

Full Length Research Paper

Multi-objective application of granular activated carbon in the production of carbonated beverage process water and bottled water

Zinabu Tebeje Zewdu

UNESCO-IHE, P. O. Box 3015, 2601 DA Delft, the Netherlands.

Accepted 25 March, 2013

There are number of issues in soft drink industries' mode of GAC operation, however, this study focuses on three issues like control of regeneration breakthrough in line with Chlorine and THM breakthrough; its frequency of regeneration and finally the competitive adsorption of different THM on two different types of GAC and extrapolation of result to full scale plant. All the experiments were conducted using rapid small scale column test (RSSCT). And for de-chlorination experiment, deionized water spiked with 2 mg/L chlorine (HOCl) was used. On the other hand, for THM's removal experiment, deionized model water was used with two THM species (chloroform, bromoform or mixture of both components) at a total THM concentration of approximately 80 µg/L. In the experiments, GAC breakthrough curves were established with RSSCT protocol. Therefore, in this study, GAC regeneration is revealed to be controlled by THMs removal. And, RSSCT suggests that in the treatment plant (THMs concentration in feed water of approximately 80 µg/L) Calgon F200 GAC (empty bed contact time (EBCT) = 7.12 min) could treat up to 12000BV before breakthrough of 10 µg/L and this would correspond to 2 months operation. In this study, both Calgon F200 and Norit GCN 1240 also demonstrated in RSSCT experiments that THMs can be effectively reduced below 10 µg/L. However, RSSCT-chloroform adsorption showed slightly higher capacity of Norit GCN 1240 at lower concentration (< 40 µg/L) and slightly higher capacity of Calgon F200 at higher concentration (> 50 µg/L) for $Co = 79.8 \pm 4.30$ µg chloroform/L and EBCT of 0.31 min.

Key words: Granular activated carbon (GAC), rapid small scale column test (RSSCT), bromoform, chloroform, de-chlorination and trihalomethanes (THMs).

INTRODUCTION

In many developing and developed countries, drinking water quality is a crucial factor to safeguard human health. Many water sources contains contaminates (micro-organisms) which can easily be managed by disinfection process. Chlorine for example is a cheap but strong disinfectant (Roy, 1995). In 1974, researchers in

the Netherlands and the United States demonstrated that disinfectant by-products (DBPs) like trihalomethanes (THMs) were being formed from the interaction of chlorine/ bromide with various organic substances in water (USEPA, 1999; Al-Naseri and Abbas, 2009). These chlorinated organic compounds and other DBPs

potentially cause cancer, miscarriages and are mutagenic. Some studies also linked THMs to heart, lung, kidney, liver, and central nervous system damage (Baruth, 2005; Fearing et al., 2004; Tchobanoglous et al., 2003).

Different countries set specific limits for THM concentrations in potable water. The permissible value for chloroform recommended by WHO is 30 µg/L (Gallard, 2002). The European commission has proposed a new council directive with parametric values of 40 µg/L for chloroform (Capar and Yetis, 2002). The current regulations of the United States Environmental Protection Agency (USEPA) demand Stage 1 Disinfectants / Disinfection by Products Rule (D/DBPR) target of 80 µg/L for total THMs (TTHMs) (Alicia and Alvarez, 2000; Lin et al., 1999). A more stringent level of 40 µg/L is proposed to be in effect as the stage two targets (Alicia and Alvarez, 2000; Lin et al., 1999). Some companies like Coca-Cola have a vigorous aim to meet guide line value of 10 µg/L. Hence, removal of THMs is necessary and this is mostly achieved by applying GAC filtration (Edward, 2005; Fearing et al., 2004; Qasim et al., 2004; Tchobanoglous et al., 2003).

In general, THMs are hydrophobic and have low molecular weight. These characteristics make them difficult to remove by most physicochemical processes, but they can be effectively removed by GAC. Thus, removal of THM species using GAC filtration is in the order $\text{CHCl}_3 < \text{CHBrCl}_2 < \text{CHBr}_2\text{Cl} < \text{CHBr}_3$ (Letterman, 1999; Potwora, 2006). The more number of bromine atoms attached to THM species means the more adsorbability by GAC (Potwora, 2006). Since chloroform has no bromine atoms it is the least adsorbed species of THMs. Beside chloroform is the most common THMs, due to these reasons chloroform was considered as trihalomethanes (THMs) basic indicator compound (Potwora, 2006). And bromoform was added to account and see the interaction of other THM species.

Adsorption isotherm is extremely valuable in evaluating the effectiveness of GAC for treating contaminated water. A rapid method for the design of full-scale absorbers from small scale column studies known as rapid small scale column test (RSSCT) was developed by Crittenden et al. (1987). However, the design of full scale GAC adsorption / reduction process can involve time consuming and expensive pilot plant studies. Therefore, RSSCT can be applied to simulate a full scale GAC filter in 1.05% of the time and one hundredth of the cost of standard pilot test (Crittenden et al., 1986; McGuire, 1991). Thus, this study was initiated to check and compare the suitability of two GACs (bituminous based Calgon F200 which is used in Coca-Cola plant and the other Norit GCN 1240) that are recommended by their manufacturer for the best adsorption of THM species. Soft drink's water quality criteria for carbonated beverage process water include an absence of chlorine residual and total trihalomethanes (TTHMs) that are below local drinking water standard or,

in the absence of a local standard, the WHO standard. The goal of this study is to get better understanding of water treatment that could lead to possible optimization of use of GAC in Coca-Cola Company in focus on the attenuation of chlorine residual and THMs. The specific objectives of this study are to identify the main factors that control GAC regeneration (either chlorine reduction or THM adsorption); to examine THM adsorption capacity of two commercially available GACs; and, to investigate competitive adsorption of chloroform and bromoform, using two types of GAC.

MATERIALS AND METHODS

RSSCT experiments were performed using two different GACs namely Calgon F200 and Norit GCN 1240 with characteristics mentioned in Table 1. Calgon F200 GAC is selected because it is currently used in the Antwerp Coca-Cola treatment plant, Belgium. Norit GCN 1240 (coconut based activated carbon) is selected since it has preference for low molecular weight than bituminous based activated carbon like Calgon F200 GAC (Potwora, 2006). To address the research objective RSSCTs were applied in UNESCO-IHE Laboratory, the Netherlands.

Rapid small scale column test (RSSCT)

Real scenario of the full scale adsorber is scaled down to small scale by the help of mathematical model. By selecting the proper empty bed contact time (EBCT), hydraulic loading rate (HLR) and particle size of a small-scale adsorber, the effluent breakthrough curve of the RSSCT will be similar to that of the full-scale column. RSSCT bed life is used for the prediction of full scale bed life, bed volume carbon usage rate and specific volume (volume of water that may be treated per mass of carbon) as per the following equation (Crittenden et al., 1991):

$$BV = \frac{t_{sc}}{EBCT_{sc}} = \frac{t_{LC}}{EBCT_{LC}}; \quad BV = \frac{QT}{V} = \frac{t}{EBCT} \quad (1)$$

Where EBCT = empty bed contact time, min; t = run time; dp = particle diameter, mm; BV = bed volume; LC = Large column (Full scale GAC); A = cross sectional area; SC = short column (RSSCT); \dot{u} = approach velocity

The specific throughput of the full scale and RSSCT are also similar and the carbon usage rate is the reciprocal of specific throughput. Full scale specific throughput is equal to the volume of water fed to RSSCT divided by mass of GAC in RSSCT. Bed life times the flow rate gives the volume of water treated.

Constant diffusivity (CD) model

In CD it is assumed that the mass transfer occurs because of film diffusion (represented by Stanton number) in addition it assumes that the inter-particle diffusivity is same for both small and large column (Crittenden et al., 1987). CD-RSSCT were more effective in simulating humic substances and SOCs desorption (Crittenden et al., 1991); in other words as Badruzzaman (2005) stated CD-RSSCT is valid for smaller molecular weight organics (that is, SOC) adsorption on to GAC. As Crittenden et al. (1991) stated Equations 3 to 9 applied to calculate different design parameters for RSSCT of CD as tabulated in Table 3:

Estimate the EBCT for the RSSCT:

Table 1. Specifications and general characteristics of GACs used for the study.

Specifications		
Supplier	Norit	Calgon
GAC name	Norit GCN 1240	Calgon F200
Iodine number -	1050	850
Total surface area (B.E.T.) 2 m/g	1150	850

Table 2. Composition of THM's stock solution and model water used in RSSCT.

No.	Stock solution in 10.52 L glass bottle	Model water (feed water) prepared in 10.52 L mixing tank
1	-	Chlorine (2 mg/L)
2	Chloroform (200 mg/l)	Chloroform (79.8 ± 4.3 µg/L)
3	Bromoform (200 mg/l)	Bromoform (76.45 ± 10.55 µg/L)
4	Chloroform and Bromoform (200 mg/L each)	Chloroform and Bromoform (41.3 ± 3.5 and 49.65 ± 1.55 µg/L, respectively)

Table 3. Design parameters of CD-RSSCT; Norit GCN12x40 and Calgon GAC 12x40.

Design parameter	Full scale	RSSCT	RSSCT
Type of GAC	F200	GCN1240	F200
Supplier	Chemviron Carbon	Norit	Chemviron Carbon
Particle diameter (mm)	1.0(12x40)	0.21(60x80)	0.21(60x80)
Apparent density (gm/ml)	0.5	0.45	0.5
EBCT (min)	7.12	0.31	0.31
Loading rate (m/h)	9.95	47.38	47.38
Flow rate (ml/min)	630,067	79.16	79.16
Column diameter (cm)	220	1.13	1.13
Column length (cm)	118	24.8	24.8
Mass of adsorbent (gm)	-	11.18	12.43

$$EBCT_{sc} = EBCT_{LC} \left[\frac{d_{sc}}{d_{LC}} \right]^2$$

(2)

Estimate time of operation for the RSSCT:

$$\left(\frac{EBCT_{sc}}{EBCT_{LC}} \right) = \left(\frac{t_{sc}}{t_{LC}} \right)$$

(3)

Estimate the loading rate for the RSSCT:

$$V_{sc} = V_{LC} \times \frac{d_{LC}}{d_{sc}}$$

(4)

Estimate the flow rate for RSSCT:

$$(A) = \frac{\pi}{4} d_{sc}^2$$

(5)

$$Q_{sc} = (V_{sc}) \times (A)$$

(6)

Estimate column length for the RSSCT:

$$L_{sc} = \frac{Q_{sc} \times EBCT_{sc}}{A}$$

(7)

Estimate mass of adsorbent required for the RSSCT of CD:

$$M_{sc} = EBCT_{LC} \left[\frac{d_{sc}}{d_{LC}} \right]^2 (Q_{sc}) (\rho_{sc})$$

(8)

Estimate volume of water required for the RSSCT:

$$V_W = (Q_{sc}) \times (t_{sc})$$

(9)

Small scale column test experimental setup

Two RSSCTs were operated in parallel; one column was filtered with Calgon F200 GAC and the other with Norit GCN1240 GAC. Continuous feed of THM containing model water was provided.

Additional RSSCT were made to study chlorine removal by Norit GCN1240 GAC.

To avoid THM's adsorption of RSSCT set up components only silicon tubing, glass and stainless steel were used. Glass column with internal diameter of 1.1 and 50 cm in length was used in the RSSCT studies. 1 cm deep white (silver) sand, which acts as a support to the GAC media, was placed over stainless steel screen (100 mesh). On top of the sand media GAC (60x80 US mesh size) was placed. The dried GAC stored in dark amber bottles was dry weighted and subsequently pre wetted with de-ionized water to allow packing of the column as slurry. The wetted GAC was transferred to the column using laboratory spatula and as the column was loaded it was taped slightly to pack the GAC. The GAC bed was submerged with de-ionized water during and after the packing process.

After packing of GAC was finished the RSSCT was checked for leaks by running de-ionized water. Once the setup was properly adjusted the influent reservoir containing the targeted component (THM or chlorine) was connected to the RSSCTs by pump (KNF Diaphragm pump; LIQUIPORT[®] type NF 1.100 TT.18S) and any air in the influent line was removed. The desirable flow rate was set and checked twice daily with stop watch and measuring cylinder. Flow rate was maintained with in $\pm 10\%$ of the desired flow rate.

Influent and effluent samples were taken daily for THMs (chloroform, bromoform and mix of both) or chlorine. 3 g ascorbic acid was added in each 125 ml glass bottles before taking samples in order to preserve THM's. To avoid contact and creation of air water interface as bottles were covered with parafilm before closing the cap. Finally, THM samples were stored in a dark room at a temperature of 4°C until samples were sent for analysis to Coca-Cola Laboratory in Brussels, Belgium. For chlorine measurements samples were taken from influent and effluent of RSSCT followed by direct quick analysis at the UNESCO-IHE laboratory, the Netherlands.

Experimental process conditions and procedures

Model water preparation for RSSCT experiment

Model water was prepared from de-ionized water (NOM-free) with one millimole of NaHCO_3 and the target concentration of selected compound (THMs) stock solution was prepared in 10.52 L brown glass bottle and covered with parafilm to make air free surface. To achieve complete mix of THMs, the stock solution was mixed with a mechanical stirrer 24 h prior to the first usage. From stock solution the required amount is taken and added to prepare model water (feed water) (Table 2). Maximum storage time of stock THM solution was 10 days to minimize loss of volatile THM compounds. Model water in the 150 L mixing tank was adjusted to pH (7 ± 0.2) by adding a few drops of concentrated HCl and using METROHM-691 pH meter. The feed water was divided in to two parallel feed tanks, which were connected to the RSSCTs. For chlorine removal experiment with RSSCT model, water was prepared from demi water, introducing sodium hypochlorite solution in 150 L feed tank.

RSSCT design parameters

Preliminary screening tests were run to model an EBCT of 7.12 min corresponding to the contact time in the full-scale GAC filters. This EBCT is recommended and commonly applied in Coca-Cola water treatment plant. From the two options of RSSCT design approaches namely, constant diffusivity (CD) and proportional diffusivity (PD) the assumption that applied in constant diffusivity was applied. CD mathematical models were used to convert full scale operational parameters to RSSCT.

GAC preparation

The grain size of GAC used RSSCT experiments was 60x80-mesh. This grain size was obtained by crushing 12x40 mesh GAC as supplied by Calgon F200 and Norit GCN 1240 GACs. After GAC grains were crushed, the appropriate size for RSSCT was achieved by sieving. The GAC grains that did not pass the upper sieve was returned and crushed again until it passed the sieve. GAC grains of appropriate size were stored in a beaker covered with aluminum foil. Fines produced during crushing and sieving were removed by washing and storing of GAC of appropriate size in a clean beaker filled with de-ionized water. The GAC was stirred with a glass rod and allowed to settle. For preparation of 60x80 mesh size GAC, at the beginning 10 s ultrasonic bath was applied for the removal of fines. Use of ultrasonic bath was restricted to once to avoid formation of new fine particles. After the GAC particles settled (1-3 min), the supernatant was poured off and new de-ionized water added. The stirring and settling was continued by fresh de-ionized water until clear supernatant was achieved. The wet GAC was placed in an oven at 105°C, dried and stored. The storage of the GAC was in a dark amber bottle with teflon lined caps in a decicator.

Residual chlorine measurement (N, N-diethyl-p-phenylenediamine (DPD) method)

Chlorine is not stable in aqueous solution and the chlorine content of particularly weak solutions, decreases rapidly. Therefore chlorine determination was executed immediately after sampling. An effort was made in order to avoid excessive light and agitation. After standardization of sodium hypochlorite solutions was finished, functionality of chlorine measuring comparator was checked with spectrophotometer. The measurements were carried out using chlorine measuring test kit and DPD-1 tablets. For measuring free chlorine N,N-diethyl-p-phenylenediamine (DPD) 1R was used. The test tube was rinsed with sample water and chlorine DPD 1R tablet was added to a test tube followed by addition of sample water. The test tube was capped and mixed until tablet disintegrate (preferably crush tablet before usage). Immediately the test tube was inserted into DPD chlorine comparator (Hellige Comparator). The slide viewer at the back of the chlorine comparator should be held so non direct light enters through the back of the comparator. With sample tube inserted at top, slide the bar through the viewer and match with color standard and recorded as ppm free available chlorine. The maximum and minimum detectable limit of the method applied was 0.1 and 4 mg/L, respectively.

Trihalomethanes (THM) measurement using gas chromatography (GC)

Gas chromatography (GC) method use headspace for the determination of volatile halogenated hydrocarbons in the samples. Chloroform was detected by an electron capture detector (ECD). Identification was based on retention time while quantification is based on the intensity of the ECD signal using a five-point calibration.

During sample preparation 5 ml of sample using pipette was added into a 20 ml headspace vial and the vial was closed with a crimp cap with a silicon septum. The sample was heated in a closed headspace vial in order to obtain equilibrium between the concentration of the volatile halogenated hydrocarbons in the headspace above the sample and the concentration in the sample. By purging the headspace with Helium, the volatile hydrocarbons in the headspace were transferred to the GC where they were separated. The components were detected by an ECD and calibration curve and control standards were observed using

software (Turbochrom). Identification was based on retention time (5.26 and 11.16 min for chloroform and bromoform respectively) while quantification was based on the intensity of the ECD-signal using a five-point calibration. These retention times slightly vary due to aging of the column and were corrected. The quantification of the components was done automatically by the software using linear regression of the second order. Finally results for chloroform $< 0.5 \mu\text{g/L}$ was reported as $< 0.5 \mu\text{g/L}$. When the total THM result was $< 2 \mu\text{g/L}$, the sum of the THMs was reported as $< 2 \mu\text{g/L}$. But, when the result of one of the components was $> 50 \mu\text{g/L}$, the samples were diluted and re-analyzed.

RESULTS AND DISCUSSION

RSSCT laboratory study

Once each individual GAC's breakthrough curves were developed, the average mass loading of chloroform and bromoform (q in mg THM/g GAC), on the carbon were calculated. The experimental breakthrough curve results were scaled to model the full-scale adsorber with an EBCT of 7.12 min. The scaling equations for the constant diffusivity case as developed by Crittenden et al. (1986) were used to predict adsorption capacity. Since, CD assumes no change in the inter-particle diffusivity with particle size ($X=0$) hence exact similarity between RSSCT and full-scale/ pilot plant can be predicted for smaller molecules like THM (Crittenden et al., 1986; Crittenden, 1991). From these equations, the full scale operating time was determined by $t_{LC} = t_{SC} (\text{EBCT}_{LC}/\text{EBCT}_{SC}) = 23t_{SC}$.

RSSCT experiment for removal of chlorine

Column tests were run to analyze for free chlorine and chlorine breakthrough curve using Norit GCN1240 GAC. Removal of chlorine by GAC reduces the chlorine to non-oxidative chloride ion. The reaction is very fast and takes place in the few centimeters of a new GAC bed where the limiting factor is the rate at which the free chlorine approaches the GAC surface, which leads to a higher reaction for a smaller carbon particles because of its higher surface area or inter-pore diffusivity (Lee and McClure, 1996). Lee and McClure (1996) stated that de-chlorination efficiency is improved by high temperature and lower pH values and the reaction between free chlorine and surface of GAC is represented as $C^* + \text{HOCl} = \text{CO}^* + \text{H}^+ + \text{Cl}^-$ or $C^* + \text{OCl} = \text{CO}^* + \text{Cl}^-$, Where C^* and CO^* represent the carbon surface and the oxidized carbon surface respectively. This is true since the free chlorine species depends pH value where pH less than 6.6 the dominant species of free chlorine is HOCl and at a pH values higher than 8.6 it is OCl^- (Faust and Aly, 1983).

The experiments were conducted for 14 and 8 days with loading rates of 23.69 and 47.38 m/h, respectively. Throughout the experiment the level of free chlorine

concentration in effluent was below the detection limit of 0.1 mg/L as shown in Figure 1. This is in agreement with result from literature which suggest that with 7.5 min EBCT complete de-chlorination (non detectable) can be achieved (Lee and McClure, 1996). GAC removes chlorine by reduction process (not adsorption) and reduction of chlorine occurs in the top few centimeters of GAC filter media which is in agreement with having value (half reduction of chlorine provided by the manufacturers) of 2 and 2.5 cm for Calgon F200 and Norit GCN 1240, respectively.

RSSCT experiment for removal of chloroform

With the help of CD-RSSCTs scaling approach the chloroform breakthrough curves have been established, for Norit and Calgon GAC. RSSCT were operational for seven days with additional of three days at the beginning of the experiment to stabilize the flow. Calgon F200 GAC developed much higher head loss in comparison to Norit 1240 GAC leading to operational problem of bursting fittings of RSSCT, expansion of inlet pipe diameters up to twice their size. During preparation of powdered granular activated carbon (PGAC) it was noticed that Calgon F200 GAC had brittle nature comparing to Norit GCN 1240. This brittle nature of Calgon F200 might contribute to the development of high head loss. However, both Calgon F200 and Norit 1240 GAC's show more or less similar capacity to reach 90% breakthrough point.

Samples were taken from two RSSCTs operated in parallel for Calgon F200 and Norit 1240 GAC's and breakthrough curves were developed as shown in Figure 2. Before reaching $10 \mu\text{g/L}$ RSSCTs were operated up to BVs of about 12,000 and 15,500 for Calgon F200 and Norit 1240 GAC's respectively. However after the $10 \mu\text{g/L}$ breakthrough point is passed both GACs showed similar capacity up to 90 percent breakthrough.

In this research RSSCTs were operational up to 30 thousands BVs (about 21 weeks in full scale) that resulted in 90% breakthrough of chloroform at the end of the experiment. Published result for most of the pilot and full scale studies indicated that the carbon bed life or time to breakthrough of the THMs ranged from 4 to 26 weeks depending on influent concentration, type of THMs removed or EBCT. Previous research conducted on lignite-based GAC (type HD10x30, 9 min EBCT, 76 cm bed depth) for removal of chloroform from tap water showed 4 weeks operation of GAC before breakthrough of $10 \mu\text{g/L}$ (Faust and Aly, 1983).

Based on results of RSSCT experiment the service life of GAC filters, in Coca-Cola treatment plant at Antwerp, before reaching a breakthrough point of $10 \mu\text{g/L}$ can be predicted by the equation: Service time of large column to reach breakthrough point (t_{LC}) = $23t_{SC}$:

Service Life (days) for Calgon F200 = $23t_{SC}$ = 60 days and

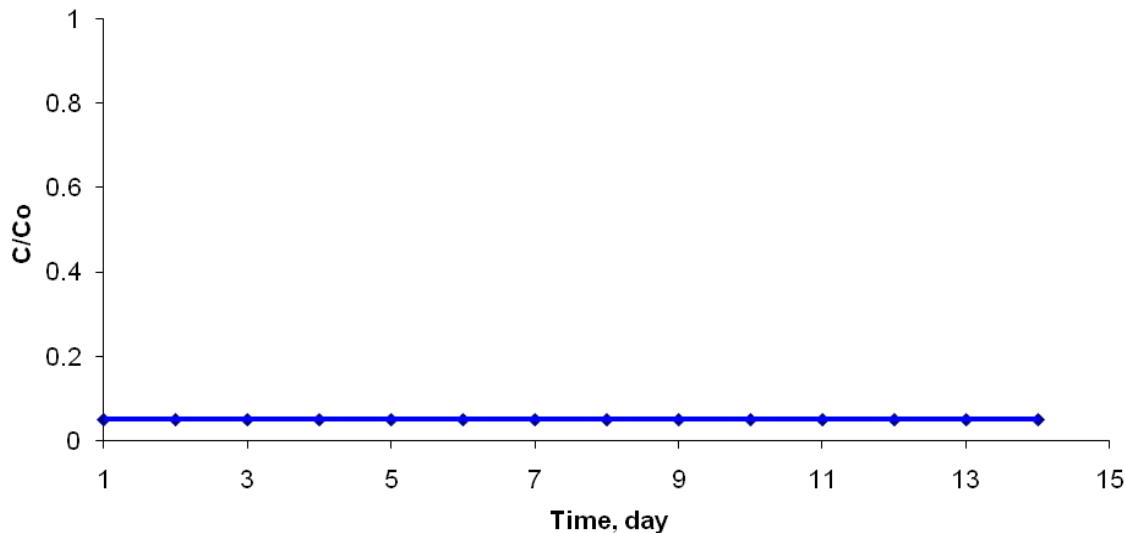


Figure 1. Free chlorine removal during CD-RSSCT experiment, EBCT of 0.62 min, Norit GCN 60×80 GAC; model water: deionized water, 2000 µg Chlorine/ L, pH of 7 ± 0.2 , $T = 20^\circ\text{C}$.

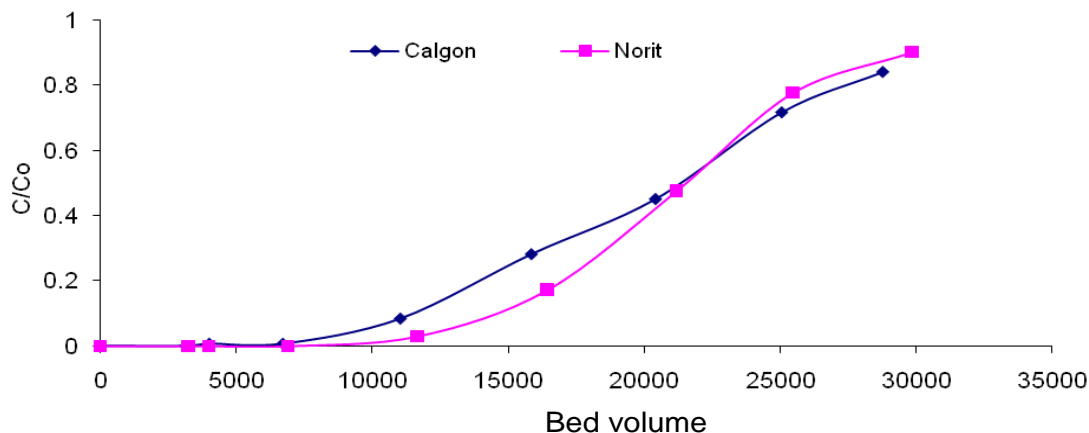


Figure 2. Comparison of chloroform breakthrough curves for Norit GCN1240 and Calgon F200 RSSCT experiment with 60×80 mesh US standard grain size, EBCT of 0.31 min; model water: deionized water, pH of 7.0 ± 0.2 , influent concentration (C_0) = 79.8 ± 4.30 µg/L, 20°C temperature.

Service Life (days) for Norit GAC = $23t_{SC} = 74$ days.

This relative short operational period before breakthrough comparing to years breakthrough for taste and odor compounds implies frequent replacement or regeneration of exhausted GAC. This is in agreement with result from literature that supports GACs need of regeneration every 8 to 10 weeks for removal of THM (chloroform) (Faust and Aly, 1983).

Results obtained in RSSCT (Figure 2) are valid for prediction of full scale plant (Crittenden, 1986). To predict performance of steam regenerated GAC, a separate set of RSSCT should run with steam regenerated GAC. Possible decrease of THM's adsorption capacity of steam

regenerated GAC is not well defined. Hence it is recommended to operate RSSCTs after steam regeneration to predict the actual capacity, with much care during crushing. However, it should be noted that unlike virgin carbon, used carbon cannot be ground to a smaller size without affecting the capacity (Letterman, 1999).

RSSCT experiment for removal of bromoform

Model water with bromoform concentration of 76.45 ± 10.55 µg/L was prepared batch wise and used to feed two RSSCTs, one with Norit 1240 GAC and another with

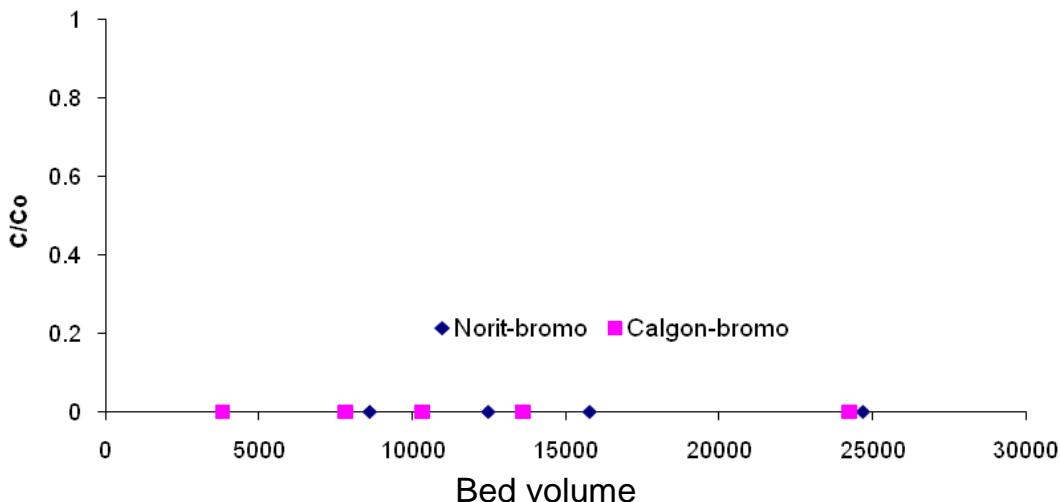


Figure 3. Bromoform removal in RSSCT with Norit and Calgon (60×80 US Standard mesh) GAC for EBCT of 0.31 min; model water: deionized water, $C_o = 76.45 \pm 10.55$ μg bromoform/l, pH of 7.0 ± 0.2 , 20°C temperature.

Calgon F200 GAC. Neutral pH = 7.0 ± 0.2 was maintained by introducing NaHCO_3 buffer and addition of HCl acid. Influent and effluent samples were taken once per day for a total filter run period of five days. RSSCT experiment with Calgon GAC had to be terminated early due to development of very high head loss which makes it difficult to provide consistent feed of model water to the column. Throughout the whole experiment effluent bromoform concentration was below the detection limit of 0.5 $\mu\text{g}/\text{L}$ for both columns.

The results of bromoform (Figure 3) are in agreement with results from literature that suggest following that GAC has much higher adsorbing capacity for bromoform compared to chloroform in the order $\text{CHCl}_3 < \text{CHBrCl}_2 < \text{CHBr}_2\text{Cl} < \text{CHBr}_3$. The more the brominated the compound is, the more it is adsorbed (Faust and Aly, 1983; Letterman, 1999; Potwora, 2006). Potwora (2006), showed bituminous GAC capacity of 16 mg/L for equilibrium concentration of 76.45 $\mu\text{g}/\text{L}$, based on this information RSSCT is expected to run more than two weeks to reach exhaustion. Experimental single solute adsorption value of Calgon F200 and Norit GCN 1240 shows adsorption capacity of 36 mg/g at equilibrium concentration of 76.45 $\mu\text{g}/\text{L}$. Based on batch isotherm experiment before reaching breakthrough of 76.45 $\mu\text{g}/\text{L}$, RSSCT experiment should run more than a month time (two years time in full scale). Up to four months operation time of lignite-based GAC (type HD10×30, 9 min EBCT, 76cm bed depth) for tap water showed complete removal of dibromochloromethane in the effluent. For bromoform large operation time is expected since GAC has high affinity for bromoform than dibromochloromethane the result from literature is in agreement with the result of this research (Faust and Aly, 1983).

RSSCT experiment for removal of combined chloroform and bromoform

Model water with bromoform and chloroform with 49.65 ± 1.55 and 41.30 ± 3.50 $\mu\text{g}/\text{L}$, respectively, was prepared in batch and used to feed RSSCs filled with Norit 1240 GAC and Calgon F200 GAC's. Neutral pH of 7.0 ± 0.2 was maintained by introducing NaHCO_3 buffer and addition of HCl acid. Influent and effluent samples were taken once per day for six days. After four days of operation Calgon F200 GAC showed very high head loss as shown in Figures 4 and 5. The head loss further increases with prolonged run time resulting in early termination of the run at the end of fourth day. Before reaching a breakthrough of 10 $\mu\text{g}/\text{L}$ both GACs showed very similar THM's adsorption capacity (Figures 4 and 5).

During the filter run the effluent bromoform concentration was below the detection limit of 0.5 $\mu\text{g}/\text{L}$ however, effluent Chloroform concentration exceeded the breakthrough value of 10 $\mu\text{g}/\text{L}$ after 19,000 BV for both GACs. From the RSSCT it can be predicted that under similar conditions (e.g. THM's composition and concentrations) the full scale GAC filters in the Coca-Cola plant in Antwerp will operate for 92 days (or 13 weeks) before breakthrough of 10 $\mu\text{g}/\text{L}$ is reached.

The observed increase in operation time compared to the experiment conducted in the previous section for chloroform is mainly due to the substitution of 50% of the chloroform by bromoform. McGuire (1991) also stated that a decrease in concentration of THM and substitution of chlorinated THM by brominated ones increased operation time of GAC filter since GAC has higher affinity to the brominated THMs. The ratio of bromide ion to the chlorine dose affects the formation of THM and

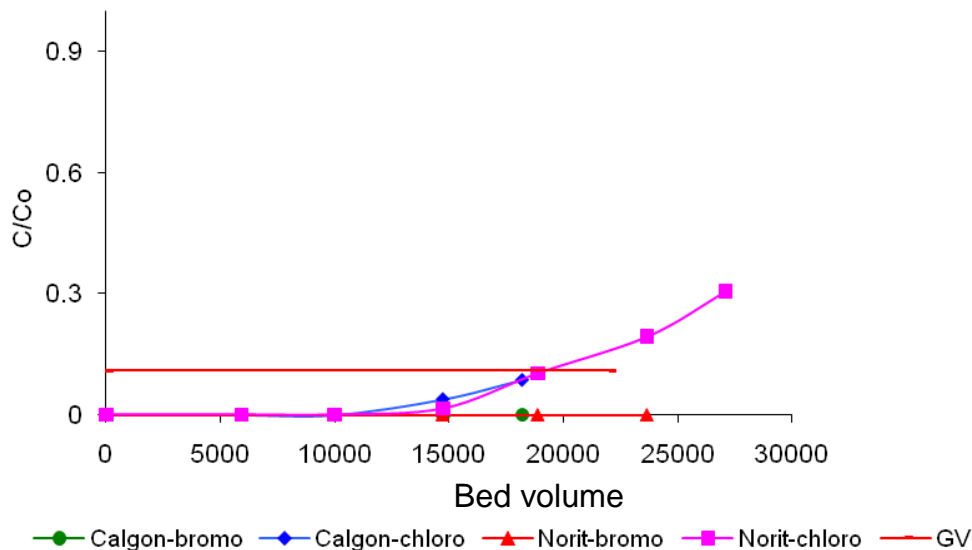


Figure 4. Comparison of bromoform and chloroform breakthrough curves per TTHM; Norit and Calgon (60x80 mesh) GAC obtained in RSSCT for EBCT of 0.31 min; model water: deionized water, pH of 7 ± 0.2 , 20°C temperature.

substitution of chlorine. During treatment steps (transportation) chlorine decrease leading to increase in the ratio of bromide to chlorine hence the TTHM shifts from chlorinated to brominated THMs leading to high adsorption of THMs (USEPA, 1999).

Comparison of Calgon F200 and Norit GCN 1240 media GACs

As per the Chemiviron carbon supplier product bulletin Calgon F200 is prepared by steam activation of selected grade of bituminous coal that have first been pulverized and then agglomerated. Calgon F200 GAC is recommended by the Calgon especially for removing chlorinated compounds and de-chlorination. On the other hand, Norit GCN 1240 is produced from coconut shells by steam activation. Norit GCN is suitable for removal of dissolved organics, including compounds causing taste and odor problems and trihalomethanes (THMs). Calgon F200 and Norit GCN 1240 have a de-chlorination halving value of 2 and 2.5 cm and using EBCT of 7.12 min complete de-chlorination can be achieved. GAC is applied in Coca-Cola Antwerp treatment plant for removal of chlorine, THMs and possibly other contaminants. Considering de-chlorination and THMs removal need for GAC regeneration is controlled by THM breakthrough.

Even though Norit GCN 1240 has a higher surface area (B.E.T) (Table 1) of 1150 m² than Calgon F200 (850 m²) both GACs showed similar adsorption property of THMs. The reason for this might be undeveloped pore structure. Based on laboratory results of RSSCT experiment for THM removal there is no preference of either of GAC

because of similarity in all the experiments. In all the RSSCT Calgon F200 GAC developed high head loss which leads to termination of operation. However, taking in to account previous studies on the origin of materials possibly bituminous material (Calgon F200) might have more macropores structure and Coconut material (Norit GCN 1240) might have more micropores (Crittenden et al., 1991; Potwora, 1978; Letterman, 1999). The micropores result in better adsorption of small size organics like THMs. On the other hand, macroporous carbon is preferred for steam regeneration since activated carbon with large volume of coarse pores usually reactivated better at lower temperature than activated carbon with smaller pores. Since the larger pores may adsorb the adsorbate molecule easier, oxidizing gases may easily reach the deposits of carbonized adsorbate. However, experimental data and information including steam regeneration are required to further examine the best fit GAC.

Conclusions

GAC is applied in carbonated beverage water industry for removal of chlorine, THMs and possibly other contaminants. Considering de-chlorination and THMs removal need for GAC regeneration is controlled by THM breakthrough. Both Calgon F200 and Norit GCN 1240 demonstrated in RSSCT experiments that THMs can be effectively reduced below 10 µg/L. Both Calgon F200 and Norit GCN 1240 showed much higher capacity for bromoform in comparison to chloroform. However, result from RSSCT showed slightly higher (15%) chloroform

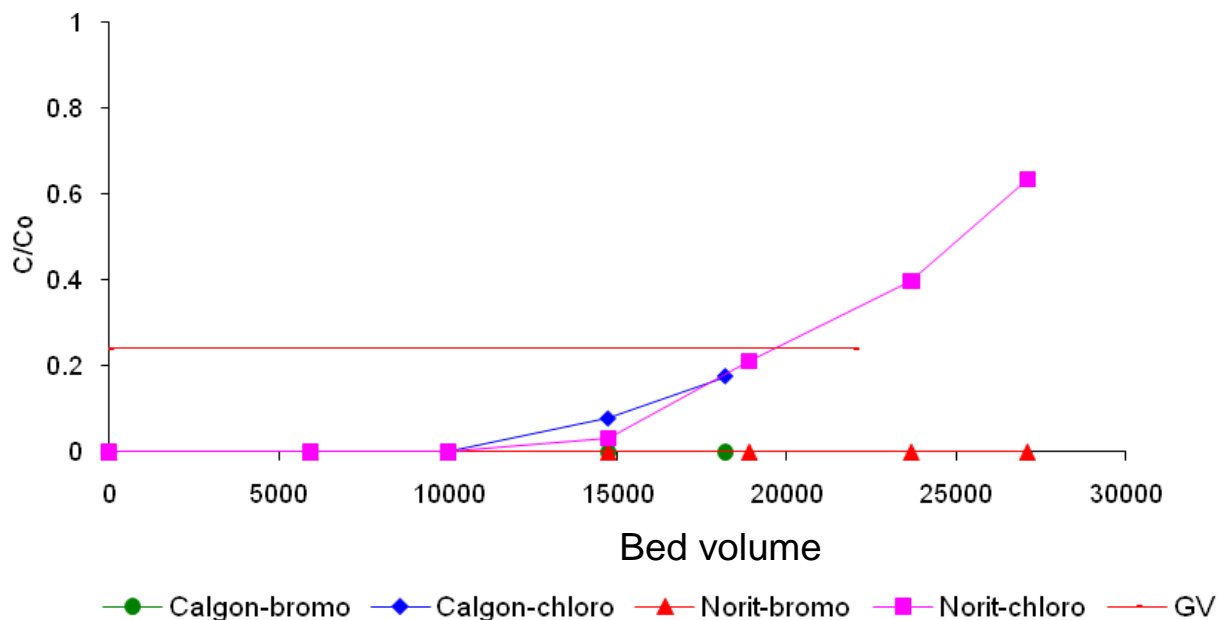


Figure 5. Comparison of bromoform and chloroform breakthrough curves per species; Norit and Calgon (60x80 mesh) GAC obtained in RSSCT for EBCT of 0.31 min; model water: deionized water, pH of 7 ± 0.2 , 20°C temperature.

adsorption capacity of Norit GCN 1240 in comparison to Calgon F200 for $C_0 = 79.8 \pm 4.30 \mu\text{g}$ chloroform/L to reach a breakthrough point of $10 \mu\text{g/L}$. Bromoform breakthrough was not observed in RSSCT Calgon F200 and Norit GCN 1240 GACs during runtime of six days (corresponding to 3.5 months in full scale plant). Extrapolation of results from RSSCT with Calgon F200 GAC suggests that approximately 12,000 BV (2 months operation) could be treated in the full-scale water treatment plant of Coca-Cola in Antwerp (EBCT of 7.12 min) before chloroform ($C_0 = 79.8 \pm 4.30 \mu\text{g/L}$) breakthrough of $10 \mu\text{g/L}$ is achieved. Assuming more realistic chloroform concentration ($C_0 = 41.30 \pm 3.50 \mu\text{g/L}$) in the feed water and mix with bromoform ($C_0 = 49.65 \pm 1.55 \mu\text{g/L}$) much longer service life of 92 days can be expected.

ACKNOWLEDGEMENTS

This work was co-funded by Coca-Cola Company for optimization of Coca-Cola Company treatment plants, which uses chlorinated water. The author would like to thank UNESCO-IHE, the Netherlands for assisting the author to conduct laboratory experiment and analysis of water samples; and Brussels laboratory of Coca-Cola Company for the analysis of trihalomethanes. The support from staffs of UNESCO-IHE, Coca-Cola Company of Antwerp and Haramaya University, Ethiopia are highly appreciated. Author thanks anonymous reviewers for their constructive comments.

REFERENCES

- Alicia C, Alvarez J (2000). DBP Formation during Chlorination. *Am. Waste Water Assoc. J.* 92(6):76-90.
- Al-Naseri SK, Abbas TR (2009). Predicting NOM Removal by Fixed-Bed GAC Adsorbers. *Jordan J. Civil Eng.* 3(2):172-183.
- Badruzzaman M (2005). Mass Transport Scaling and the role of Silica on Arsenic Adsorption on to Porous Iron Oxide (Hydroxide). A Ph. D. Dissertation, Arizona State University, December 2005, Arizona, U. S. A.
- Baruth EE (2005). *Water Treatment plant designn*, 4th edition. Tata McGraw-Hill Publishing Company Limited, New York.
- Capar G, Yetis U (2002). Removal of THM precursors by GAC. *Water Resour. J.* 36(10):1379-1384.
- Crittenden JC, Berrigan JK, Hand DW (1986). Design of Rapid Small Scale Adsorption Test for a Constant diffusivity. *Water Pollut. Control Fed.* 58(4):312-319.
- Crittenden JC, Berrigan JK, Hand DW (1987). Design of Rapid Fixed Bed Adsorption Tests for Non-Constant Diffusivities. *Environ. Eng.* 113(2):243-259.
- Crittenden JC, Reddy PS, Arora H, Trynoski J, Hand DW, Perram DL, Summers RS (1991). Prediction of GAC Performance with Rapid Small-Scale Column Tests. *Am. Water works Assoc.* 83(1):77-87.
- Edward EB (2005). Technical Editor, *Water Treatment Plant Design*, New York.
- Faust SD, Aly OM (1983). *Chemistry of Water Treatment*, Butterworth publisher, Woburn, U. S. A.
- Fearing DA, Banks J, Wilson D, Hillis PH, Campbell AT, Parsons, SA (2004). NOM Control Options: The Next Generation. *Water Sci. Technol.* 4(4):139-145.
- Gallard H (2002). Chlorination of Natural Organic Matter: kinetics of THM formation. *Water Resour. J.* 36(1):65-74.
- Lee MW, McClure AF (1996). Choosing and Sizing. *Water Technology* (<http://www.watertechnonline.com/article.asp?IndexID=5190501>, date accessed: August, 2010).
- Letterman RD (1999). *Water Quality and Treatment: A handbook of community water Supplies*. American Water Works Association, McGraw-HILL Companies, USA.
- Lin CH, Huang Y, Hao O (1999). *Ultrafiltration Processes for Removing*

- Humic Substances. *Water Resour. J.* 33(5):1252-1264.
- McGuire M (1991). Evaluating GAC for Trihalomethanes Control. *J. Am. Water Works* 83:38-48.
- Potwora JR (2006). Trihalomethanes Removal with Activated Carbon, Water conditioning and purification (<http://www.wcponline.com/pdf/Potwora.pdf>, date accessed: May 2008).
- Potwora LS (1978). *Water Treatment Plant Design for the Practicing Engineer*. Butterworth, Stoneham, U. S. A.
- Qasim SR, Motley EM, Zhu G (2004). *Water Works Engineering Planning, Design And Operation*. Prentice Hall PRT, New Jetsy, U. S. A.
- Roy GM (1995). *Activated Carbon Applications in the Food Pharmaceutical Industries*. Technomic Publishing Company, Inc., Lancaster, Pennsylvania, U.S.A.
- Tchobanoglous G, Burton FL, Stensel HD (2003). *Wastewater Engineering Treatment and Reuse*, 4th edition. Tata McGraw-Hill Publishing Company Limited, New Delhi.
- United States Environmental Protection Agency (USEPA) (1999). *Alternative Disinfectants and Oxidants Guidance Manual*, Office of Water (4607), U. S. A.