in Fig. 4(c), clearly the degradation efficiencies of both the

| Table 8 | Kinetic constants, MBE, and dechlorination of TCAA and DCAA in Fe(VI)/UV process. |
|---------|----------------------------------|---------|---------|
|         | TCAA | DCAA | Combination |
| Time (min) | 40 | 40 | 38 | 38 |
| pH | 8 | 8 | 7.5 | 7.5 |
| HAA (μg L⁻¹) | 550 | 550 | 500 | 500 |
| k (min⁻¹) | -0.0179 | -0.0362 | -0.006 | -0.0149 |
| R² | 0.995 | 0.96 | 0.988 | 0.998 |
| MBE% | 4.21 | 4.07 | – | – |
| Dechlorination% | 22.82 | 43.63 | – | – |
compounds significantly decreased compared to those obtained when studied separately. In the mixture study, the maximum chloride concentration was 23 μg L⁻¹, which was very low compared to the separate TCAA and DCAA studies (see Fig. 4). After 100-min contact time, the highest reductions observed for TCAA and DCAA were 47.2% and 78%, respectively. Notably, when two HAAs were simultaneously present in the solution, the reduction efficiency of TCAA (35% less than the separate study) was significantly affected compared to DCAA (19% less than the separate study), and the results were in good agreement with those reported by Wang et al. (2009).

The kinetic constants, MBE, and dechlorination % of each HAA and their combination are shown in Table 8. The reduction of both HAA compounds followed real first-order reaction rate with higher R² values of 0.99 and 0.96 for TCAA and DCAA, respectively. It can be inferred from this Table that the individual DCAA reduction rate was two times higher than TCAA. On the other hand, when a combination of the two HAAs was studied, the degradation rate of both the compounds significantly decreased. However, the DCAA reduction rate was ~2.5 times higher than TCAA. Notably, in the mixture study, the degradation rates of TCAA and DCAA were 33% and 41% of their previous state, respectively.

Dechlorination of HAAs is the most common factor for comparing the degree of degradation of organochlorine pollutants. Based on the results obtained under the experimental conditions shown in Table 7, chloride formed by DCAA oxidation in Fe(VI)/UV process is much higher than TCAA degradation. Table 8 shows that DCAA dechlorination is two-fold higher than TCAA. The phenomenon can be explained by the fact that no hydrogen atom is present in the α-C bonds (Hirano et al., 2005) of TCAA, and the three chlorine atoms provide a larger space block, protecting it from the attack of oxidative agents. However, in the case of DCAA, one hydrogen atom is present in the α-C bond and could be easily broken by the attack of Fe(VI) or a stronger oxidative agent Fe(V). In addition, notably the dechlorination of TCAA achieved by Fe(VI)/UV process is almost three times higher (22.82% compared to 8.24%) than the amount obtained by Hu et al. (2014) using a sonophotolytic catalytic process for TCAA degradation. A comparison of the degradation rates for TCAA and DCAA in different oxidation processes is shown in Table 9. The Fe(VI)/UV process is more efficient than other processes, except O₃/UV process for DCAA degradation, which is almost 2.5 times more efficient than the Fe(VI)/UV process.

5. Conclusion

Degradation of the two most common HAAs, TCAA and DCAA, in drinking water was investigated either separately or in a mixture using the Fe(VI)/UV process. The results obtained in the individual study showed that DCAA can be easily degraded than TCAA. Both the degradation rate and dechlorination % of DCAA were almost two times higher than those obtained for TCAA. Mass balance analysis between the initial HAAs and byproducts formed during the treatment was completely successful. When both the compounds were simultaneously present in the solution, their degradation rate dramatically decreased. The degradation rates of TCAA and DCAA in their mixture were 33.5% and 41% of the individual degradation rates, respectively. Finally, it can be concluded that the Fe(VI)/UV process is promising for the degradation of recalcitrant organic pollutants. C–Cl and C–C bond cleavage is suggested as the main mechanism of HAA degradation; however, further studies on the exact degradation pathways are necessary.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2017.07.072.

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