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WATER QUALITY ASSESSMENT, STATISTICAL ANALYSIS AND KINETICS OF TRIHALOMETHANES FORMATION IN DRINKING WATER SUPPLIES - A COMPLETE BATCH STUDY

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Abstract

The study attempted to identify the best suited models to determine the kinetics of chlorine decay and trihalomethanes (THMs) formation in drinking water supplies. Batch experiments were conducted on synthetic water samples to simulate the characteristics of raw water collected from Maithon water treatment plant (MWTP), Dhanbad, Jharkhand, India. Influence of various parameters like total organic carbon (TOC), reaction time, pH and chlorine dose on the rate of THMs formation were analysed. The studies revealed that above 50% of THMs were formed within the first 83.65 min. Later on the reaction rate decreases and it takes 7.32-9.26 hours for 99% formation of total THMs. Pearson correlation matrix dictated strong correlation of reaction time followed by pH, dose and TOC with THMs formation. Principal component analysis (PCA) demonstrated that dissolved organic carbon (DOC) is the most influencing parameter for THMs formation. Chlorine decay kinetics followed second order reaction and the rate constant was found to be 0.0131 L/mg.min⁻¹. THMs formation kinetics was analysed by Clark and Kavanaugh model. Validation results indicated lower error of prediction (< 6%) for Clark's model than Kavanaugh model (< 20%). Thus, it was observed that Clark's model more suitably predicts the formation of THMs in Indian drinking water supplies.

Key words: chlorine decay, drinking water, kinetics, model, trihalomethanes, validation

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1. Introduction

Disinfection of water is performed to achieve the removal of pathogenic micro-organisms and safeguard the environment and public health. Chlorination is the most widely used procedure for the disinfection of water (Kunigk et al., 2018; Lu et al., 2009). Rules and regulations have been developed under the Safe Drinking Water Act (SDWA) and has been included in standard guidelines for drinking water (IS 10500, 2012) to ensure that the protection is maintained. Surface water treatment requires a minimum level of 0.2 mg/L residual chlorine when

water enters the distribution system. Studies show that aqueous chlorine reacts with a wide variety of organics such as methyl ketones, acetaldehydes, ethanol, secondary alcohols etc., in water to form a byproduct of chlorination i.e. trihalomethanes (THMs) in water which are designated as probable human carcinogens (USEPA, 2011). Literature studies reported that the rate of THMs formation is significantly affected by various environmental factors such as pH, temperature, dissolved organic carbon (DOC), type of organic precursor, presence of inorganic species such as bromide/iodide, and water quality operational factors like applied chlorine dose

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and contact time (Lu et al., 2009; Roccaro et al., 2014; Uyak et al., 2007; Zhang et al., 2009). Amongst these, DOC is the most important factor in the formation of THMs and designated as an indirect measure of disinfection by-product (DBPs) precursors by the U.S. Environmental Protection Agency (USEPA). The presence of halogenated species i.e. bromine and iodine also play an important role in the formation of various types of halogenated byproducts such as chloroform, bromoform, iodoform etc. The formation of THMs takes place via the classical “haloform reaction” (March, 1992). However, there is some disagreement regarding quantitative reactions between chlorine concentration and rate of THMs production.

Over the years, many mathematical models have been reported in literature to predict THMs in chlorinated drinking water (Clark and Sivaganesan, 1998; Dippong et al., 2019; Gang et al., 2002; Kumari and Gupta, 2015; Ohar and Ostfeld., 2014). These models can be classified into two main categories, one based on empirical and another based on kinetics during chlorine reaction (Bixiong et al., 2011; Di Cristo et al., 2013). Empirical models are based on THMs and water quality parameters, which affects their formation (Abdullah et al., 2003; Kumari and Gupta, 2015; Singh et al., 2012). Kavanaugh et al. (1980) conducted batch chlorination experiments for determining the rate of THM formation as a function of precursor type, chlorine dose, TOC levels, and pH. But the applicability of these models become inappropriate and uncertain as the water quality parameters and environmental conditions varies from one country to another (Hong et al., 2007; Samios et al., 2007). Kinetic models are based on the chlorine decay and THMs formation kinetics, and can be effectively used only if the kinetic rate constants are known (Di Cristo et al., 2013). A number of chlorine decay model have reported in literature (Clark and Sivaganesan, 1998; Di Cristo et al., 2014; Kavanaugh et al., 1980). Hua et al. (1999) reported the effect of water quality parameters on the bulk decay constant of free chlorine and found an empirical relationship

between initial chlorine concentration and the bulk decay constant (k_b) for a fixed temperature. Peters et al. (1980) found that the rate of THMs formation highly dependent on chlorine concentration. A linear relationship observed between chlorine concentration and THMs levels in drinking water (Hua and Vasyukova., 2015). Rossman et al. (2001) defined bulk chlorine decay based on reactions with dissolved and suspended organic matter in the water. Clark (1998) showed that THMs formation can be characterized as a function of chlorine demand based on second order reaction kinetics.

Presence of large number of variables limits the applications of chlorine decay models. Hence, it becomes quite difficult to identify appropriate models for predicting the chlorine decay or formation of THMs. The present study is an attempt to identify the applicability of best suited empirical and kinetic models for chlorine decay and THMs formation in drinking water. The study also analyzed the role of water quality operational parameters such as NOM, reaction time, pH and chlorine dose on the rate of THMs formation.

2. Material and methods

2.1. Study area

Raw and treated water samples were collected from Maithon water treatment plant (MWTP), Dhanbad, Jharkhand, India. MWTP is located at a latitude of 23°46'47.13 N & longitude of 86°48'42.11 E. MWTP was established in the year 2011 with a capacity of 14.5 MLD, but it supplies only 7 MLD of treated water to the nearby local population. Barakar river is the source of raw water to MWTP. The location map of WTP was developed using ARCGIS 10.5 and depicted via Fig. 1. The WTP follows the conventional method of treatment which comprises of coagulation-flocculation, sedimentation, filtration, and chlorination/disinfection. The flow diagram of MWTP unit operations is shown in Fig. 2.

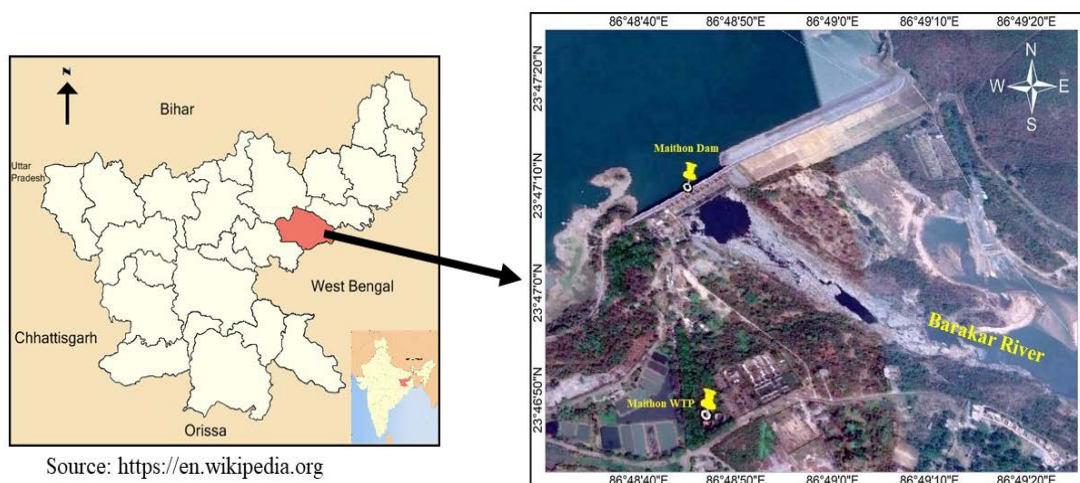


Fig. 1. Location map of Maithon water treatment plant (MWTP), Dhanbad, Jharkhand

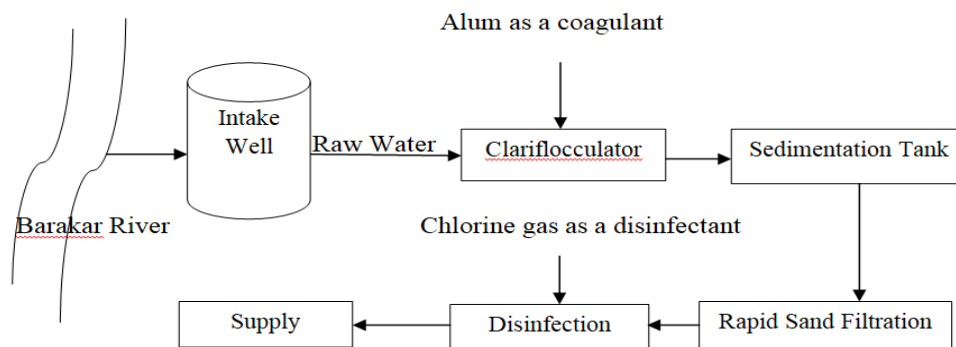


Fig. 2. Flow diagram of Maithon water treatment plant (MWTP), Maithon, Dhanbad, Jharkhand, India

Triplicates water samples were collected from two sampling points (raw and treated water) for a period of two months. The samples were collected in clean and dry 1 L polypropylene bottles. For THMs analysis, the samples were separately collected in 125 mL glass bottles and ascorbic acid, a quenching agent was added to stop further reaction (Kristiana et al., 2014). pH, temperature and residual chlorine were analyzed at the time of sample collection. On site analysis of residual chlorine was carried out using HACH Kit. For analysis of other parameters, the samples were brought to laboratory at Indian Institute of Technology (ISM) Dhanbad, stored at under 4°C and analyzed within 2-3 days.

2.2. Experimental protocol for batch experiments

Batch experiments were conducted on synthetic water samples to simulate the raw water characteristics as a function of pH, chlorine dose, TOC and reaction time on the rate of THMs formation. Synthetic water was prepared by mixing treated water collected from MWTP and distilled water in 1:1 ratio. Humic acid solution (10 mg/L) was prepared by adding 1g of powdered humic acid (analytical grade, Lobachemie) in 0.1M NaOH (100 mL) and diluted to 1L. In order to achieve complete dissolution of particles, the solution was stirred @ 25 rpm for 1 hour followed by pH adjustment using 0.1M HCl/NaOH. The synthetic kaolin turbid suspension was prepared by adding 2.5 g of kaolin powder in 500 mL of distilled water and stirred @ 30 rpm for 1 hour (Ndabigengesre et al. 1995). The supernatant of the suspension was used as a stock solution for the preparation of synthetic water. Humic acid solution was added to the synthetic water and turbidity was adjusted using kaolin suspension. The study was conducted at variable TOC concentration (2, 3, 4, 5, 6 mg/L), chlorine dose (0.5, 1, 2, 3, 4, 5, 10 mg/L) and pH (5, 6, 7, 8, 9).

For the chlorine decay tests, the samples were stored in zero-head-space, amber bottles at ambient temperature. Stock solution of sodium hypochlorite (NaOCl, 4% active chlorine, Sigma Aldrich) was prepared. Ascorbic acid (0.1g) was added to each bottle at the end of the desired reaction time to stop further reaction. Individual bottles were then opened

at different times, chlorine residuals measured, and the residual values were plotted against time.

2.3. Statistical analysis

The data obtained were statistically evaluated for mean, standard deviation (SD) and coefficient of variation (CV %) using Microsoft Office Excel 2010 (Microsoft, USA). Statistical Package of Social Sciences (SPSS, version 22.0) was used for determining the correlation of various water quality parameters on THM formation. Principal component analysis (PCA) based on observed THMs concentration was performed to determine their distribution pattern in the sampling area and in water sources, using SPSS software (Version 22.0). The principal components were extracted with Eigen values > 1.

2.4. Kinetics of chlorine decay

Chlorine decay kinetics was evaluated using first-order and second-order equations as mentioned via Eqs. (1-2), respectively (Clark et al., 1993):

$$C(t) = C_0 e^{-kt} \quad (1)$$

$$C(t) = \frac{C_0}{1 + C_0 k t} \quad (2)$$

where: $C(t)$ is the chlorine concentration (mg/L) at time t ; C_0 is the initial chlorine concentration (mg/L); t is the reaction time, and k is the rate constant of the reaction.

2.5. Kinetic model for THMs formation

Batch experiments were conducted as a function of reaction time, TOC, pH and chlorine dose for determining the rate of THMs formation. Clark's and Kavanagh's second order model were evaluated to analyse the kinetics of THMs formation using Eqs. (3-4), respectively.

$$TTHM = T \left\{ C_{Ao} \left[\frac{C_{Ao}(1-R)}{1 - R e^{-kt}} \right] \right\} + M \quad (3)$$

where: T is a dimensionless parameter; C_{A_0} is the initial chlorine residual (mg/L); R (dimensionless) and u (min^{-1}) are the parameters of chlorine decay model; M represent the estimated value of TTHM at time zero.

$$\frac{1}{A_0 - \frac{3C}{f}} = \frac{3k_3 B t}{f} + \frac{1}{A_0} \quad (4)$$

where: A_0 is the initial chlorine dose; B is the concentration of organic precursor (TOC); C is the concentration of total THMs; f is the moles of THMs formed per moles of chlorine consumed; k is the reaction rate constant. The concentrations of all the parameters are in molar units (e.g., m M).

2.6. Analytical methods

pH measurements were carried out using a Multi-parameter water analysis kit. TOC was analysed by high-temperature Combustion-Infrared method 5310-B (APHA, 2012) using SHIMADZU TOC-L/CSH/E200 with NDIR detector equipped with Pt catalyst. For dissolved organic carbon (DOC) content, samples were filtered through 0.45 μm Millipore filter paper and analysed by combustion-infrared method 5310-B (APHA, 2012). Residual chlorine concentration in the samples was determined by DPD colorimetric method, standard method 4500-Cl-G (APHA, 2012). Turbidity was analyzed by Nephelometric method, 2130 B (APHA, 2012). The determination and quantification of THMs was carried out using Chemito CERES 800 Plus Gas Chromatograph (Thermo Fischer) equipped with an electron capture detector (ECD) and Ni^{63} as catalyst. Liquid-liquid extraction using pentane as a solvent was used for the recovery of THMs from aqueous samples. The analytical procedure for THM analysis is adopted from elsewhere (Kumari et al., 2015). Trihalomethane formation potential (THMFP) was measured as per standard method, 5710-B (APHA, 2012).

2.7. Quality control

For THMs analysis, a 6-point calibration curve was used to identify the linearity of the method. The regression coefficient for all the THMs ranged from 0.992 to 0.999 and precision in terms of coefficient of variation ranged from 5 to 7 %. Limit of quantification (LOQ) and limit of detection (LOD) was determined from the standard deviation (s) of the response from

0.1 $\mu\text{g/L}$ THM standard solution. Calibration standards of THMs (Purity 99.5%) was purchased from Sigma Aldrich (Germany). If the relative per cent difference between the two samples was more than 5%, the instrument was recalibrated and samples were re-analyzed. All chemical reagents used were of analytical grade available.

3. Results and discussion

3.1. Characterisation of raw and treated water

The physiochemical parameters like pH, turbidity, conductivity, alkalinity, TOC, DOC, UV_{254} and specific ultraviolet absorbance (SUVA) in the raw and treated water were assessed to determine the water quality (Table 1). The free residual chlorine concentration in the treated water was found to be 0.14ppm, which is less than the prescribed standard of 0.2 ppm (IS 10500, 2012).

Concentration level of THMs in the treated water samples was found to be 484 ± 2.5 $\mu\text{g/L}$. Amongst different THMs, CHCl_3 was the predominant one (461 ± 1.9 $\mu\text{g/L}$) and exceeded the prescribed USEPA regulatory standard of 80 $\mu\text{g/L}$. Other THMs compounds, CHBr_2Cl (13 ± 1.6 $\mu\text{g/L}$) and CHCl_2Br (10 ± 1.1 $\mu\text{g/L}$) falls within the prescribed regulatory standards whereas Bromoform was not detected in any of the analysed samples. The study indicated that chlorinated THMs are more predominant than brominated THMs and followed the order: $\text{CHCl}_3 > \text{CHCl}_2\text{Br} > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$. The observed order is consistent with other studies reported in the literature (Karim et al., 2011; Legay et al., 2011; Pardakhti et al., 2011).

3.2. Reaction kinetics of THMs formation

3.2.1. Influence of reaction time on THMs formation

The study revealed that the rate of formation of THMs was fast in the first 90 min of the reaction and thereafter the rate of increase was marginal (Fig. 3a). More than 94% of the THMs were formed within the first 90 min beyond which it did not vary significantly and took approximately 7.32 hrs for 99% formation. This may be attributed to the rapid rate of reaction between chlorine and active group which leads to the quick formation of THMs in the beginning whereas, as the reaction proceeds, a marked reduction in the amount of free chlorine and reactive groups occurred which slowed down the formation of THMs (Hong et al., 2013).

Table 1. Physiochemical characteristics of raw and treated water samples (N=180, average values are reported)

Sample	pH	Turbidity (NTU)	Conductivity ($\mu\text{S/cm}$)	Alkalinity (mg/L)	Residual Chlorine (Cl_2/L)	TOC (mg/L)	DOC (mg/L)	UV_{254} (/cm)	SUVA (L/mg/m)	THM ($\mu\text{g/L}$)
Raw water	7.8	34	167	105	-	4.87	4.41	0.189	4.28	-
Treated water	7.2	1.8	123	78	0.14	4.15	3.97	0.134	3.37	484

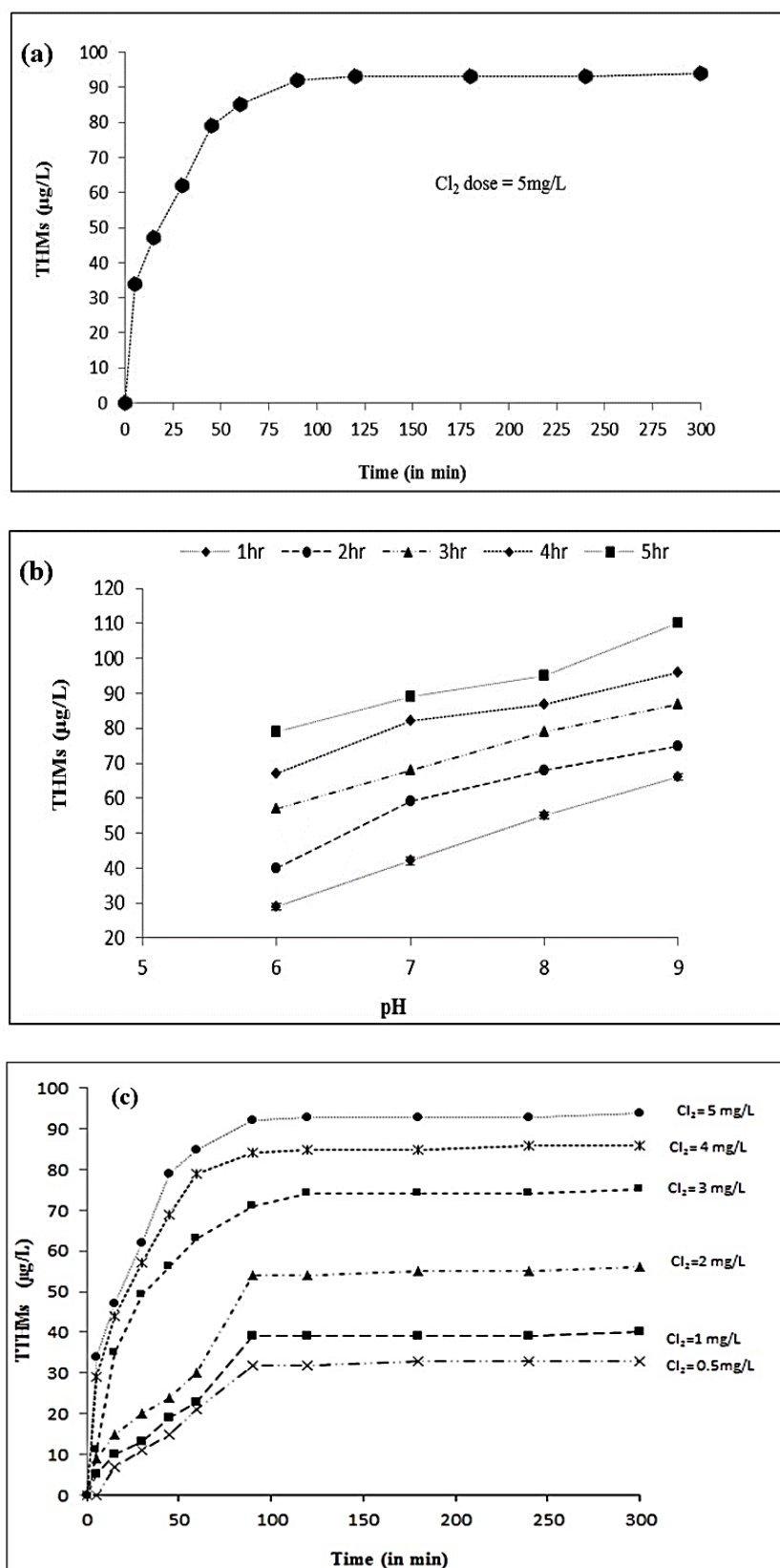


Fig. 3. Effect of parameters on rate of THMs formation (a) Reaction time (b) pH (c) chlorine dose

Thus, the formation of THMs mainly occurred in two different stages i.e. an initial faster stage wherein the reaction was completed within the first few hours and a slower, later, stage was marked by a steady rate of increase. Peters et al. (1980) reported

that during chlorination, organo-chlorine intermediates are formed which undergo slow conversion to THMs. The overall rate of THMs formation followed pseudo-first order reaction and the rate constant (k) was found to be 0.0035 min^{-1} , which

is line with the values reported by other researchers (Amy et al., 1991; El-Dib and Ali, 1995).

3.2.2. Influence of pH on reaction rate

The study observed that formation of THMs was found to depend on pH and increases with increase in pH as can be seen in Fig. 3b. The maximum percentage increase (44.82%) occurred between pH 6-7, thereafter, the rate of increase decreased with increase in pH. This may be attributed to the fact that at pH 5-7, the HOCl will generally exist without dissociating into OCl⁻ ions which is 80 times more reactive than OCl ions.

As the pH increases, the percentage of OCl⁻ increases which in turn reduces the rate of THMs formation. Below pH 5, chlorine remains in elemental form and the acidic functional groups of NOM molecule are not ionized, thereby reducing their solubility and stability leading to the accumulation of unreacted NOM. Thus, fewer sites of NOM molecules are available for attack by chlorine thereby reducing THMs formation (Adin et al., 1991). Chen et al. (2005) also reported the THMs concentration increased with increasing pH value in the range of 5-10.

3.2.3. Influence of chlorine dose on THMs formation

The effect of variable chlorine dose on THMs formation with respect to time was studied at fixed precursor concentration. The study revealed that an increase in the chlorine dose leads to increase in the rate of THMs formation (Fig. 3c). 50% of the THMs was formed within the first 66.08-83.65 min, indicating faster rate of reaction.

However, remaining 49% of THMs were formed in 9.26 hours (Table 2). Jedas-hecart et al. (1992) and Ventresque et al. (1990) reported that chlorine decay occurs into two different phases, i.e., an initial phase of immediate consumption and the second phase of its slower consumption. An overall decrease in reaction time was observed at higher doses which may be attributed to increase in the rate of reaction i.e. from 0.0113 to 0.0165 min⁻¹.

Table 2. Kinetic data of THMs formation as a function of chlorine dose

Parameter	Kinetic data		
	k (min ⁻¹)	$T_{0.5}$ (min)	$T_{0.99}$ (hr)
Chlorine dose			
0.5 mg/L	0.0113	83.65	9.26
1 mg/L	0.0119	82.22	9.10
2 mg/L	0.0123	79.08	8.76
3 mg/L	0.0141	74.44	8.24
4 mg/L	0.0163	67.08	7.43
5mg/L	0.0165	66.08	7.32

Therefore, it was found that the formation of THMs is not directly proportional to the applied chlorine dose. According to Trussell and Umphres (1978), the formation of THMs with respect to chlorine follows first order reaction while it is the third order with respect to organic precursors. This may be

attributed to the fact that not all organics act as THMs precursors besides several other halogenated compounds were also formed (Rook, 1979; Sontheimer et al., 1978; Summerhayes et al., 2011). At low chlorine dose, substituted chloro-products dominated whereas at higher doses oxidation and cleavage products (Johnson and Jensen, 1986).

3.2.4. Influence of TOC on THM formation

The study revealed that the rate of THMs formation increases with an increase in initial TOC concentration (Fig. 4). The higher the amount of organic matter the higher was the THMs formation. However, it was observed that the rate of reaction was fast till the first 90 mins after which the rate of increase was marginal. This is mainly due to decrease in the concentration of chlorine and organic matter as the chlorination proceeds, leading to slow formation of THMs. Literature studies reported that an increase in initial TOC concentration usually leads to increase in THM formation (Arora et al., 1997; Chang et al., 2001; Hassani et al., 2010). Moreover, a higher TOC will form more THM if residual chlorine is enough. High concentration of organic matter will produce more THMs (Babcock and Singer, 1979).

Reckhow et al. (1990) also found that THMs formation was related to the activated aromatic content and was correlated with chlorine consumption. Thus, the rate of chlorine decay in drinking water is primarily a function of NOM concentration, water temperature and the initial chlorine concentration.

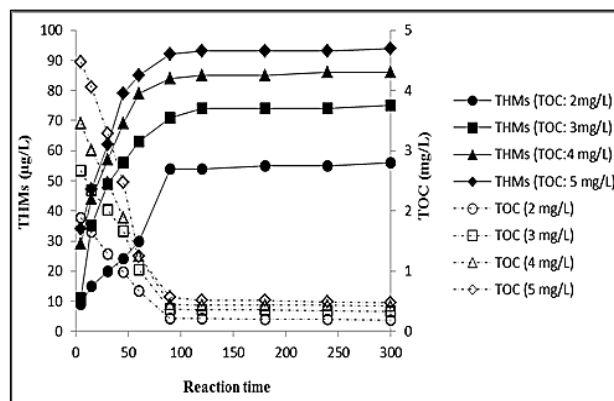


Fig. 4. Effect of TOC on THM formation

3.3. Correlation analysis

Pearson correlation matrix (SPSS, version 22.0) was used to determine the correlation of various water quality operational parameters on the rate of THMs formation. Strong and high correlation coefficient was obtained for reaction time with THMs ($R^2=0.920$) (Table 3). The other parameters like TOC and chlorine dose also showed good correlation with THMs. Babcock and Singer (1979) also reported that water samples having a higher concentration of TOC will form more THMs. The correlation analysis revealed that THMs formation is greatly influenced by reaction time followed by pH, TOC and chlorine dose.

Reaction time and pH were highly correlated ($R^2=0.997$) indicating pH would also influence the formation of THMs. Garcia-Villanova et al. (1997) reported linear relationship of pH with THMs. Kim et al. (2002) and Roccaro et al. (2014) also described that THMs formation increases formation with increase in pH. The applied chlorine dose also showed strong correlation with reaction time ($R^2=0.990$) indicating that THMs formation can be also controlled by regulating the applied chlorine dose in addition to organic matter concentration and pH. Higher is the reaction time, faster is the rate of reaction of chlorine with TOC, leading the formation of THMs (Sadallah, 2014; Scheili et al., 2015). The overall results demonstrate that reaction time is the most influencing parameter followed by pH, chlorine dose and TOC.

Table 3. Correlation matrix of major water quality parameters with THMs (N=180)

	Reaction Time	TOC	Chlorine dose	pH	THMs
Reaction Time	1	0.770**	0.990**	0.997**	0.920*
TOC		1	0.897**	0.985**	0.876**
Chlorine Dose			1	0.994**	0.866**
pH				1	0.902**
THMs					1
**. Correlation is significant at the 0.01 level (2-tailed).					
*. Correlation is significant at the 0.05 level (2-tailed).					

3.4. Principal component analysis

Principal component analysis serves as an exploratory method for data analysis suitable for complex mixtures such as disinfection by-products (Feder et al., 2009). The advantage of PCA is that generates a set of independent variables (components) that are linear combinations of the original variables. In our study, we observed that the THMs mixture is simplified in three main components explaining more than 80% of variance (Table 4). The first component explained 44.62% of variance and correlated with NOM precursors dominated by DOC followed by TOC and UV₂₅₄. The second component explained 19.40% of variance and showed highest correlations with SUVA followed by UV₂₅₄. However, TOC and DOC showed negative correlation. The third component explained 16.58% of variance and showed maximum correlation with SUVA followed by UV₂₅₄. Both TOC and DOC in this case also showed negative correlation with THMs.

An alternative PCA using residuals from linear regressions of chemicals adjusting for area was conducted, to control for the effect of area. Analysis of the data shows that most of the variance was explained by UV₂₅₄ and SUVA. These parameters explained the largest part of variability overall,

although it differed by area. In areas where UV₂₅₄ and SUVA showed low concentrations, THMs precursors (DOC and TOC) were dominant parameters.

Table 4. Principal component analysis of THMs precursor (N=180)

Component	1	2	3
Explained variance	44.62	19.40	16.58
Component-variable correlation			
TOC	0.853	-0.331	-0.072
DOC	0.919	-0.311	-0.084
UV ₂₅₄	0.781	0.513	0.240
SUVA	0.102	0.890	0.368

3.5. Chlorine decay kinetics and its validation

To determine the kinetics of chlorine decay, the data were fitted in first order and second order chlorine decay model. Second order model showed higher correlation coefficient ($R^2 = 0.969$) whereas the first model failed as evident from its low R^2 value (0.284) (Fig. 5). Accordingly, the chlorine decay rate constant (k) was calculated for second order model and was found to be 0.0131 L/mg.min⁻¹. The obtained result is in line with those reported in literature (Clark et al., 1998; Hua and Vasyukova, 2015; Kowalska et al., 2006). Dharmarajah and Patania (1991) also suggested the second-order decay equation during the initial phase due to initial rapid decay of chlorine.

The applicability of the model was further tested by validating it on field scale data. *t*-test was performed to determine the skewness biasness of the developed model. The t_{cal} value (-0.347) of the model was lower than the $t_{critical}$ value (2.09) with *p* values more than 0.5. This indicated that the model bias is insignificant. The standard deviation and standard error of estimated mean were also very little. Similarly, mean square error of prediction (MSEP) for second-order model was also found to be very little (0.00018) (Table 5). The chlorine decay rate constant (k) was used for predicting the actual chlorine concentration in the field scale data. The plots between the observed and predicted residual chlorine resulted a good fit with high R^2 value (0.967) (Fig. 6). This indicates that second order model can be precisely used for predicting the actual chlorine levels in chlorinated drinking water samples.

3.6. Empirical kinetic model for THMs formation

THMs formation kinetics was determined by using empirical models proposed by Clark et al. (1998) and Kavanaugh (1980). These are the baseline models developed for ascertaining the kinetics of THMs formation. The results revealed that the plot of Kavanaugh et al. (1980) model showed a good correlation ($R^2=0.945$) (Fig. 7a). The value of 'f' was determined for a set of water samples and was compared with the theoretical value obtained from the stoichiometric relation between TOC concentration and chlorine.

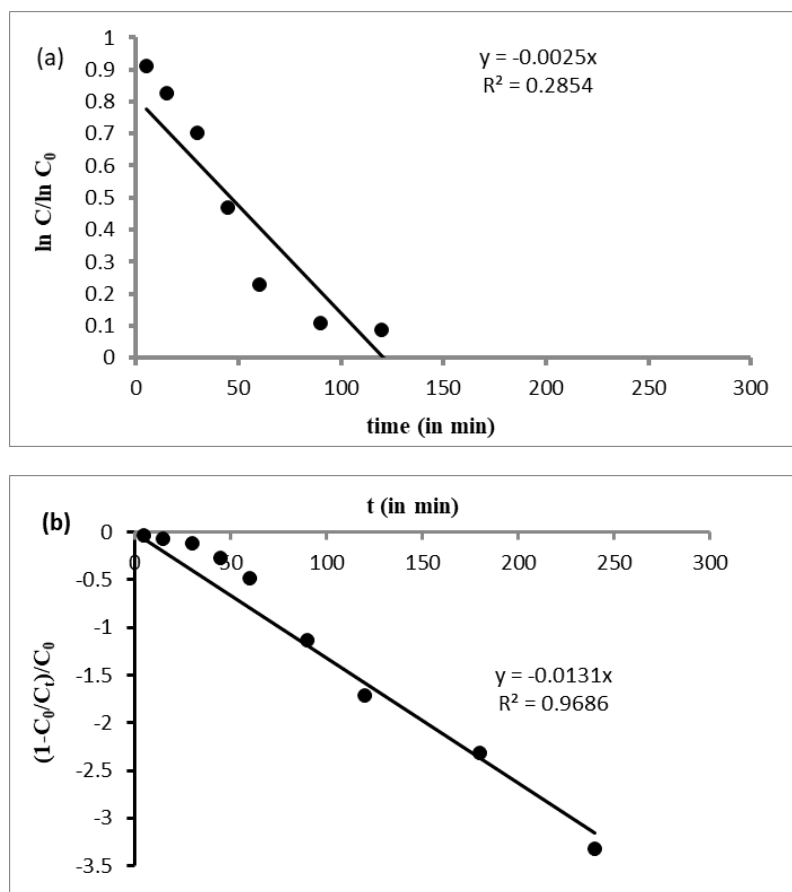


Fig. 5. Chlorine decay kinetics (a) First-order model (b) second-order model

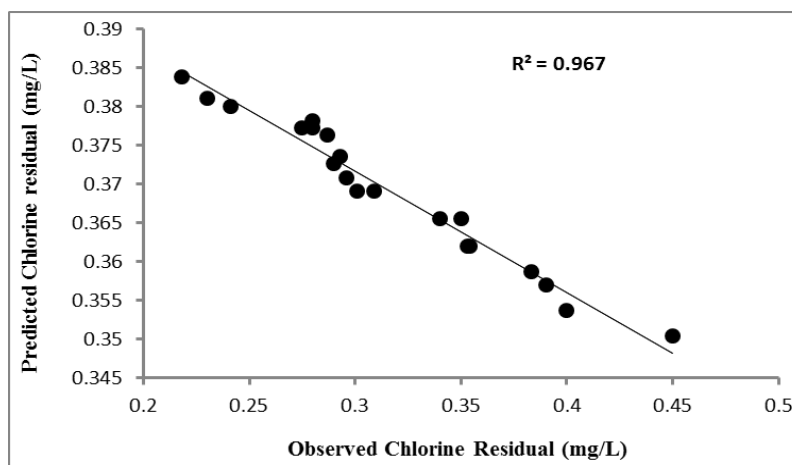


Fig. 6. Correlation between observed and predicted chlorine residual concentration for second-order model

The experimental value of 'f' (0.030) was observed to be similar with the stoichiometric value (0.033). This shows that the experiment was in line and perfectly simulated the actual reaction conditions. The reaction rate constant (k) for the model was found to be $2.26 \times 10^{-6} \text{ L } \mu\text{M}^{-1} \text{ min}^{-1}$. The value of constants i.e. T (0.898) and M ($0.009 \mu\text{g/L}$) in Clark's model were determined from the slope and intercept of the model plot (Fig. 7b). This model gave relatively higher correlation coefficient ($R^2=0.997$) than Kavanaugh model.

Table 5. Validation statistics of the chlorine decay second order model

Parameters	Values
Degree of freedom, df	19
Std. Deviation of prediction errors	0.009
Std. Error of estimated mean bias	0.002
Mean Square Error prediction (MSEP)	0.00018
t Calculated	-0.347
t Critical	2.09
Significant	No

The M value, which is the estimated THM concentration at time zero, was found to be 0.009 µg/L which is significantly much less than those reported by Clark (10-17 µg/L) in his study (Clark, 1998). Theoretically, M must be close to zero. Thus, very low value of M obtained in the present study dictated better accuracy and applicability of the model.

3.6.1. Validation of THM formation model

Similar to validation of chlorine decay, *t*-test was performed to validate the model. Validation was carried on different set of experimental data used in the model kinetics. The model was validated on the basis of R^2 values, t_{Cal} , mean square error of predication and prediction error. The observed t_{Cal} for Clark's model (1.13) was less than Kavanaugh (1.97) and were subsequently less the $t_{Critical}$ value (2.09). This indicated that the biasness is insignificant for both these models however, t_{Cal} value in case of Clark's model was lower than Kavanaugh model. The percentage error of prediction was also low (< 6%) in Clark's model than Kavanaugh model (20%). Higher the error of prediction, the less significant the model is (Kumari and Gupta, 2015).

The plot between the observed and the predicted THMs values for these models revealed high correlation coefficients for Clark's model ($R^2=0.986$) while Kavanaugh model failed in predicting the THMs levels for field scale data with low R^2 value (0.886) (Fig. 8). This implied that Clark model is better suited for predicting the THMs formation kinetics in drinking water supplies. Even though, the model may not be applicable for different environmental conditions since the water quality parameters vary from location to location.

4. Conclusions

The study revealed that rate of THMs formation is a function of reaction time, pH, organic matter concentration and applied chlorine dosage. THMs concentration increased with increasing chlorine dosage and reaction time. Correlation and regression analysis indicated that reaction time is the most influencing parameter ($R^2 = 0.920$) for the formation of THMs followed by pH, chlorine dosage and organic matter concentration.

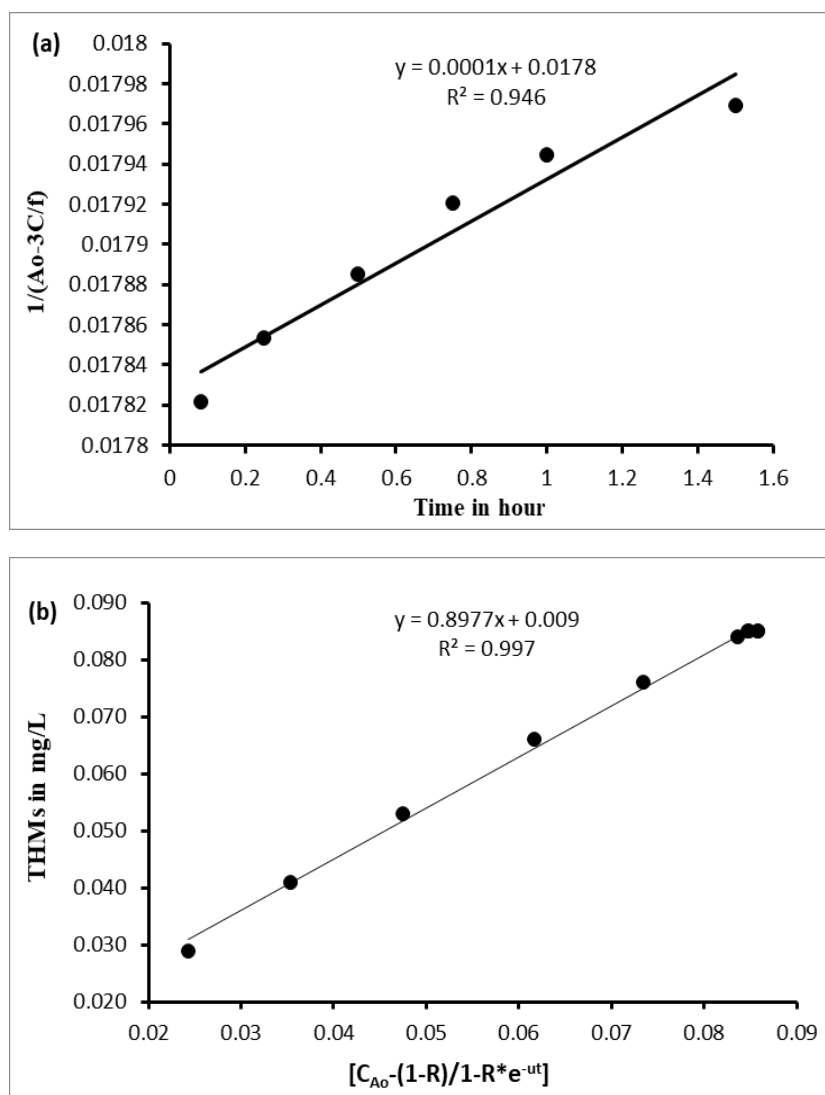


Fig. 7. Kinetic model for THMs formation (a) Kavanaugh's (b) Clark's

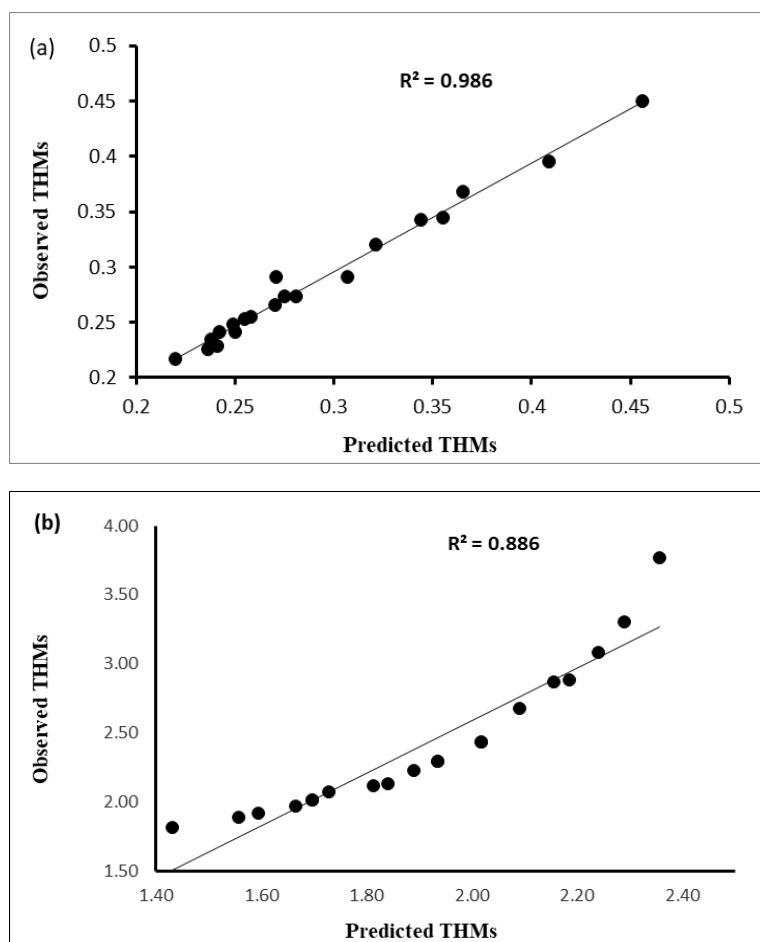


Fig. 8. Relationship between observed and prediction values (a) Clark (b) Kavanaugh

The study observed that THMs formation occurred in two different stages, an initial fast reaction between chlorine and active groups leading to the quick formation of THMs in the beginning although, as the chlorination proceeds, the quantity of free chlorine diminishes which further slows down the formation of THMs. PCA demonstrated that DOC is the major precursor for the formation of followed by TOC and UV_{254} .

The chlorine decay kinetics followed second order reaction during the initial phase due to initial rapid decay of chlorine. Validation statistics indicated that second order model can be precisely used for predicting the actual chlorine levels in chlorinated drinking water samples. Clark's empirical model was found to be most appropriate for determining the THM formation kinetics with low error of prediction (< 6%) and high R^2 value.

Usually, mathematical models are established empirically or semi-empirically. Each distribution system should be considered individually according to different environmental and geo-climatic conditions as the models are site specific. A more detailed knowledge of actual relationships between kinetic parameters will provide a better understanding of the true effects of free chlorine on the formation of THMs. The models can reduce the necessity of further complex and expensive examination, and will help in

executing appropriate quality control measures in drinking water supplies.

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