Optimization of total trihalomethanes’ (TTHMs) and their precursors’ removal by granulated activated carbon (GAC) and sand dual media by response surface methodology (RSM)

Sajida Rasheed, Luiza. C. Campos, Jong. K. Kim, Qizhi Zhou and Imran Hashmi

ABSTRACT

A response surface methodology (RSM) applying central composite design with rotatable full factorial (14 non-center and six center points) was used to discern the effect of granular activated carbon (GAC), sand and pH on total trihalomethanes (TTHMs) and humic acid (HA) removal from drinking water. Results showed efficient TTHMs and HA removal by GAC while a sand column showed little effect for TTHMs but was significant for total organic carbon (TOC) removal. With GAC and a sand column of 4 cm, a pH increase from 6 to 8 caused an increase in TTHM removal from 79.8 to 83.6% while a decrease in HA removal from 26.6 to 6.6% was observed. An increase in GAC column depth from 10 to 20 cm caused a slight increase in TTHM removal from 99.4 to 99.7%, while TOC removal was increased from an average of 38.85% to 57.4% removal. The developed quadratic model for TTHM removal ($p = 0.048$) and linear model for TOC removal ($p = 0.039$) were significant. GAC column depth ($p < 0.0117$) and column depth$^2$ ($p < 0.039$) were the most significant factors. A 98% TTHMs, 30%TOC and 51% residual chlorine removal were optimized at 9 cm GAC and 4 cm sand column depth at pH 8 with desirability factor ($D$) 0.64.

Key words | chlorine, drinking water, humic acid, residual chlorine, RSM, TTHMs

INTRODUCTION

Chlorination of drinking water containing dissolved organic matter (DOM), mainly humic acids (HAs) and fulvic acids (FAs) results in disinfection by-products (DBPs) formation (Radian et al. 2011), mainly total trihalomethanes (TTHMs) e.g. chloroform (CHCl$_3$), bromodichloromethane (CHCl$_2$Br), dibromochloromethane (CHClBr$_2$), and bromoform (CHBr$_3$). These TTHMs cause kidney, liver cancer, central nervous system damage and miscarriages (Zewdu 2013). TTHMs formation in potable water supplies led tighter regulatory control; hence there is a need for proper trihalomethane (THM) management. Besides TTHMs, DOM removal is itself desirable due to color, taste/odor problems; because it is a biofilm formation accelerator (Rezaee et al. 2014) and interferes with water treatment.

Water treatment plants remove a specified percentage of DOM to reduce TTHM formation potential in the treatment process and in distribution systems (Lekkas et al. 2009). But THMs are hydrophobic and have low molecular weight, making them difficult to remove by most physiochemical processes (Zewdu 2013). Nano-filtration membranes and reverse osmosis also showed potential in removing THMs (Uyak et al. 2008). However, their application in developing countries is still limited due to the high costs of the membranes and pumping. Therefore adsorption technologies are still widely applied to efficiently remove organic and inorganic pollutant. Among them, granular activated carbon (GAC) adsorption is an effective barrier against many dissolved organic contaminants. Due to the large surface area,
its chemistry and fast adsorption kinetics, GAC is recommended by the US Environmental Protection Agency for adsorption of these compounds (Wei et al. 2008). Nowadays, GAC column adsorbers are used for taste/odor, toxic organics and/or DBP precursor removal (Narbaizt & Karimi-Jashni 2009). GAC is applied as a fixed bed column, water is passed through and organic compounds or contaminants are adsorbed due to intermolecular attraction between dissolved chemicals and the GAC surface (Erto et al. 2013). In addition, the hydrophobic properties of HAs makes GAC an adsorbent of choice for HAs. GAC as a post-disinfection is reported to remove residual chlorine besides TTHMs. Chloroform (CHCl₃) removal was reported at around 71.2% and 76.4% in deionized and chlorinated water, respectively, while 100% residual chlorine was removed when initial chlorine concentration was 0.5 and 0.8 ppm (Samadi et al. 2004). Removal of THMs and DOM (HA + FA) was attributed to adsorption while dechlorination was caused catalytically by the carbon surface in a pilot study from Athens, Greece (Babi et al. 2007). Lower molecular weight species of HA/FA were more adsorbable; presumably more surface area was accessible to these species (McCreary & Snoeyink 1980). GAC adsorption capacity can be estimated by fitting Freundlich and Langmuir adsorption isotherms and the Freundlich isotherm was fitted well for adsorption of chloroform by Zewdu (2011).

Adsorption performance is governed by a number of parameters, i.e. carbon type, organic matter type, adsorbent particle size, water temperature and pH (Auta 2012), pH being the most influential, inducing not only surface charge on GAC but degree of ionization of contaminant (El-Haddad et al. 2013). Hong (1998) reported that TTHM adsorption on GAC increased with decreasing pH from 8.5 to 5.5. GAC adsorption efficiency has also been reported to vary from chlorinated species to brominated species. The brominated THM compounds were removed more significantly than chlorinated THM compounds resulting from the stronger adsorption bonds between the brominated species and GAC (Babi et al. 2011). GAC and sand has also been investigated for TTHMs and their precursor’s removal and GAC and sand as a dual media, with 30 cm GAC and 90 cm sand depth showed 87% TTHM removal (Mohammed et al. 2006). Although GAC and sand adsorption individually as well as in dual media is reported, their isotherms fitted well but due to the complicity of contaminants, absorber media and treatment processes, the effect of various factors on a process design, performance and their optimization can better be understood by application of mathematical models. These models could establish a mathematical relationship between interacting variables and the resulting responses (TTHM and total organic carbon (TOC) removal). So the specific objectives of this study were: (a) to evaluate the performance of GAC and sand dual media with variable pH for TTHMs’ and their precursors’ removal, (b) to optimize the process using response surface methodology (RSM) and its subsequent modeling for better water distribution system management.

**MATERIALS AND METHODS**

**Design of experiment by RSM**

RSM was applied for optimization of three effective parameters, i.e. GAC and sand column depths and pH. It provided a new perspective approach for investigating adsorption with better results reproducibility, process optimization and predictive model building (Rezaee et al. 2014). In RSM, for each response, a model is defined, predicting individual as well as interactive effects of different parameters with the unit factor effect, two factors interaction and quadratic factor’s impact on the resultant model (Auta 2012). RSM coupled with central composite design (CCD), is used to study interaction, optimization and modelling of process variables with a minimum number of experiments (Danbaba et al. 2015).

Design Expert (DX, Version 9; Stat Ease Inc., Minneapolis, USA) was used for optimum independent parameter design in relation to dependent responses. The design of the experiment consisted of a rotatable full factorial (14 non-center and six center points) with various levels of each factor viz. −α, −1, 0, +1 and +α (Table 1) with 20 experimental runs (Table 3). The experimental sequence was randomized to minimize the effect of uncontrolled factors (Salman 2013). All experiments were performed according to statistical designs to develop predictive regression models used for optimization.

**Determination of surface characteristics of GAC**

Specific surface area, particle size and volume of GAC were determined through Brunauer–Emmett–Teller (BET) analysis.
by low temperature nitrogen adsorption method using a Micromeritics ASAP 2420 Accelerated Surface Area and Porosimetry System. A scanning electron microscope (SEM) (JEOL JSM-6480LV) was used for GAC surface morphology.

Standards and reagents

Prepared TTHM standards (Supelco) with 99.9% purity (5,000 μg/ml) dissolved in methanol were used with fluoro-benzene (2,000 μg/ml) as internal standard. Stock solution of HA (Sigma-Aldrich) and commercial sodium hypochlorite (10.5%) were freshly prepared and applied as per experimental requirement.

Rapid small scale column test

A fixed bed adsorption system consisting of a small-scale column made up of Plexi glass (internal diameter = 50 mm, height = 30 cm), with a Teflon cap and stainless steel base was established (Figure 1).

GAC was washed with deionized water and dried at 105 °C overnight. Feed water containing HA (as precursor) and TTHMs was fed to the column in a downward direction. Samples were collected with a peristaltic pump through silicon tubing from inlet and outlet at different GAC and sand column depths, as shown in Table 3. Water pH, temperature and free residual chlorine were measured immediately after sampling by DPD-FAS titrimetric method (APHA 2005) using a Spectroquant Picco colorimeter while TOC was analyzed by TOC analyzer (Shimazdu, TOC-L).

TTHM extraction and analysis

TTHM extraction was performed by liquid–liquid extraction using Methyl-tert-butyl ether (MtBE; Sigma-Aldrich). In 6 ml of water sample, 0.45 g sodium sulfate (anhydrous) was added, to enhance organic layer separation, and mixed vigorously for 30 sec followed by addition of 1 ml MtBE, mixed on a vortex mixer for 90 sec and left undisturbed for 160 sec. Gas chromatography/mass spectroscopy (GC/MS) (Model Claurus 500, Perkin Elmer) with a column (Restek Rxi-5 ms, 30 m × 0.25 mmID) was used for TTHM detection/quantification. GC analytical conditions were: oven temperature was 50 °C for 5 min; temperature ramp was from 50 to 180 °C at the rate of 6 °C/min, injection volume: 1 μl.

The percent removal of TTHMs and TOC was calculated as below:

$$\% R(\text{TTHMs}) = \left(\frac{C_{\text{in}} - C_{\text{eff}}}{C_{\text{in}}}\right) \times 100$$

$$\% R(\text{TOC}) = \left(\frac{C_{\text{in}} - C_{\text{eff}}}{C_{\text{in}}}\right) \times 100$$

where $C_{\text{in}}$ is concentration of TTHMs (μg/L) and TOC (mg/L) in influent water, while $C_{\text{eff}}$ is concentration of TTHMs (μg/L) and TOC (mg/L) in effluent water respectively after a known length of column.

Table 1 | Independent variables with low/high-level by CCD

<table>
<thead>
<tr>
<th>Coded values</th>
<th>Symbols</th>
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</tr>
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<tr>
<td>Variables</td>
<td>Symbols</td>
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<td>Low</td>
<td>Centre</td>
<td>High</td>
<td>Highest</td>
</tr>
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<tr>
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<td>10.0</td>
<td>16.0</td>
<td>20.0</td>
</tr>
<tr>
<td>pH</td>
<td>C</td>
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<td>6.0</td>
<td>7.0</td>
<td>8.62</td>
<td>8.68</td>
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</table>

Figure 1 | Schematic diagram of the small-scale GAC and sand dual media column.
RESULTS AND DISCUSSION

Characterization of GAC

The BET surface area of GAC was 774 m²/g. The other parameters are given in Table 2. The SEM image showed ions on the GAC surface such as Ca²⁺, Al³⁺, O⁻² and Si²⁻ (Figure 2). The Ca²⁺ was specifically reported to increase the capacity of granular activated carbon for adsorption of contaminants, as suggested by Daifullah et al. (2004). These cations/anions show greater adsorption capability due to electrostatic forces between the carbon surface and contaminant molecules. The ‘electrostatic attraction’ and ‘surface complex formation’ are responsible for efficient adsorption (Radian et al. 2011). These interactions are significantly influenced by pH (Auta 2012). Sand was Aqua sand of density 2.6 g/cm³.

Table 2 | BET analysis data

<table>
<thead>
<tr>
<th>Sr. #</th>
<th>Characteristics</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>Mesh size</td>
<td>20 × 30</td>
</tr>
<tr>
<td>2.</td>
<td>GAC particle size</td>
<td>0.001–0.002 m</td>
</tr>
<tr>
<td>3.</td>
<td>Surface area</td>
<td>779.15 m²/g</td>
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<tr>
<td>4.</td>
<td>Single point surface area at P/Po</td>
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</tr>
<tr>
<td>5.</td>
<td>BET surface area</td>
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Table 3 | Experimental layout with respective results

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<th>Run</th>
<th>GAC column depth (cm)</th>
<th>Sand column depth (cm)</th>
<th>pH</th>
<th>% TTHM removal</th>
<th>% TOC removal</th>
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<td>7.0</td>
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<tr>
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<td>6.0</td>
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<td>18.3</td>
</tr>
<tr>
<td>4</td>
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<td>8.0</td>
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<tr>
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<tr>
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<td>6.0</td>
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<td>10.0</td>
<td>7.0</td>
<td>2.1</td>
<td>5.2</td>
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For results analysis, optimization, simulation and modelling, DX Version 9 was used. Three parameters, i.e. GAC and sand column depth with pH contributed positively and showed significant TTHM and HA removal (measured as TOC). The design matrix with actual factors, types of run and respective responses (TTHM and TOC removal) are given in Table 3. It was observed that GAC absorbance was comparatively more significant for TTHMs and TOC than sand. In the case of the 10 cm sand column alone, TOC removal was 5.2%, while TTHM removal was 2.1% (Run 20). It doubled, i.e. to 12.6% for TOC when GAC of the same column depth was used (Run 14), while TTHM removal was also significantly increased up to 89.0% (Table 3). The reason could be the type of adsorbent as sand showed less attraction for TOC and TTHMs than GAC. On the other hand, increasing the GAC column depth resulted in more efficient TTHM and TOC removal simultaneously. The amount of TTHMs adsorbed was observed to be correlated to stronger surface hydrophobicity of adsorbent (Nakamura et al. 2003) and was proportional to available GAC surface. For pH 7, there was a significant increase in TTHM removal from 2.1 (Run 20) from the top of the GAC to 99.7%, at 20 cm depth of GAC (Run 6) (Table 3). While an increase in GAC column depth from 10 to 20 cm caused a small increase in TTHM removal from 99.4 (Run 7) to 99.7% (Run 6), TOC removal was increased from an average of 38.85% (Runs 7–10, 12 and 13) to 57.4% removal (Run 6). When pH was increased from 6 to 8 with GAC and sand depth of 4 cm, TTHM removal was increased from 79.8% (Run 5) to 83.6% (Run 11) while TOC adsorption was decreased from 26.6% to 6.6%. This decrease could be explained by increasing pH; GAC particles tend to adsorb negative charges and HAs are negatively charged naturally so reduced electrostatic attraction resulted in less adsorption, as emphasized by Al-Neseri & Abbas (2009).
To analyze the combined effect of three factors on TTHM removal, three-dimensional (3-D) surface plots and contour graphs were employed (Figure 3(a) and 3(b)), which are the graphical representation of the regression equation. In Figure 3(a) the legend X1 (x-axis) and X2 (y-axis) show GAC and pH respectively and curvature and color from blue to red in the contour graph (Figure 3(b), X1 (x-axis) = GAC, X2 (y-axis) = Sand) revealed that removal of TTHMs increased up to a certain limit (99.7%) (Run 6) with increasing GAC layer length up to 20 cm, then decreased. This may be due to the saturation of the adsorptive site on GAC.

Statistical data analysis for GAC removal

Data competence and significance of the model was assessed by analysis of variance (ANOVA) (Chowdhury et al. 2014). A significant quadratic model was fitted with a $p$ value of 0.0486 with GAC column depth being the most significant factor ($p = 0.0117$) (Table 4). Beside $p$, determination of the coefficient ($R^2$) and adjusted $R^2$ (adj. $R^2$) were also used as statistical tools to evaluate model adequacy (Rezaee et al. 2014). The closer the $R^2$ value to unity and the smaller the standard deviation (16.67), the better the model in predicting response (Danbaba et al. 2015). The values of $R^2$ and adj. $R^2$ were 0.73 and 0.49, respectively. The statistical results showed that the model was well defined to predict the TTHM removal within the range of variables applied.

Efficiency of sand for the TOC removal

The adsorption of TTHMs and HA on sand occurs due to the bonding between oxygen atoms on the sand surface and the hydroxyl radical present on TTHMs and HA (Site 2001). The 3-D surface plots depicted TOC removal behavior by GAC

Figure 2 | (a) SEM view for GAC surface morphology, (b) GAC chemical analysis.

Figure 3 | 3-D response and 2-D contour surface graph showing the effect of GAC layer depth on TTHM removal. Refer to the online version of this paper to see this figure in color: http://dx.doi.org/10.2166/ws.2015.175.
and pH (Figure 4(a)) and by sand and GAC dual media column (Figure 4(b)). From Figure 4(a) it is evident that pH showed no appreciable effect on TOC absorption as removal percentage remained almost constant from pH 6 to 8 on the x-axis. These results are in accordance with Erto et al. (2013), who reported a negligible effect of pH on GAC adsorption for TOC. While increasing GAC column length (y-axis) the percent TOC removal increases up to almost 52%. In Figure 4(b), as expected, the sand column showed a slight TOC removal (almost 15%) represented as B on the y-axis as compared to GAC (approximately 52%) at the GAC column length of 16 cm (A: x-axis).

While in Figure 4(b) GAC demonstrated a linear effect for TOC removal as by increasing GAC column depth, TOC removal increased proportionally. Therefore it was evaluated that the sand column showed a less efficient effect on TOC removal as compared to GAC.

### Statistical data analysis for TOC removal

In the case of TOC removal, a linear model was fitted to data which was significant ($p = 0.0018$) with GAC column depth again the most significant factor ($p = 0.011$) (Table 5). The $R^2$
for the model was approximately 0.60 while pred. $R^2$ was 0.524.
A very high F-value ($F_{model} = 7.98$, much greater than unity) and a very low probability value ($p = 0.0018$) with small standard deviation (SD = 13.61) indicated that the model obtained is appreciably significant (Appavoo et al. 2014).

### Efficiency of GAC for residual chlorine removal

According to the literature, GAC removes chlorine by reduction (Babi et al. 2011). The trend of Figure 5(a) and 5(b) shows that by increasing GAC and sand column individually and together, increase in residual chlorine removal was observed. The curvature in the 3-D surface showed a minimum removal at 4 cm depth of each column and increased as column depth increased (Figure 5(a)) and was triggered catalytically by the carbon surface (Babi et al. 2011).

Zewdu (2013) reported that chlorine reduction occurred in the top few centimetres of GAC column, while the present study showed that for residual chlorine removal, both the GAC and sand column were more or less equally effective and a substantial part of it was removed from the feed water.

### The Pareto chart of variables

To observe the contribution of the most significant factor towards effective removal of TTHMs, TOC and residual chlorine, a Pareto chart of variables was plotted, (Figure 6). Here bar lengths are proportional to value of...
effect, showing their relative importance (Tuncel & Topal 2014). In this chart, the maximal effect was presented in the upper portion, then progressed down to minimal effect. A, B, and C are coefficients with one factor for GAC column depth, sand column depth and pH, respectively, while the coefficients with two factors (AB, BC, AC) and with second-order polynomial (A^2, B^2 and C^2) terms show interaction between two factors and a quadratic effect, respectively (Chowdhury et al. 2015). The chart shows that almost 48% removal was contributed by GAC column depth (A^2).

Evaluation of the model

The adequacy of the model was tested by correlation between normal plots of residuals versus percent removal of TOC and TTHMs respectively, as shown in Figure 7(a) and 7(b) (Singh et al. 2011). It is also used to validate accuracy of the predictive model. The figures depict a fairly good correlation between the obtained results and predicted values by statistical model and a reasonable agreement between observed data and determined values was observed indicating suitability of model.

The data points are aligned on the diagonal depicting that the fitted regression equation showed a satisfactorily good fit for the model using rapid small scale column testing (Appavoo et al. 2014).

TTHM removal modelling

In RSM/CCD, each response was used to develop an empirical model that correlates response (percent TTHM and TOC removal) to the three studied factors, i.e. GAC, sand and pH. Based on the quadratic polynomial equation (suggested by the software) and normal plots of residuals, the empirical relationship between independent variables

![Figure 6](https://iwaponline.com/ws/article-pdf/16/3/783/412420/ws016030783.pdf)

**Figure 6** | Pareto chart showing contribution of variables for THM removal.

![Figure 7](https://iwaponline.com/ws/article-pdf/16/3/783/412420/ws016030783.pdf)

**Figure 7** | (a) Normal plot of residuals for TOC, (b) normal plot of residuals for TTHMs.
and percent removal of TTHMs and TOC may be expressed by the mathematical model equation given below.

\[
\text{TTHM removal \%} = \frac{99.56 - 16.41A^2 - 6.01 AB + 5.62 AC}{16.41} + 4.44 BC
\]

where \( A = \) GAC column depth, \( B = \) Sand column depth, \( C = \) pH.

Based on the evaluation of the data by normal plot of residuals, it is estimated that the model had a good prediction effect for the removal of TTHMs and HA TOC. This mathematical model may be used to predict performance of a fixed bed GAC and sand column to remove/reduce TOC and TTHMs from drinking water (Danbaba et al. 2015). Although the other water quality parameters may vary, the use of natural water instead of one-solute solution is considered to make no significant difference to model prediction by activated carbon filtration (Babi et al. 2011).

**Numerical and graphical optimization**

Process optimization is important in determining values of factors for which response is at a maximum (Sagbas 2011) by solving a regression equation. So removal efficiency became an objective function or performance index called the desirability function \( D \), whose value closer to 1 is considered fair enough. For numerical optimization, the goal is to optimize all variables together for a numeric value for collective response (percent TTHM and TOC removal).

Numerical optimization was done for maximum removal of TTHMs, TOC and residual chlorine with minimum GAC and sand column depth (0 to 20 cm) and an optimized pH (pH 5.32 to 8.68) (ranges given in Table 1). This will reduce capital costs related to columns and operational costs related to pH correction. The top row in Figure 8 depicts recommended factor settings, and predicting responses are shown in the second row. The model predicted 98% TTHM, 30% TOC removal and 51% residual chlorine removal which could be achieved simultaneously at 9 cm GAC and 4 cm of sand depth as dual media with a pH value of 8 with \( D = 0.64 \) (Figure 8).

The maximum predicted value for TTHM and TOC removal for independent variable ranges may also be represented graphically by graphical optimization (Figure 9). The surface confined in the smallest eclipse region colored yellow, in the contour diagram, illustrated the area where all the variables meet the required criteria (Trinh & Kang 2016). The grey part depicts the areas where only a part of the criteria are met.

**CONCLUSIONS AND RECOMMENDATIONS**

The present study was conducted to optimize and model various factors for maximum TTHM removal from water using GAC and sand dual media using RSM coupled with CCD.
The following conclusions may be drawn:

1. TTHM removal increased with increase in pH ($p < 0.48$) while a decrease in HA removal from 26.6 to 6.6% was observed at GAC and sand dual column of 4 cm each.
2. With increasing GAC column depth, TOC removal increased due to increase in number of binding sites irrespective of high pH.
3. Maximum TTHM and TOC removal were 99.7% and 57.4% respectively at GAC and sand column depth of 20 cm and 10 cm, respectively, at pH 7.
4. The quadratic model for TTHM removal was significant ($p = 0.048$) with $R^2 = 0.73$, while linear model for TOC removal had $p = 0.0018$ and $R^2 = 0.59$.
5. GAC column depth ($p < 0.0117$) and column depth$^2$ ($p < 0.039$) were the most significant factors for both TTHM and TOC removal while sand showed a less significant effect for TTHM removal.
6. A 98% TTHM, 30% TOC and 51% residual chlorine removal was optimized at GAC and sand column depth of 9 cm and 4 cm, respectively, at pH 8 with $D = 0.64$.

Based upon the conclusions, a detailed study at a pilot plant is suggested for further insight into removal efficiency.

Furthermore treatment performance to remove these contaminants should be evaluated using the specific water of the area to be treated.

REFERENCES


