Species-specific interaction of trihalomethane (THM) precursors in a scaled-up distribution network using response surface methodology (RSM)

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Abstract:

Response surface methodology (RSM) coupled with central composite design (CCD) was used to monitor and optimize species specific interaction of trihalomethane (THM) precursors in a scaled up distribution network (DN). Independent variables such as applied chlorine (Cl_2), contact time (t), humic acid (HA) and bromide ions (Br^-) were analyzed using full factorial CCD. Analysis of variance (ANOVA) revealed a good agreement between experimental data and proposed a two factor interaction (2FI) model (p = 0.04, R^2 = 0.7983). As a precursor, Cl^- and Br^- interaction with HA in various combinations was observed to affect THMs speciation. These precursor molecules were perceived least significant as discrete elements but product of HA: Br^- ratio and pH significantly impacted TTHM formation (r= 0.998, p = 0.007). This mutual interactive fraction was observed to be pH-dependent and influenced TTHM yield. Dibromochloromethane (DBCM) and Bromoform (BF) formation were observed pH dependent

provided sufficient Br^- in the system. Applied chlorine was significant (p = 0.01) while time had insignificant (p = 0.75) effect. Multiple response optimization suggested pH range between 6.0-7.6 and HA:Br^- ratio between 1.3-5.9 were satisfactory for maintaining TTHM concentration below ≤ 80µg/L in drinking water DN with a desirability function (D) of approximately 0.88.Their respective concentration may be minimized by changing precursor's individual concentration and possible combinations.

Key words: Trihalomethanes, Distribution network, Precursors, Chlorine, Response surface methodology (RSM)

1. Introduction

A water distribution network (DN) acts as a large chemical and biological reactor where numerous reactions take place. Chlorination of drinking water containing natural organic matter (NOM), mainly humic substances, leads to disinfection by-products (DBPs) formation [1-2] such as TTHM i.e., chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$). The later three brominated trihalomethanes (Br-THMs) are produced by reaction of hypo-bromite with humic acid [3]. Hassani et al.[4] showed that higher TTHM concentrations formed within DN while El-Shafeyet al.[5] reported that 45% of TTHMs were formed in treatment plant; the rest formed in pipelines. The carcinogenic and non-carcinogenic health effects showed an association between ingestion of chlorinated water and esophagus, pancreas, urinary tract, stomach, colon and rectal cancers and reproductive/developmental anomalies in laboratory animals [6-9]. Therefore recommended TTHM concentration in drinking water is set to be ≤80 µg/L by World Health Organization (WHO) [10]. This has led to the monitoring of their presence in drinking water for regulatory compliance, health risk assessment, epidemiological evaluation and water quality control purposes so measures may be taken to minimize or eliminate their presence. Moreover, as bromide ion concentration is not lowered by conventional drinking water treatment processes [11], the effect of Br^- concentration on trihalomethane formation potential (THMFP) is an important area of study.

TTHM species formation and their concentration depend on amount of organic matter, Br^- concentration, pH, water temperature (T), chlorine dose (Cl_2), residence time (t) and residual chlorine in DN [12-13]. In addition, their level in DN may increase due to continued presences of chlorine residuals [14].On the other hand, it is now accepted that pH plays a significant role in TTHM formation by affecting base-catalyzed reaction. Hua and Rekhow [15] observed TTHM concentration nearly three times higher at pH 10 than at pH 5. While discussing individual THMs species, Chaudhary et al. [16] found that by increasing pH from 6 to 8.5, chloroform increased while BDCM and DBCM formation was decreased. By increasing Br^- concentration, TTHM speciation shifted from chlorinated species to mixed bromochloro species to brominated species [17]. Zhu et al.[18] observed that when 1mg/L of Br^- was used at pH 8, TTHMs yield reached up to 270 % of that without bromide ions at pH 6. Earlier literature reports that it is not Cl^- or Br^- concentration that plays an important role in TTHM speciation in a DN but combination of TTHM precursor ratios. For instance, Nokeset al.[19] reported that formation of brominated trihalomethanes depends on (NaOBr):(NaOCl) or more simply Br^-: Cl^-. The hypochlorite ion (HClO) reacts effectively with humic acid in oxidation reactions but hypobromous acid ($HBrO^-$) is more predominant in electrophilic substitution. So in excess of NaOCl, NaOBr addition enhanced Br-THMs formation and reduced $CHCl_3$ formation. However, this formation was found to be pH independent and reaction time [3]. Working on effect of pH on TTHM formation, Singh et al.[20] in a five-factor Box– Behnken experimental design, found that water pH followed by reaction time and temperature were the most significant factors defining TTHM formation,and this is also consistent with Nikoloau [21].

Describing modeling of TTHM formation and speciation, most reported modeling and simulation were performed in closed systems like glass bottles, volumetric flasks and batch systems with high doses of chlorine for longer periods of time; from one week to twenty days. But complexity of the reactions between TTHM precursors and their relative importance could be better understood by a modeled simulation of a DN. Furthermore, a detailed insight into TTHMs formation/speciation with different precursors and various environmental conditions could be achieved relatively easily within a DN. Therefore in this workreal field conditions were replicated in the form of a DN reactor to model and simulate TTHM formation/speciation using response surface methodology (RSM). This was done by mapping the fine details in the area of

optimal response, determining the most desirable input values to get the optimal output and defining the permissible values for maximum process responses.

2. Materials and Methods

2.1 Design of Experiment (DoE) using CCD

RSMis useful for designing experiments, building models, analyzing and optimizing effects of several independent variables [22-23]. It also analyses the relationship between independent variables and resulted response [24-25]. Design Expert software (Trail version 9, Stat-Ease, Inc., MN) was used for experiment designing (DoE) tool involving CCD. The CCD is helpful to identify combined effectof independent variable by selecting experimental points at which response should be evaluated and optimized [26]. In the present study, time (A), pH (B), HA: Br^- ratio (C) and applied chlorine (D) were used as independent variables. The HA concentrations were 5, 7 and 10 mg/L while Br- ions concentrations were 0.5, 1 and 1.5 mg/L(Table 1), stated as HA: Br^- ratio. TheDoE, constructed using RSM-CCD, consisted of a fullfactorial 30 points(24 noncenter + 6 center)experimental runs to simultaneously optimize levels of these variables with optimized system performance

2.2 Construction of scaled-up DN

A scaled-up DN was built using high density poly ethylene (HDPE) pipe of 220 meters in two concentric loops connected to a main water reservoir. A continuous plug flow was maintained with a peristaltic pump and flow meter within the network (Fig. 1). Nine sampling ports, 22.5 meter apart, were provided to collect samples at various time/distance intervals. De-chlorinated tap water was introduced with various combinations of humic acid (HA) and Br^- for investigation of the factors affecting TTHM formation.

2.3 Standards and reagents

Prepared TTHM standards, dissolved in methanol, 5000µg/mL each, (Supelco; 99.9% purity) with Fluorobenzene (FB) (2000µg/mL) as internal standard were used. Stock solution of HA (Sigma-Aldrich) and commercial sodium hypochlorite (10.5 %) were freshly prepared and different dilutions were applied as per experimental design. Samples were taken at various time

intervals and residual chlorine concentration was quenched by adding 0.01N sodium thio-sulphate ($Na_2S_2O_3$) to cease further reaction [27].

2.4 TTHM extraction and analysis

TTHM extraction was performed by liquid-liquid extraction (LLE). In 10 mL of water sample, 1g sodium sulphate (anhydrous) was added and mixed vigorously for 30 sec followed by addition of 1 ml Methyl-ter-butyl ether (MtBE; Sigma-Aldrich), mixed on a vortex mixer for 90 sec and left undisturbed for two minutes. This salt addition, called salting out, enhances organic layer separation from water. One microliter (µl) of organic layer containing TTHMs was analyzed by gas chromatography (GC) (Model Claurus 500) with column (Restek Rxi-5ms, 30m x0.25mmID) coupled with mass spectroscopy (MS) for identification and quantification of TTHM composition. GC analytical conditions with MS configuration are given in Table 2 whereas respective chromatograph is illustrated in Fig. 2.

3. Results and Discussion

3.1 Effect of HA: Br^- on speciation of TTHMs

Various combinations of HA and Br^- species, as precursors of TTHMs, along with other independent variables were analyzed in a continuous system as per DoE depicted in Table 3. Results showed significant impact of both HA and Br^- species as B*C (product of HA: Br^- and pH) on TTHM formation with pH (r= 0.998, p = 0.007) as illustrated in Table 4.

Three dimensional (3D) plots were drawn to investigate the interactive effect of these factors on TTHMs speciation within experimental ranges given in Table 1. Observing the effect of HA:Br^- and pH on TTHMs formation in Fig. 3 (B = pH, C=HA: Br^-), it is evident that TTHM is high at low HA:Br^- concentration. This may be due to high availability of Br^- ions which resulted in a shift towards brominated species and an overall increase in TTHM concentration.

This fact was also explained by Hong et al. [28] that during chlorination, bromide quickly oxidized to bromine forming hypobromous acid (HOBr), a more powerful halogenating agent than hypochlorous acid (HOCl). The chlorinated species initially formed may be subsequently

attacked by HOBr to form brominated species in the presence of sufficient Br^- [29]. On the contrary, increasing the HA:Br^- ratio decreased TTHM species due to less brominated species formation. In absence or insufficient Br^- concentration, chlorinated species were the only products formed, resulting in decreased TTHM concentration, also shown by Liang et al.[30]. The role of HA:Br^- was observed to be dependent on pH of the system as at higher pH, THM formation yield was comparatively high even at the lower HA:Br^- ratios (x-axis, B=pH). The reasons for this could be the quick oxidation of bromide to highly reactive OBr^- or HOBr species, which are pH dependent [17].

Comparing pH and applied chlorine effect in Fig. 4(D = Chl., B = pH), TTHMs concentration at pH 8 was approximately 6 times higher when observed at pH 5, corroborating well with Rodriguez and Erodes [31]. This is due to the fact thatin TTHMformation,actual hydrolysis step is base-catalyzed, therefore boosted as hydroxyl concentration increases [9, 32]. Observing the individual species, BF concentration was formed almost twice times the other chlorinated species, showing thatmulti-brominated species formation is pH dependent provided sufficient Br^- within the system. On the other hand, when time was taken into consideration, TTTHM concentration increased with time (Fig. 5: C = HA: Br^-, A = Time). Hong et al.[28] also described that longer reaction times had a positive effect on TTHMs formation.

The significance of studied factors was analyzed by regression coefficients and ANOVA (Table 4). The factors having a *p* value less than 0.05 showed a positive impact on TTHM formation. The quality of the polynomial model equation was judged statistically by the coefficient of determination R^2as the model fit was controlled by the coefficient of determination R^2. The R^2value of 0.79, Adj. R^2 value of 0.57 and Pred. R^2 indicated a better response overall.

A significant two factor interaction model (2 FI, $p = 0.040$) was applied for best fit, based on 95% confidence level. The small valueof prediction error sum squares (PRESS) also signifies the present model [33], given as 7.87 suggesting that the developed model could predict response very well.Adequate precision greater than 4 is recommended by Yunardi et al.[34] and the results showed a value of 7.02 in this case. As expected, among the most significant factors, chlorine was observed to be a major contributor ($p = 0.01$) towards TTHMs formation. While product of

HA:Br^- and pH (BC) was observed significant (p= 0.007) to affect the TTHMs formation and speciation. Therefore according to the data analysis, it is a two factor interaction (2FI) model (p = 0.040) as shown in Table 4, describing the effect of two factor's mutual interaction in defining the overall process.

To represent the comparative significanceof the independent variables (Table 1) on TTHM formation, a Pareto chart of effects was created (Fig. 6). The minimal effect is presented in the upper portion which progresses to maximal effect in lower portion of the chart. These were observed as B (pH), C (HA: Br^-) and D (Chl), all being significant and BC (pH*HA: Br^-), CD (HA:Br^-*Chl) and BD (pH*Chl).

3.2 TTHM modeling

Regression modeling by RSM was performed on the responses of corresponding independent variables such as HA concentration, Br^- ion concentration, applied chlorine dose (Cl_2), pHand timeto the dependent variable i.e., TTHM concentration. Statistically significant factors are summarized in the form of a model equation for the formation and speciation of TTHMs in a distribution network as follows:

THMs (mg/L) = 2.61 +0.99 B - 0.71 C +1.74 D – 0.44 AB - 2.26 BC +0.64 BD-0.89 CD

Eq. 1

Where: A = Time (hours)

B = pH

C = HA:Br^- ratio

D = Applied chlorine (mg/L)

The proposed mathematical approach provides a critical analysis of individual and simultaneous interactive influences of the selected independent variables. The coefficient of the equation demonstrated that they were sensitive in predicting TTHM formation.

3.3Verification of model

The proposed CCD matrix was tested to analyze and compare the effects of independent variables described in Table 1 on TTHM formation, and the experimental and predicted results are summarized in Table 3. From the normal probability plots of the residuals, it is evident that the data points are situated around the same straight line (Figure 7) confirming a very good fit to the model [35]. These data points indicate that neither response transformation was required nor was there any apparent problem with normality.

4. Multiple response optimization

Optimization of the operational conditions for studying the response (TTHM formation) was carried out for practical purposes.

4.1 Numerical optimization

Numerical optimization finds one point in independent variable's range that would maximize the response (TTHMs formation/speciation) as objective function. It involves combining the goals into an overall D function that ranges from zero outside of the limits to one at the goal [36]. Having a D value closer to 1 is considered most desirable. For an HA:Br^-=7.5, pH = 7.3 and Cl_2=5.61, the probability of TTHM formation was optimized as lower than the recommended 80 µg/L in approximately 12 hours with a D value of approximately 0.88 (Fig.8).

4.2 Graphical optimization

The overlay plots allow for a visual selection of the optimum conditions according to a certain criterion, i.e., to minimize TTHMs concentration (Fig.9). The yellow/shaded areas show that the criterion was fully met in this region. The region of pH between 6.0 -7.6 and HA:Br^- between 1.3-5.9 seems safe with respect to the formation of TTHMs below the recommended level (Fig. 9).

5. Conclusions

Thecurrent study shows that CCD may be applied in modeling of the contribution of TTHM precursors and optimization of associated factors in formation and speciation of TTHMs in a scaled up DN.

TTHM formation and speciation is controlled by various factors in a DN and chlorine was observed as the most significant factor. The other important factors were pH, time and HA: Br^- ratio. These factors were observed to be least significant as discrete elements but the product of HA:Br^- ratio and pH significantly impacted TTHMs formation more than the individual contributions (r= 0.998, p = 0.007). The pH of the solution was found to be synergistic to TTHMs formation as 2FI mechanism resulted in higher yield of TTHMs, whilst brominated species formation was observed pH dependent, provided sufficient Br^- in the system. The graphical optimization and overlay plots showed formation of TTHM could be kept below the WHO recommended level i.e., 80 µg/L at a pH range between 6.0-7.6 and HA:Br^- between 1.3-5.9.

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7. References

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Table 1. DoE using independent variables with their low and high levels values by CCD

Coded values		-α	-1	0	+1	+α
Variables		**Lowest**	**Low**	**Centre**	**High**	**Highest**
Time (Hours)	A	0	4	16	24	32
pH	B	5	6	7	8	9
HA: Br-	C	1.5	3.33	4.44	6.66	7.5
Applied chlorine (mg/L)	D	1	3	5	7	9

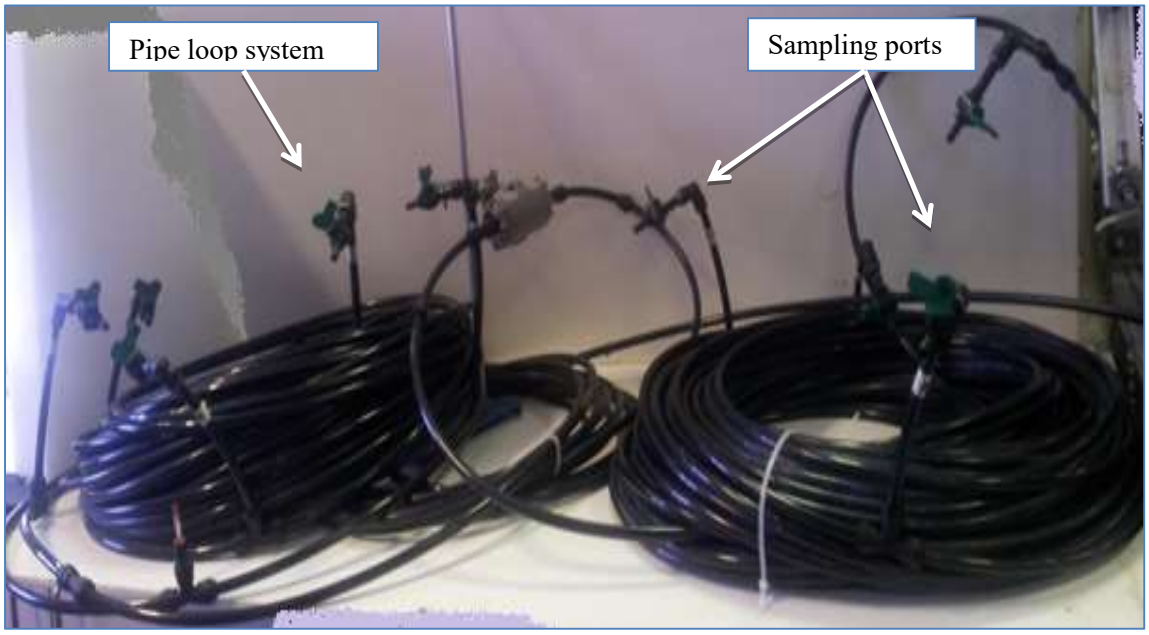

Fig. 1 Scaled-up distribution network

Table 2. GC/MS operating conditions and MS configurations for TTHMs

Injection	**Auto sampler**	
Experimental time (min)	30.0	
Injection volume (µL)	1.0	
Delay time (min)	0.00 min	
Initial temperature	52ºC for 5 min	
Ramp	7ºC/min to 180ºC	
Hold time (min)	2	
Compounds	**Retention time (min)**	**m/z**
Chloroform	3.16	50,70, 95, 96
Fluorobenzene (Internal Standard)	4.41	47, 83,85,87
Bromodichloromethane	5.44	47,48,83,85
Dibromochloromethane	8.61	47,48,127,129,131
Bromoform	11.89	91, 93, 171, 173, 175

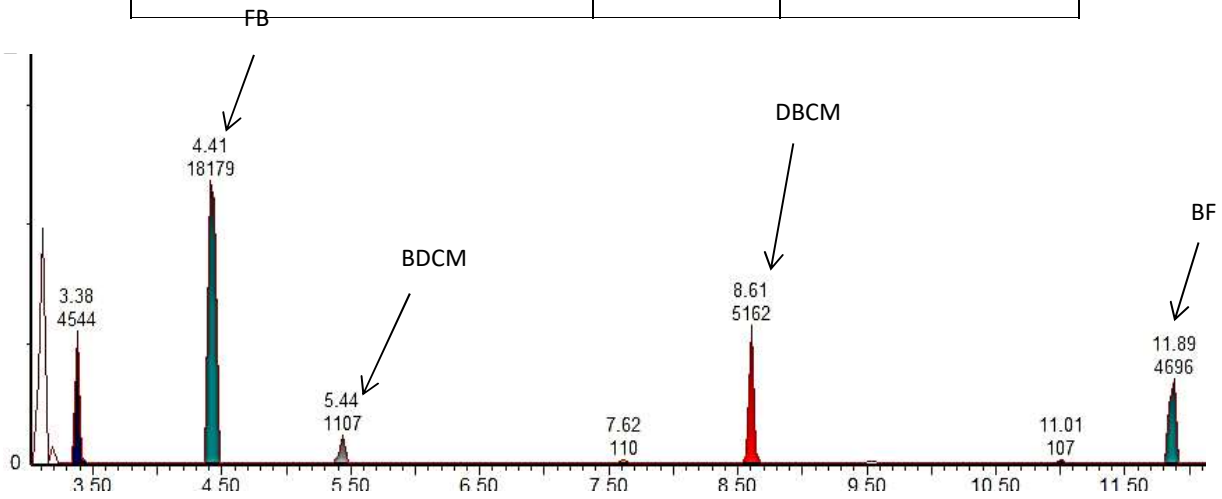

Fig. 2 The GC chromatograph of THM_4 compounds

Table 3. DoE using CCD with respective experimental and predicted results

Std. Order	Run Order	Pt. Type	Blocks	Time (Hours)	pH	HA/Br-Ratio	Applied Chl. (mg/L)	TTHMs Experimental (µg/L)	TTHMs Predicted (µg/L)
4	1	1	1	24	8	3	3	1734.78	1713.54
20	2	-1	1	16	9	4.5	5	3732.58	3700.21
13	3	1	1	8	6	6	7	10599	10500.14
12	4	1	1	24	8	3	7	34158.4	33541.7
5	5	1	1	8	6	6	3	683.344	676.75
11	6	1	1	8	8	3	7	16618.1	16435.2
28	7	0	1	16	7	4.5	5	2069.1	2054.7
6	8	1	1	24	6	6	3	101.726	99.465
7	9	1	1	8	8	6	3	2083.27	2079.8
8	10	1	1	24	8	6	3	1143.55	1134.67
9	11	1	1	8	6	3	7	1594.17	1591.7
21	12	-1	1	16	7	1.5	5	1313.73	1301.99
17	13	-1	1	0	7	4.5	5	461.358	458.67
25	14	0	1	16	7	4.5	5	2470.45	2450.99
2	15	1	1	24	6	3	3	1105.49	1100.65
23	16	-1	1	16	7	4.5	1	796.278	787.9
3	17	1	1	8	8	3	3	3815.29	3799.98
26	18	0	1	16	7	4.5	5	1298.9	1300.00
22	19	-1	1	16	7	7.5	5	1329.27	1315.90
1	20	1	1	8	6	3	3	1453.28	1440.24
31	21	0	1	16	7	4.5	5	1608.76	1600.45
15	22	1	1	8	8	6	7	1139.18	1138.69

10	23	1	1	24	6	3	7	999.099	1000.56
30	24	0	1	16	7	4.5	5	1686.82	1680.98
16	25	1	1	24	8	6	7	945.452	943.50
14	26	1	1	24	6	6	7	22973.6	22960.40
29	27	0	1	16	7	4.5	5	1789.47	1781.87
19	28	-1	1	16	5	4.5	5	658.301	656.541
27	29	0	1	16	7	4.5	5	1830.4	1827.8
18	30	-1	1	32	7	4.5	5	1869.98	1860.67

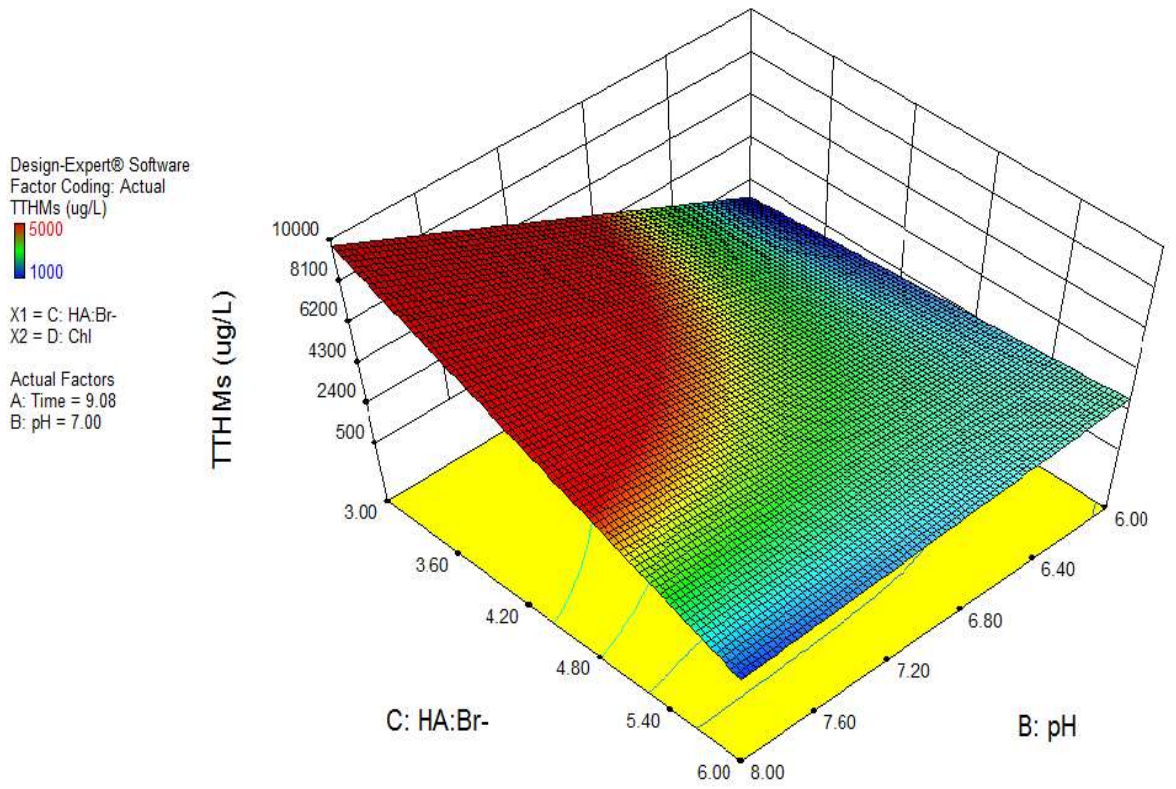

Fig.3. 3D graph of TTHM formation showing effect of HA: Br^- and pH

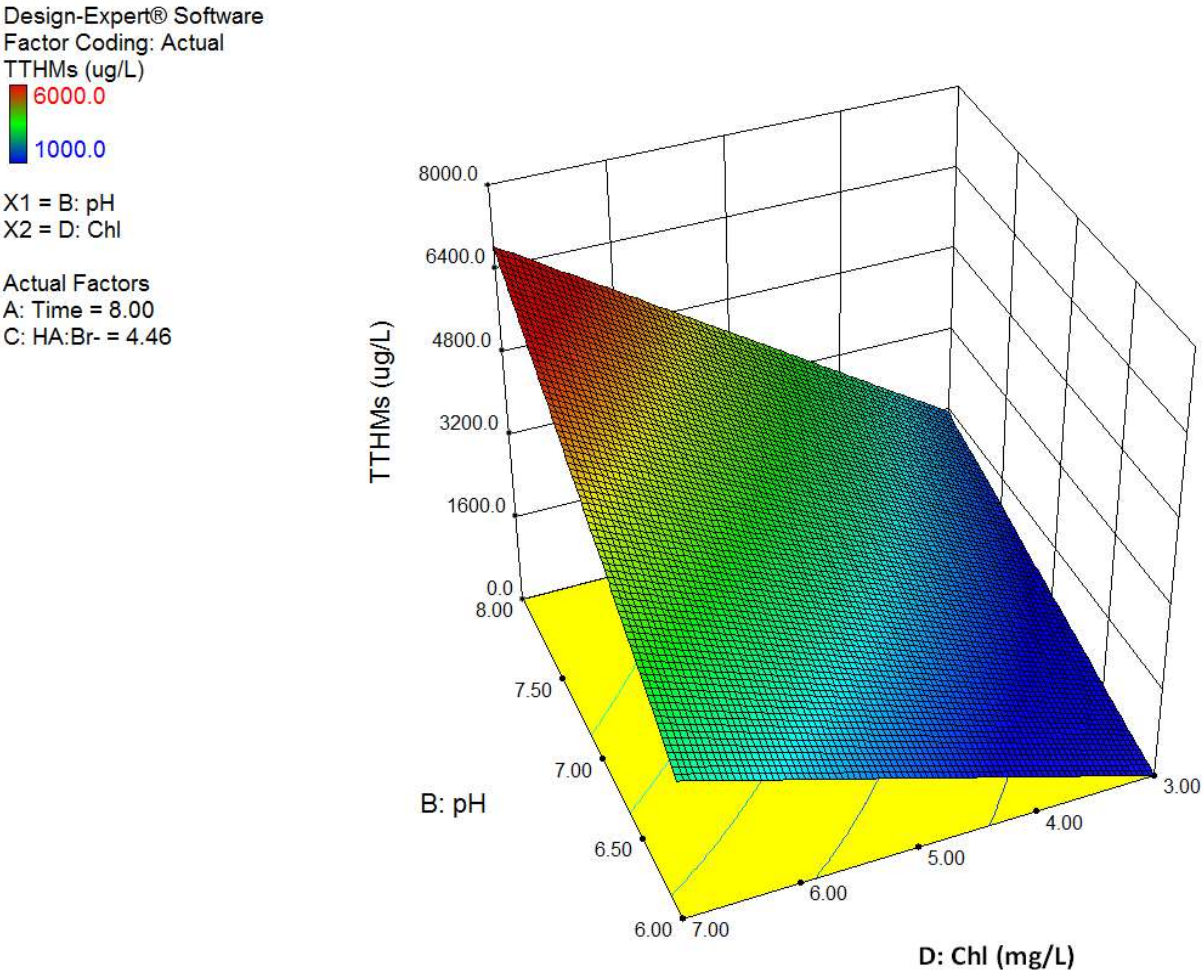

Fig.4. 3D graph of TTHM formation showing effect of pH and chlorine (mg/L)

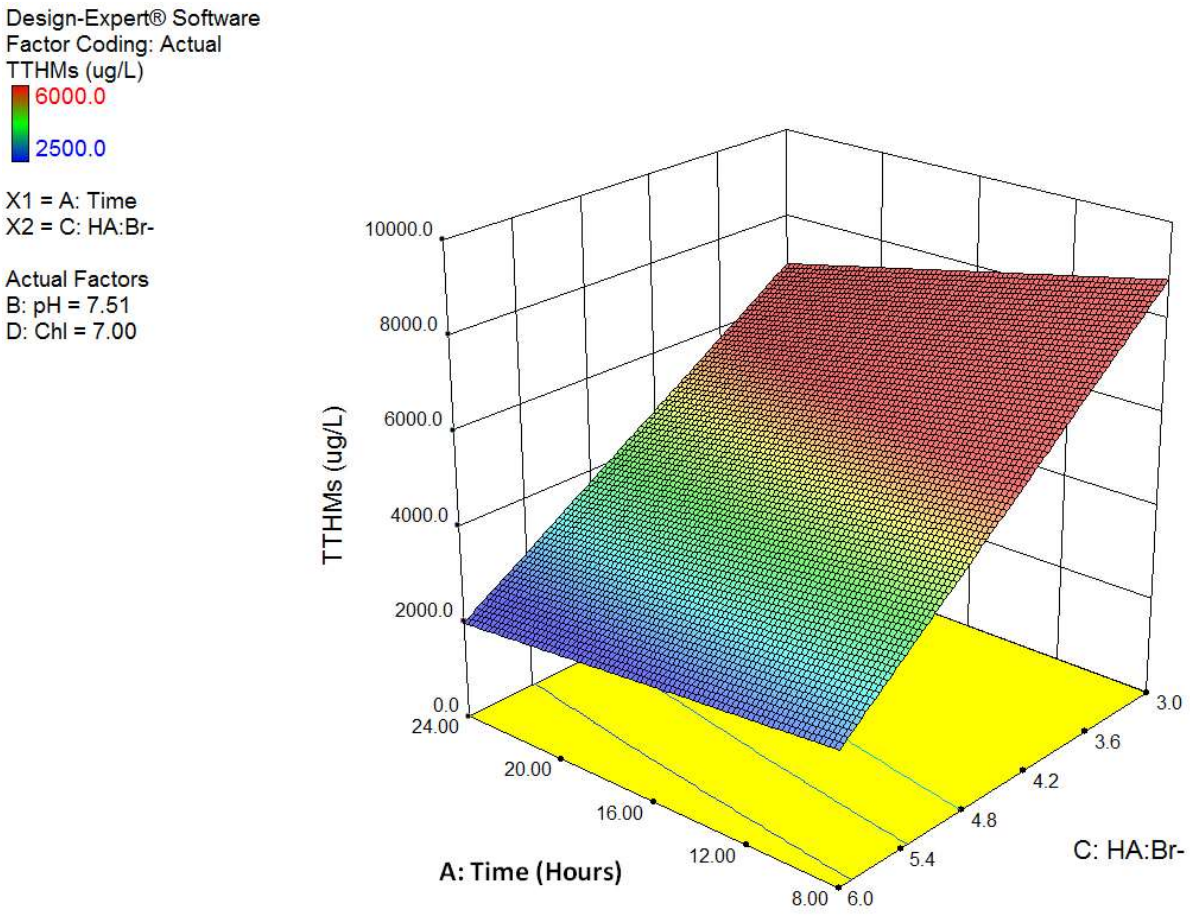

Fig.5. 3D graph of TTHM formation showing effect of HA: Br- and Time

Table 4. Analysis of Variance (ANOVA) for TTHMs formation

Source	Sum of Squares	df.	Mean square	F value	*p* value
Model	214	10	21.40	2.40	0.040
A-Time	0.89	1	0.89	0.10	0.7548
B-pH	23.38	1	23.38	2.62	0.1218
C- HA: Br-	11.98	1	11.98	1.34	0.2606
D- Chl	72.40	1	72.40	8.12	0.0102
A*B	2.70	1	2.70	0.30	0.5881
A*C	1.27	1	1.27	0.14	0.7095
A*D	0.89	1	0.89	0.10	0.7551
B*C	81.40	1	81.40	9.13	0.0070
B*D	6.46	1	6.46	0.72	0.4015
C*D	12.61	1	12.61	1.42	0.2488
Residual	169.31	19	8.91	--	--
Lack of fit	167.90	14	11.99	42.58	0.0003
Pure error	1.41	5	0.28	--	--
Corrected total	383.31	29	Mean	2.61	
SD	2.99		Press	7.87	
CV	114.42		Adeq*. Pre	7.208	
R^2	0.7983		Adj*. R^2	0.5758	
Pred. R^2			-1.0540		

Note: SD = Standard deviation, CV= Covariance, Adeq. = Adequate, Adj. = Adjusted,

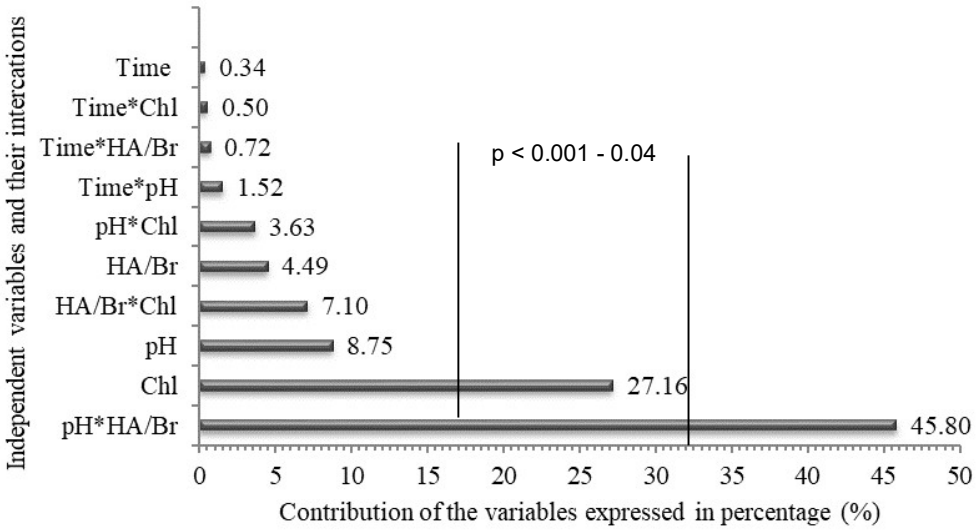

Fig.6. Pareto chart of standardized effects of independent variables and their interactions with percent contribution; Note: * is the multiplication sign.

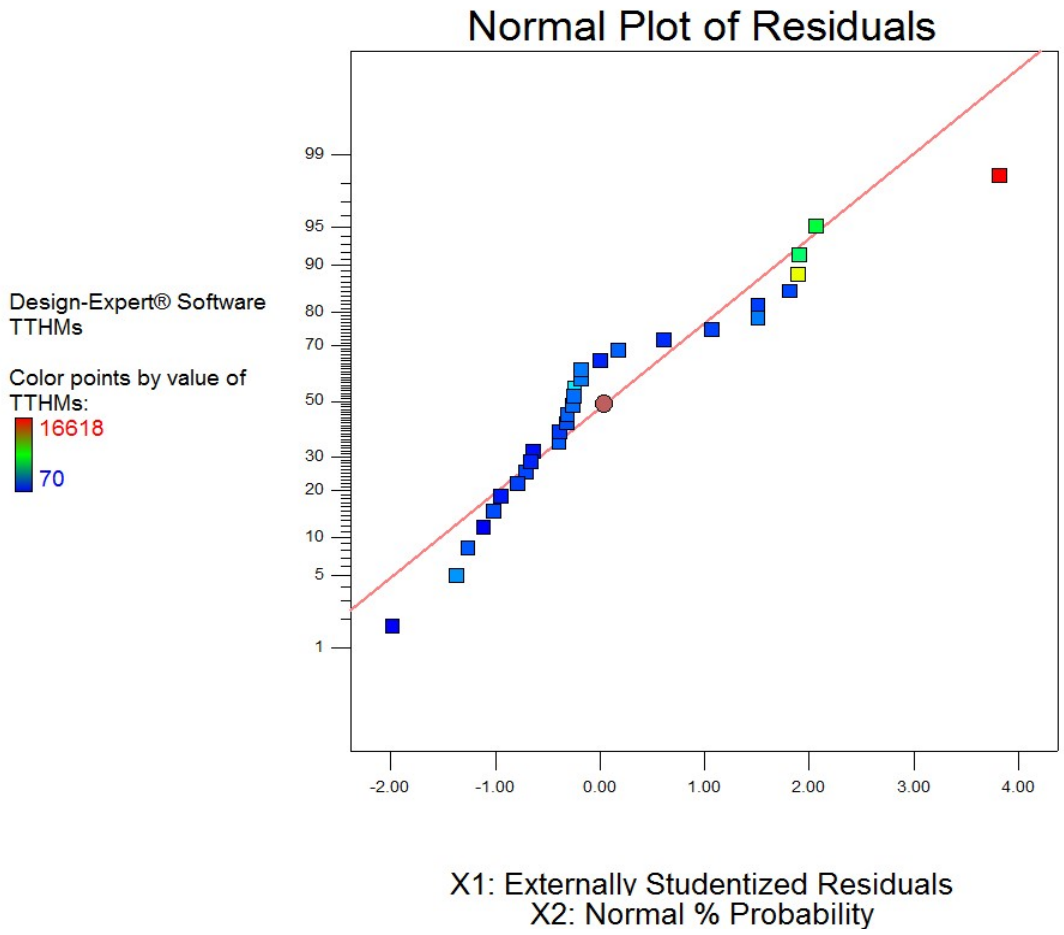

Fig.7. Verification of the model showing Normal plot of Residuals

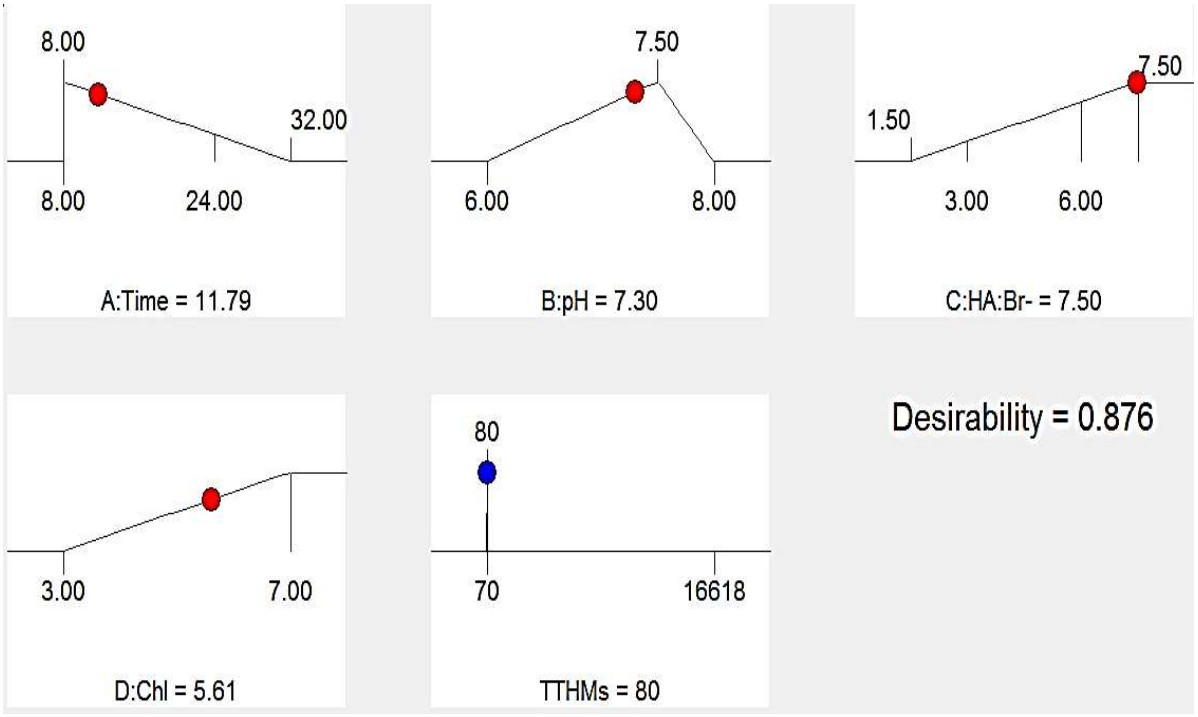

Fig. 8. Ramp function shows the region of optimal conditions of studied precurors for TTHM formation, ≤ 80 µg/L

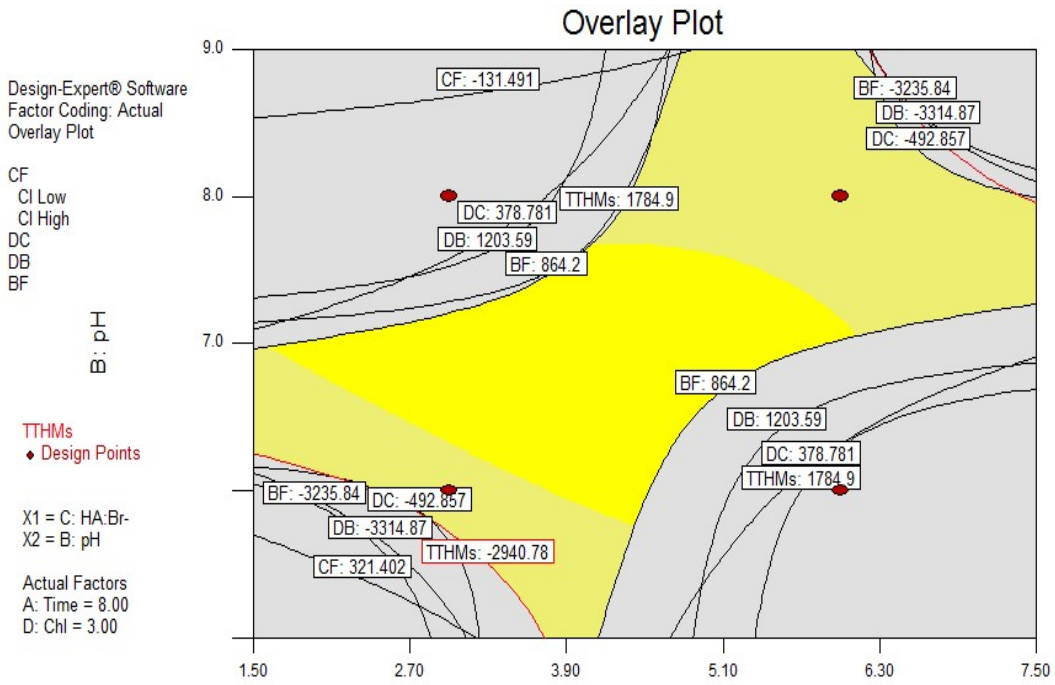

Fig. 9. Overlay plot shows the region of optimal conditions of HA/Br^- and pH for TTHM formation, ≤ 80 µg/L as response