

USE OF ACTIVATED CARBON

FROM OILY FLY ASH TO REMOVE
DISENFECTANT BY-PRODUCTS FROM
DRINKING WATER SUPPLY SYSTEMS
IN SMALL COMMUNITIES

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Executive Summary

Water utility managers in small communities face numerous challenges in protecting drinking-water supplies from water-borne diseases. To supply safe drinking water, chlorine is the most common oxidant and disinfectant used to eradicate and inactivate the pathogens that cause such diseases. Chlorine not only oxidizes iron and manganese but it also removes odour and colour and prevents biological re-growth in water distribution systems. Due to these characteristics and its relatively low cost, more than 90% of the world's water supply systems use chlorine. This disinfectant in residual form, however, reacts with the natural organic matter (NOM) present in the water, forming hundreds of disinfection by-products (DBPs), among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common groups. Some of the compounds within these groups are harmful to human health and are possible carcinogens.

The main objective of the research was to design a cost-effective and affordable filtration system to reduce NOM in the intake water source and remove THMs and HAAs in the drinking-water systems of the communities of Torbay and Pouch Cove near St. John's. To reduce the concentration of THMs and HAAs, a series of experiments were conducted on tap water with a low-cost filtration system which was developed using the carbon extracted from oil fly ash. The results show more than a 95% removal of THMs and a 35% removal of HAAs from the tap water in both communities. A significant removal of chloroform, bromodichloromethane, and bromoform in the THM group and a high

percentage removal of bromochloroacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid in HAA group was achieved during column and batch tests.

The developed adsorbent was also applied as a filtration technology to assess the removal efficiency of DBP-causing precursors such as total organic carbon (TOC) from the intake water sources in both communities before chlorination. More than a 92% removal of TOC from Pouch Cove and a 65% removal from the Torbay intake water were achieved. The filtered water was later chlorinated to assess THM and HAA formation potential. The test results showed a significant reduction in the formation potential of THMs and HAAs, making the filtration technology an effective and affordable adsorbent in supplying safe drinking water to rural communities.

Although the adsorbent used for this research has the potential to remove DBPs from drinking-water supply systems, the results reported here are based on limited data and requires an in-depth investigation before it can be used as a filtration media. It is recommended that the adsorption capacity be improved by activation and micro-sieving of the extracted carbon and by using different physical and activation processes. The regeneration and backwashing of the adsorbent once it reached breakthrough was not conducted in this research. It would be useful to develop the feasibility of regeneration of the adsorbent. Since TOC values were performed only in the summer months, more samples should be collected and analyzed covering temperature ranges in different seasons and hydrologic variations and its hydrophilic and hydrophobic characteristics should be studied covering the whole season.

The Royal Bank of Canada (RBC) research and outreach fund from The Harris Centre partially provided financial support to Masood Ahmad, a graduate student completing his M.Eng. thesis entitled “Affordable Filtration Technology of Safe Drinking Water for Rural Newfoundland and Labrador.” Masood graduated in the spring of 2013 and is currently working in Alberta, Canada.

The Harris Centre’s knowledge mobilization team provided support in the dissemination of information by arranging meetings with the news media and providing opportunities to our team in various public events:

1. Putting Waste to Work: Refreshing Research on An Innovative Water Treatment System for Rural Communities, The Harris Centre Annual Report 2012-2013, pp. 9-10.
2. Low-Cost Adsorbent to Reduce Disinfection By-products and Colour from Pouch Cove Water Supply System, An experimental set-up to demonstrate technology in MUN Buttoned Event in Downtown, 12-13 November 2013.
3. Filtration technology demonstration to the Councillors from Pouch Cove Community in October 2013.
4. ENVIRONMENT: Making clean water more affordable, The Telegram, 7 October 2014, and also in Vital Signs, 2014.
5. CBC News coverage on affordable filtration technology, 24 October 2013.

Research publications from this project include:

1. Husain, T. and Ahmad, M. 2014. Low Cost Adsorbent to Reduce Disinfection By-products from Drinking Water in Small Communities’ International Conference in Environmental Engineering and Computer Applications, Hong Kong, 26-28 December 2014.
2. Husain, T. 2014. Low Cost Adsorbent to Reduce Disinfection By-products from Drinking Water in Small Communities, International Conference on Water, Informatics, Sustainability, and Environment, Keynote Speaker, 26-28 August, Canadian Museum of History, Gatineau, Quebec, Canada.
3. Husain, T. 2014. Development of Activated Carbon from Oil Fly Ash for Water and Wastewater Treatment Systems, Invited Speaker, Proc. WSTA 11th Gulf Water Conference, Oman, 20-22 October 2014.
4. Ahmad, M., Mofarrah, A., and Husain, T. 2012. Development of cost-effective filtration technology to remove disinfectant by-products in drinking water supply system, Invited Speaker, Saudi International Environmental Technologies Conference, 13-15 May 2012, Riyadh, Saudi Arabia.

CHAPTER 1 INTRODUCTION

1.1 Background Information

Water utility managers face numerous obstacles in protecting drinking-water supplies from water-borne diseases. To supply safe drinking water, chlorine is the most common oxidant and disinfectant used to eradicate and inactivate the pathogens that cause such diseases. Chlorine oxidizes iron and manganese; it also removes odour and colour and prevents biological re-growth in water distribution systems. Due to these characteristics and its relatively low cost, more than 90% of the world's water supply systems use chlorine. This disinfectant in residual form, however, reacts with the natural organic matter (NOM) present in the water, forming disinfection by-products (DBPs) in these systems.

NOM consists of numerous organic materials such as proteins, humic substances, hydrophilic acid, lipids, carbonates, and bicarbonates. A reaction between the NOM and the residual chlorine causes the formation of more than 600 DBPs in water supply systems, among which trihalomethanes (THMs) and haloacetic acids (HAAs) are the most common groups. Some of the compounds within these groups are harmful to human health. To protect the public from exposure to these DBPs, regulatory agencies have placed limitations on their levels in drinking water to minimize their adverse effects on human health without any microbiological water quality changes and are based on the

levels of DBPs and residual chlorine at different locationsl in the drinking-water supply system. To improve the quality of water from conventional water supply systems, we need to introduce new technology to enhance water quality and reduce DBPs. Activated carbon is one such filtration technology used for the reduction of THMs and HAAs, but, due to its high cost, it is not economical. The objective of this research is to develop a cost-effective filtration technology using extracted carbon from oily fly ash (OFA) and apply this technology to the water supply of two small communities (i.e., Torbay and Pouch Cove) near St. John's, Newfoundland.

The removal of those pathogens in drinking water which cause water-borne diseases such as cholera, typhoid, and dysentery is a global issue, and water distribution supply systems are unable to provide a safe water supply to consumers unless these disease-causing pathogens are inactivated in the supply system. Even countries such as the United States and Canada with their advanced water treatment technologies must control outbreaks of water-borne diseases.

Based on World Health Organization (WHO) statistics, approximately 3,400,000 people and young children under the age of five die every year in Asia, Africa, and Latin America due to water-borne diseases (WHO, 2002). More than 100 people died and 400,000 were affected in 1993 in Milwaukee, Wisconsin, in the USA as a result of cryptosporidium in the drinking water (Mackenzie et al., 1994). Approximately 2,300 people suffered from E. coli contamination in the drinking water in Walkerton, Ontario, Canada (MOE, 2002).

Chlorine is now commonly used as a disinfectant in North American water supply systems (US EPA, 2006; Health Canada, 2007). Although other disinfectants such as chloramines, chlorine dioxide, ozone, and ultraviolet (UV) radiation are used, chlorine is the most effective and economical. However, once disinfectants have been added to the water, some DBPs are formed in the presence of NOM in the water supply system. Parameters such as NOM, pH, temperature, chlorine dose, and bromine influence the level of DBP formation in drinking water (Zhang et al., 2008).

1.2 There are hundreds of different types of known DBPs associated with various forms of disinfectants, and it is difficult to monitor all of them. Recent focus has, however, been on two groups of DBPs—THMs and HAAs—as these have been identified as the largest class of DBPs detected on a weight basis in chlorinated drinking water. Chloroform (CHCl₃), bromodichloromethane (BDCM) or CHBrCl₂, chlorodibromomethane (CDBM) or CHB₂Cl, and bromoform (CHBr₃) are four compounds within the THM group. The maximum acceptable concentration of the sum of their concentrations, known as total trihalomethane (TTHM), is 100 µg/l (Health Canada, 2012). There are nine compounds within the HAA group, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA), as well as three mixed chloro- and bromo-acetic acids, namely bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and bromochloroacetic acid (BCAA). The combined concentration of the five most prevalent HAAs (MCAA, DCAA, TCAA, MBAA, DBAA), known as HAA5, should not exceed 80 µg/l (Health Canada, 2012). According to the United States Environmental Protection Agency (U.S. EPA) Stage 1 Disinfectants/Disinfection By-Products (D/DBP) Rule, the maximum concentration level (MCL) for TTHMs and HAA5 are 80 and 60 µg/l respectively (U.S. EPA, 1998). Objectives

The main objective of this research is to optimize the effectiveness of activated carbon from OFA to remove trihalomethanes (THMs) and haloacetic acids (HAAs) which are

DBPs of concern in the drinking-water supply systems in small communities in Newfoundland and Labrador, Canada. The objectives of the study are (a) to identify the physical and chemical parameters involving activated carbon and their relationships that affect the removal of DBPs in drinking water, (b) to develop techniques for imaging and quantitation of the chemical interactions in the removal process, and (c) to develop an activated carbon filter as a potential future technology. This study will be useful in understanding the chemical processes for the removal of DBPs by the activated carbon being developed by the proponent and his team and to assess the economic and technical feasibility of the activated carbon filter for rural communities on a commercial scale.

1.3 Rationale of the Study

There are about 480 drinking-water systems in the province, 95% of which use chlorination as a disinfectant. According to CCME guidelines, the limits for acceptable concentrations of total THMs and HAAs are 0.10 ppm and 0.080 ppm respectively and 23% of the province's systems exceed the total THMs concentrations, while the exceedances for HAAs is 34.3% (Government of Newfoundland and Labrador, 2009). This study will help in reducing THMS and HAAs in drinking-water supplies for these public water systems to a safe level by introducing activated carbon as a filter technology in tap water. The proposed technology is simple and also economically viable because it uses activated carbon, which can easily be extracted and purified from OFA, which is an abundant waste from the burning of heavy fuel oil (Mofarrah and Husain, 2010). This study also fits with the program priority areas in the provincial government mandate: (a)

to provide an economically sustainable in-home treatment as a source of drinking water in Newfoundland and Labrador; and (b) to provide this technology as a cost-effective treatment option for delivering clean, uninterrupted drinking water in rural communities.

This proposal also fits in the broad category of the environment and deals with treatment technologies that minimize DBPs in drinking water and supply safe drinking water to small communities where other water treatment options are not cost-effective. The results from this proposed study will provide research evidence for the use of activated carbon from OFA as a technology for the removal of THMs and HAAs. This will help local decision-makers to adopt this technology to minimize DBPs in the drinking-water supply systems.

1.4 DBP Levels in the Province's Water Supply Systems

The Department of Environment and Conservation in Newfoundland regularly monitors THMs and HAAs in the province's water supply systems (MOENL, 2011). The results are plotted in Figures 3.2 and 3.3. As demonstrated in these figures, THMs and HAAs in various communities exceed the Health Canada guidelines of 100 µg/L for THMs and 80 µg/L for HAAs; the THM levels in a few communities even exceeded 400 µg/L. More than one-third of the communities have higher HAAs levels than the Health Canada guidelines, and 27 communities exceed 300 µg/L in their water supply systems.

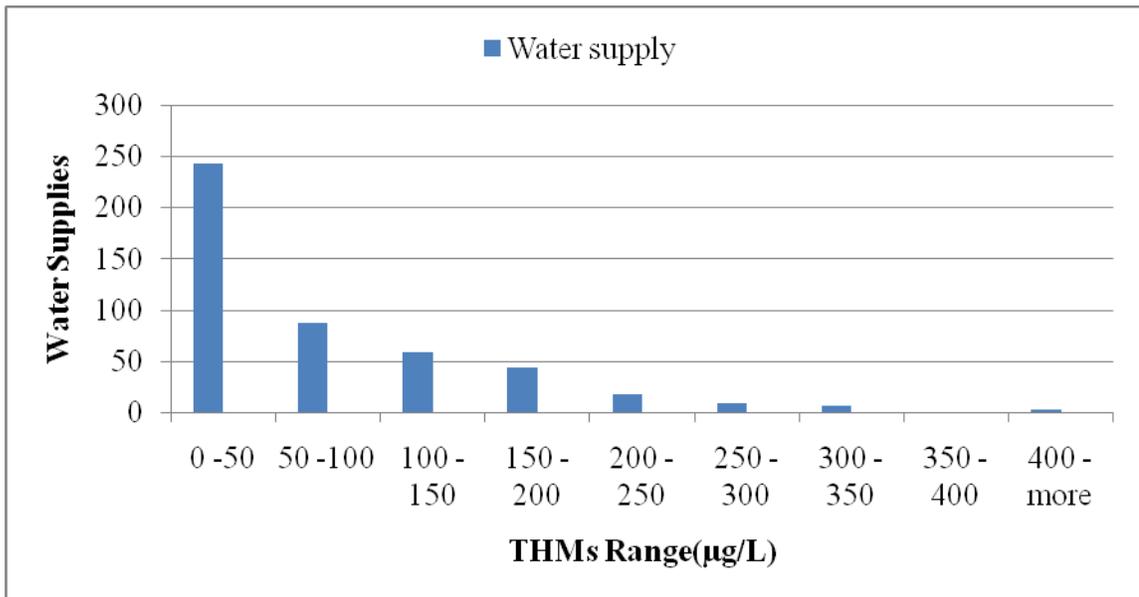


Figure 1.1 Distribution of THMs in Newfoundland & Labrador communities (MOENL, 2011)

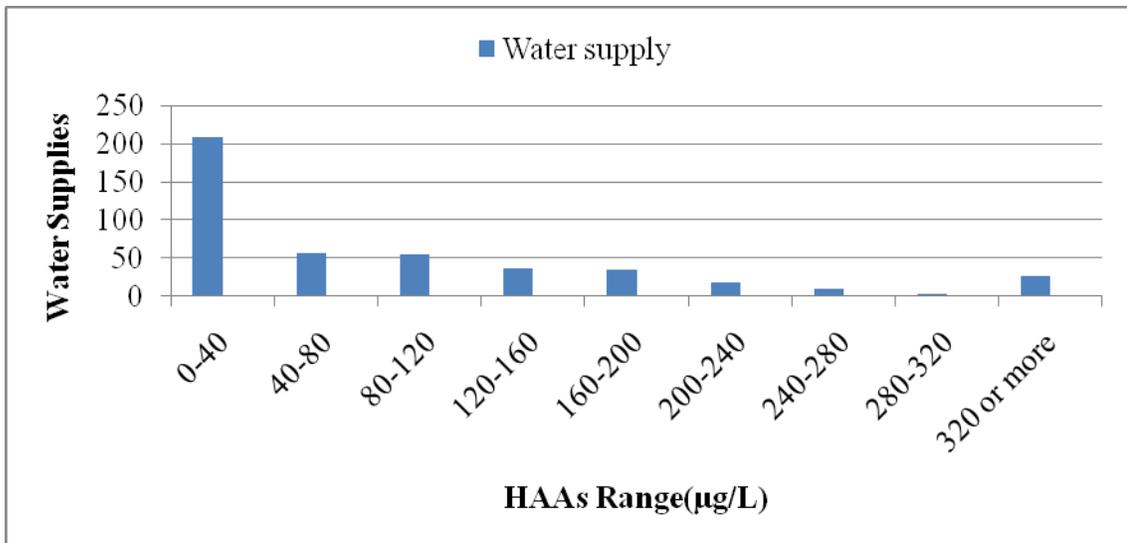


Figure 1.2 Distribution of HAAs in Newfoundland & Labrador communities (MOENL, 2011)

CHAPTER 2 RESEARCH METHODOLOGY

2.1 Sample Collection

This research focuses on two communities: Pouch Cove, with a population of 1,900, located about 30 km northeast of St. John's; and Torbay, located 15 km north of St. John's, with more than 7,000 residents. These communities do not have water treatment plants and, instead, rely solely on chlorination of the intake water and pH adjustment.

Tap water samples from both communities were collected from different locations and raw water samples collected from the intake sources before chlorination.

All bottles, lids, and Teflon liner septa were cleaned with laboratory detergent and washed with tap water and rinsed three times with ultrapure water for sample collection. The tap water samples from Pouch Cove and Torbay were collected in glass bottles. Before the samples were collected, 100 mg of granular ammonium chloride (NH_4Cl) per litre of tap water was added to the sample containers to convert free chlorine to residual chlorine. The tap was drained for 3 to 5 minutes to allow the temperature to stabilize. Sample bottles were filled to their head space but preventing the flushing out of ammonium chloride. The bottles were capped and agitated for 15 seconds after collection. They were kept in a chilled container to maintain a temperature below 4°C , and transported to the laboratory within a few hours of collection. In the laboratory, the samples were protected from light, kept below 4°C , and analyzed within 14 days.

2.2 Sample Analysis

The TOC was measured with TOC analyzers (Model TOC-5000A) equipped with an infrared detection system. Dissolved organic carbon (DOC) was determined after passing the sample through a 0.45 µm membrane filter. TOC was calculated by subtracting the inorganic concentration from total carbon concentration:

$$\text{Total organic carbon} = \text{Total carbon} - \text{Inorganic carbon}$$

An ultraviolet (UV254) experiment was performed on a HP 8453 Spectrometer with a 1 cm quartz cell. The spectrophotometer wavelength was set at 254nm and samples were analyzed. ChemStation software was used to generate the absorption data and the Specific Ultraviolet Absorbance (SUVA) was calculated with the following equation:

$$\text{SUVA} = \text{UV}/\text{DOC} * 100 \text{ (L/mg-m)}$$

A Model 3000 pH meter was used for pH determination. Buffer solutions of pH 4.0, 6.0, and 10.0 with +/- 0.1 sensitivity were used for calibration purposes before measuring the pH values.

A 93703 Portable Microprocessor Turbidity Meter measured turbidity; it comes with two calibration standards, and a monthly calibration is recommended.

The concentration of free chlorine was measured with a HACH pocket colorimeter II analysis system using U.S. EPA-approved Method 8021 (free chlorine) for water, treated water, and sea water samples. Method 8167 determined the total chlorine in

water, treated water, and wastewater. The estimated detection limit (EDL) = .02 mg/L and the precision at 95% confidence interval = 1+/- .05.

A micro-electron capture detector (μ -ECD) is installed in the GC/ECD to analyze all nine HAA compounds: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA). To measure the concentration of four THM compounds in the drinking water—i.e., chloroform (CHCl_3), bromodichloromethane (CHCl_2Br), dibromochloromethane (CHClBr_2), and bromoform (CHBr_3)—EPA Method 501.3 (EPA 500-Series) with a purge and trap procedure was used. GC/MS and StratUm PTC measured the THM values in the drinking water.

CHAPTER 3 RESULTS AND DISCUSSION

3.1 Development of Low Cost Filtration Technology

In this research, carbon extracted from heavy oil fly ash (HOFA) was used as a filter media. HOFA is collected directly by the electrostatic precipitators of power plants which use heavy fuel oil or crude oil as its fuel source. Such fly ash is available in abundance worldwide and is mainly disposed into landfills. The chemical composition of HOFA varies from plant to plant, but it contains a significant amount of unburned carbon which can be used as an adsorbent for water and wastewater treatment processes. Impurities from HOFA obtained from a power plant were removed using the following cleaning procedures.

1. HOFA was washed with distilled water, with a ratio of 1 gram of fly ash to 10 ml of water, and stirred at 10 rpm using a Birds & Philips stirrer 7790-400 for 12 hours with the magnetic bar dipped in the solution to capture the contamination at room temperature.
2. After filtration, the washed raw HOFA was thoroughly mixed with an aqueous acid solution, in a ratio of 1 gm of fly ash to 5 ml distilled water, with a 28% nitric acid solution at 60°C for 2 hours and then rinsed several times with distilled water to remove the nitrate ions.

3. The washed HOFA was then treated with HCl in the ratio of 1 gm of fly ash to 5 ml distilled water with 15% HCl at 60°C for one hour and rinsed several times with distilled water to remove the chloride ions.

4. After filtration, the wet, clean carbon was oven-dried for 24 hours at 105°C.

A detailed analysis was conducted for raw fly ash and treated carbon for heavy metals as listed in Table 3.1. As shown in the table, most of the metals are removed, but research is in progress to remove nickel, vanadium, and zinc from the fly ash to make clean carbon free from trace metals.

Table 3.1 Metals in heavy oil fly ash (HOFA)

Metal (mg/kg)	Raw HOFA (mg/kg)	Washed HOFA(mg/kg)	US EPA Limit (mg/kg)
Arsenic (As)	ND	ND	0.01
Cadmium (Cd)	ND	ND	0.005
Cobalt (Co)	1.23	ND	-
Copper (Cu)	3.6	ND	1.3
Mercury (Hg)	.094	ND	0.002
Nickel (Ni)	2176.32	331.91	-
Lead (Pb)	2.593	ND	-
Selenium (Se)	ND	ND	-
Vanadium (V)	5251.471	221.321	-
Zinc (Zn)	46.947	14.858	5.0
Carbon	86.12%	89.65%	

ND = Not detectable

The particle size of HOFA was measured with Horiba Particle Laser Scattered Particles Size Analyzer model LA-950 with a wet dispersion method in a NaPO_3 solution. It showed that the mean diameter of the collected washed fly ash is $59.395 \mu\text{m}$ with a standard deviation of $31.54 \mu\text{m}$ (Figure 3.1).

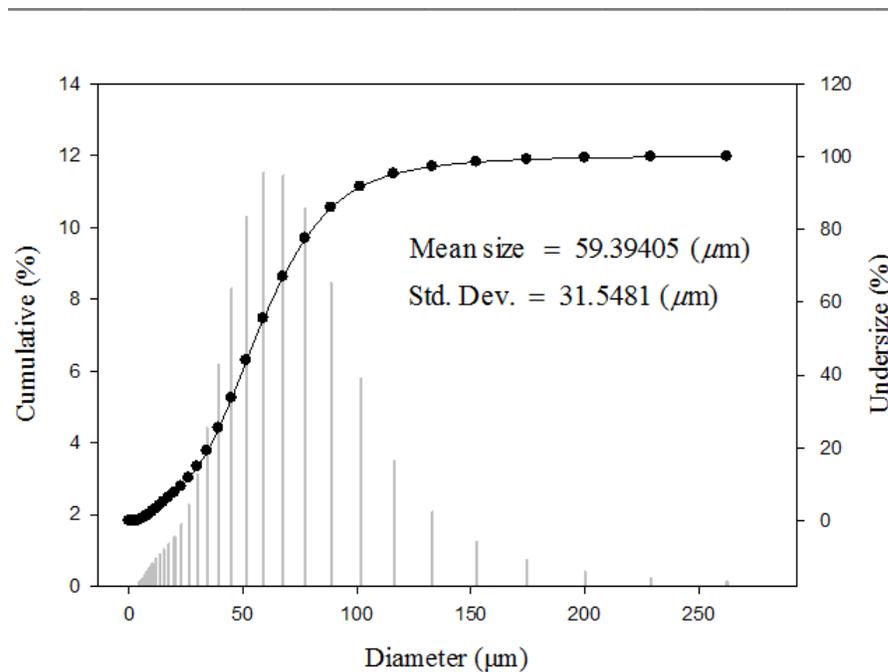


Figure 3.1 Particle size graph

3.2 Experimental Set-up

A column test experiment was designed using a Pyrex glass column 30 cm in length and having an internal diameter of 40 mm. Sixty-four grams of extracted clean carbon was used in the column. In order to prevent leaching of the fine particles into the

filtered water, glass wool and a 1 μm filter at the outlet of the column were used. The column test was conducted using the same tap water as that used in the batch test. A flow rate of 3.5 ml/min was maintained using a peristaltic pump. The advantage of using a peristaltic pump is that there is no cross-contamination, since water flowing through the column does not touch any mechanical part of the pump but passes through the internal tubing system. The filtered sample was collected and analyzed for THM and HAA concentrations in Torbay and Pouch Cove.

3.3 Removal of THMs from Pouch Cove Tap Water

The results for chloroform, BDCM, and bromoform removal as listed in Table 3.2 are very encouraging. The adsorbent used in this experiment helped significantly in the removal of THMs. As shown in Table 3.2, chloroform comprised 219 $\mu\text{g/l}$ of the total THMs in the reference tap water. While running water through the filter media for 1440 minutes, the total THM concentration was reduced to 70 $\mu\text{g/L}$ (Figure 3.2). After 2880 minutes of filtration, the concentration of chloroform was reduced by 50%. BDCM constitutes 27.45 $\mu\text{g/L}$ of the reference tap water; even after 1440 minutes of filtration, its concentration was less than half of the reference water concentration. The bromoform concentration in the reference water was 22.28 $\mu\text{g/L}$, but after filtration it showed zero concentration in the filtered water. Only the DBCM percentage contribution remained unchanged in the filtration process.

Table 3.2 THM compounds in tap water before and after filtration in Pouch Cove ($\mu\text{g/L}$)

	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C_o/C_i
REF	219	27.45	19.86	22.25	288.57	1
30	0	15.84	20.63	0	36.48	0.12
60	0	14.75	19.67	0	34.42	0.11
120	0	15.54	20.21	0	35.76	0.12
180	0	14.75	19.59	0	34.35	0.11
240	0	15.17	20.12	0	35.30	0.12
300	0	15.10	19.70	0	34.81	0.12
420	0	14.79	19.69	0	34.48	0.11
540	0	14.77	19.59	0	34.36	0.11
750	0	14.79	19.60	0	34.39	0.11
930	0	0	19.59	0	19.59	0.06
1170	0	14.84	19.62	0	34.46	0.11
1440	0.47	15.57	20.32	0	35.89	0.12
2160	70.21	26.96	19.77	0	116.95	0.40
2880	127.8	0	19.66	0	147.48	0.51

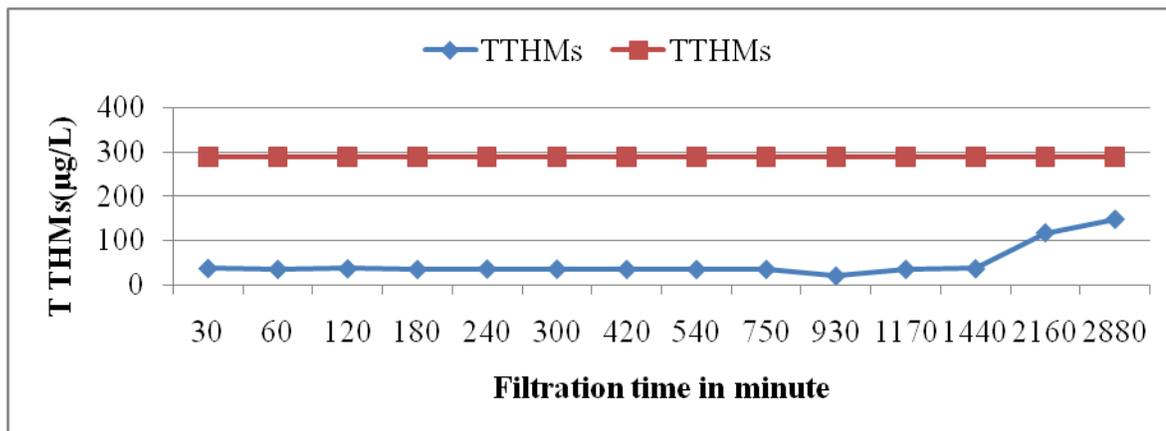


Figure 3.2 TTHM concentrations in filtered water with times of filtration

3.4 Analysis of HAAs in Pouch Cove Water

The adsorbent was very effective in removing HAA compounds, especially DCAA, TCAA, BCAA, and DBCAA. Table 4.3 shows the concentration of these compounds as 163 µg/L, 7.14 µg/L, 233.85 µg/L, 25.31 µg/L, and 20.47 µg/L in the reference tap water respectively. After filtration for up to 480 minutes, these compounds were removed completely. TBAA was completely removed in the filtered water supply system even after 2880 minutes of filtration (Figure 3.3).

Table 3.4 HAA compounds in tap water and filtered water in Pouch Cove (µg/L)

	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	C ₀ /C _i
Tap water before filtration	0	0	163.69	7.14	233.85	0	25.31	0	20.47	450.48	1
Filtered water (30)	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0
120	0	0	0	0	0	0	0	0	0	0	0
180	0	0	0	0	0	0	0	0	0	0	0
240	0	0	0	0	0	0	0	0	0	0	0
300	0	0	0	0	0	0	0	0	0	0	0
420	0	0	0	0	0	0	0	0	0	0	0
540	0	0	105.05	0	0	0	0	0	0	105.05	0.23
750	0	0	209.45	7.20	0	0	0	0	0	216.66	0.48
930	0	0	141.46	10.28	58.20	0	0	0	0	225.60	0.50
1170	0	0	204.31	9.72	55.46	0	0	0	0	343.49	0.76
1440	0	0	168.60	8.82	51.12	0	21.48	0	0	299.22	0.66
2160	0	0	29.99	4.88	31.92	0	22.65	0	0	109.61	0.24
2880	0	0	150.56	6.57	40.17	0	23.8	0	0	210.49	0.46

In Figure 5.44, the reference tap water had 450.5 $\mu\text{g/L}$ of total HAAs, but after filtration the concentration was considerably reduced. As shown in Figure 5.45, the curve shows that after 2880 minutes of filtration the concentration was very low in the filtered water. This means that the adsorption efficiency of clean carbon was very high compared to that of activated carbon.

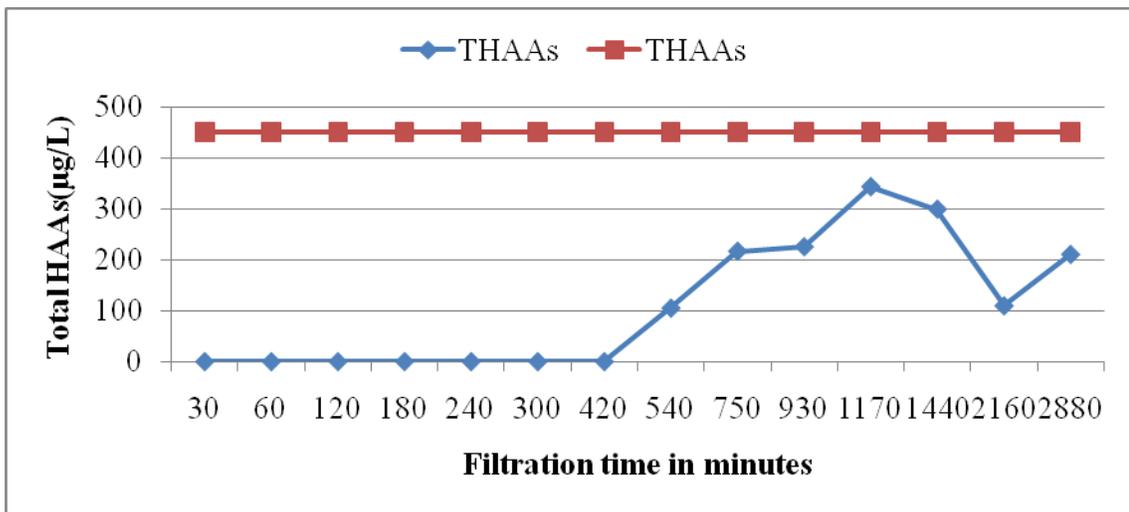


Figure 3.3 Graph of times and THAA concentrations

3.4.1 THM data in Torbay tap water

The trend of the Torbay water system filtration with the adsorbent was observed to be very effective in removing chloroform (Table 3.5 and Figure 3.4). The chloroform in the raw water was 259.36 $\mu\text{g/L}$, which, after filtration for 740 minutes, was reduced to 56.06 $\mu\text{g/L}$. The initial concentration of other compounds such as BDCM was 38.41 $\mu\text{g/L}$ and was reduced to 5.17 $\mu\text{g/L}$. This indicates that the activated carbon is very effective in removing

these two THM compounds. The level of reduction for the other two compounds, DBCM and bromoform, was not significant.

Table 3.5 Individual THM compounds in unfiltered and filtered water in Torbay

TIME (min)	Chloroform	BDCM	DBCM	Bromoform	TTHMs	C _o /C _i
Tap water before filtration	259.36	38.41	10.39	12.47	320.65	1
Filtered water 20	5.43	0	4.16	5.23	14.84	0.04
40	0	2.41	4.16	5.23	11.42	0.03
60	4.20	2.720	4.18	5.23	16.34	0.05
80	194.43	32.42	5.66	8.59	241.12	0.75
100	13.01	4.51	4.79	5.24	27.56	0.08
120	101.57	20.24	5.94	5.30	133.06	0.41
140	8.1	4.70	4.58	5.23	22.34	0.04
260	63.62	5.31	4.30	5.23	78.47	0.24
380	65.77	4.87	4.33	5.68	80.66	0.25
500	5.57	5.62	4.33	5.30	20.83	0.06
620	58.01	4.57	4.25	5.50	72.36	0.22
740	56.06	5.17	4.30	5.35	70.90	0.22

As shown in Figure 3.4, reference tap water had a total THM concentration of 332.24 µg/L before filtration. However, after continuous filtration through activated carbon for 740 minutes, its total THM concentration was, on average, less than 50 µg/L; this indicates that the filtration was very effective in removing chloroform and BDCM, because these two compounds are dominant. As shown in Figure 3.4, the trend shows that the filtered water

THM concentration gradually increased, but it is much below the level in the unfiltered water, even for 740 minutes of filtration.

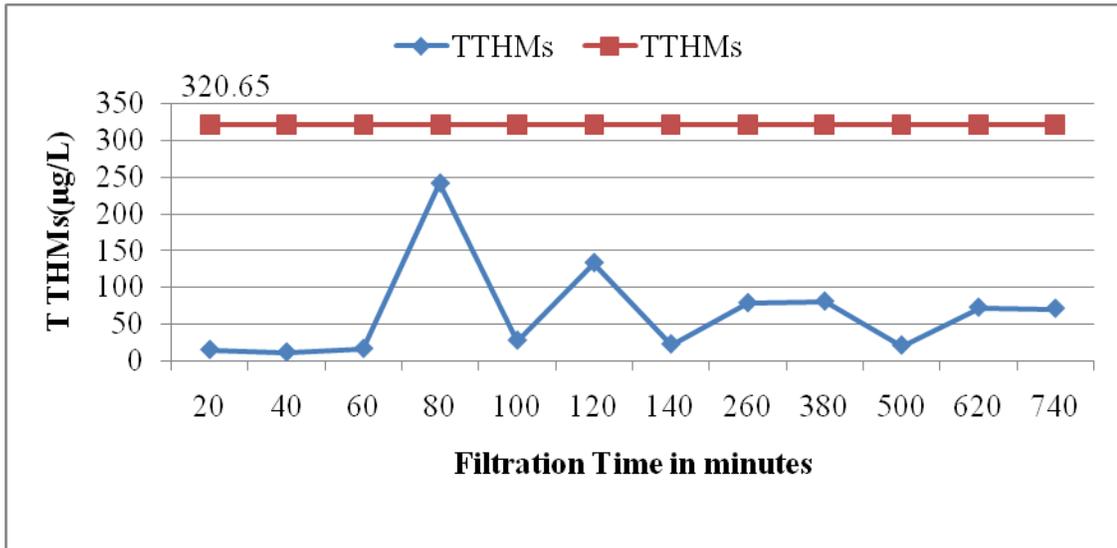


Figure 3.4 Total THM variation with time in filtered water in Torbay

3.4.2 HAAs in Torbay water before and after filtration

The adsorbent does not have much effect on removing HAA compounds from the Torbay water supply system (Table 3.6).

Table 3.6 HAAs in tap water before and after filtration in Torbay (µg/L)

	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	C _o /C _i
Tap water before filtration	0	0	51.01	5.48	48.71	0	36.39	0	0	141.60	1
Filtered water (20)	0	0	55.06	0	32.53	0	0	0	0	87.59	0.61
40	0	0	59.46	6.06	51.68	0	35.80	0	0	153.02	1.08
60	0	0	50.73	5.41	52.30	0	36.60	0	0	145.06	1.02
80	0	0	48.26	5.32	46.34	0	36.39	0	0	136.32	0.96
100	0	0	0	5.98	54.61	0	37.23	0	0	97.83	0.69
120	0	0	52.88	5.69	52.07	0	35.27	0	0	145.92	1.03
140	0	0	50.31	5.52	45.23	0	36.14	0	0	137.21	0.96
260	0	0	61.02	66.98	15.94	0	1.76	0	0	145.72	1.02
380	0	0	57.57	64.89	16.24	0	1.78	0	0	140.50	0.99
500	0	0	62.75	68.82	17.03	0	1.82	0	0	150.44	1.06
620	0	0	59.79	69.86	16.75	0	1.78	0	0	148.20	1.04
740	0	0	61.48	66.21	16.50	0	1.78	0	0	145.99	1.03

3.5 Removal of Precursors in Pouch Cove Intake Water

There are two ways to reduce DBP formation: apply a filtration media to tap water, and reduce organic precursors in the raw water, mainly total organic carbon (TOC) from the source water. These methods are discussed below.

The raw water samples used in this research were collected from the intake source. Parameters such as TOC, pH, UV₂₅₄, turbidity, and water colour were measured and the results tabulated in Table 3.7. The results show a high level of TOC in the intake water and a turbidity above 1 NTU.

The filtered samples were analyzed for TOC concentration, pH, turbidity, and UV₂₅₄. As shown in Table 3.7, raw water passes through the column and is filtered through clean carbon. The TOC of the raw and filtered water was analyzed to determine the removal efficiency of TOC, as tabulated in Table 3.7. The adsorbent was effective in removing TOC from the Pouch Cove raw water.

Table 3.7 Intake water quality and reduction in TOC in Pouch Cove before and after filtration

Time (min)	pH	Uv254 (cm)	Turbidity (NTU)	TOC (mg/L)	% TOC Reduction	C_o/C_i
Raw water before filtration	6.61	0.13	1.45	13.64	0	1
After filtration 240	6.14	0.007	0.35	1.16	92	0.08
540	6.7	0.01	0.34	1.04	93	0.076
900	6.63	0.03	0.34	2.10	85	0.15
1620	6.43	0.01	0.36	5.7	58	0.41
2940	6.4	0.005	0.4	6.73	53	0.49
3720	6.51	0.01	0.38	4.90	64	0.35
4020	6.71	0.05	0.34	5.49	60	0.40
4440	6.72	0.005	0.33	5.64	50	0.41
5100	6.65	0.001	0.36	5.45	52	0.40
6000	6.72	0.001	0.35	6.84	39	0.50
7500	6.74	0.001	0.37	5.56	50	0.40

As shown in this table, TOC, UV₂₅₄, and turbidity levels were high in the raw water and the pH value was within the range of 6.5 and 8.5. The TOC reduction was 92% for 240 minutes of filtration but, after this, the TOC removal efficiency decreases and, after 7500 minutes of filtration, the TOC concentration removal reached 50%.

The pH, turbidity, and UV₂₅₄ concentration were within the ranges established by the Canadian drinking-water guidelines. The pH should be between 6.5 and 8.5 and the turbidity less than 0.5 NTU. There is no specific guideline for UV₂₅₄. However, as shown in the table, UV₂₅₄ and turbidity were reduced significantly in the filtered water.

3.6 Removal of DBP Precursors in Torbay Intake Water

Raw water samples were collected from North Pond, which is the distribution source for the community of Torbay, and the values of the measured parameters such as TOC (mg/L), pH, UV₂₅₄, and turbidity are listed in Table 3.8. The TOC of the raw water was 5.41 mg/L, while the turbidity was lower than that of raw water from the Pouch Cove intake source.

Table 3.8 Intake water quality and reduction in TOC in Torbay before and after filtration

Time (min)	pH	UV254 (cm)	Turbidity (NTU)	TOC (mg/L)	% Reduction	C ₀ /C _i
Raw water before filtration	6.23	0.02	0.59	5.41	0	1
After filtration 240	5.64	0.04	0.31	1.31	76	0.24
540	5.79	0.002	0.35	1.86	66	0.34
900	5.8	0.003	0.42	1.70	69	0.31
1560	5.76	0.04	0.43	1.83	66	0.18
2880	5.99	0.06	0.39	3.37	38	0.62
3600	6.01	0.042	0.33	2.37	56	0.43
3960	6.43	0.02	0.42	2.08	40	0.38
4200	6.51	0.009	0.35	2.57	55	0.47
4740	6.75	0.007	0.36	2.74	52	0.50
5700	6.74	0.13	0.37	2.87	49	0.53
7200	6.82	0.003	0.34	3.31	41	0.61

3.7 Formation of THM Potential – Pouch Cove Intake Water

Samples collected after 4, 16, 74, and 125 hours of filtration were chlorinated in order to study the DBP formation potential in the filtered water. Similarly, the raw water was also chlorinated. An attempt was made to maintain the same residual chlorine level in both the filtered and raw water samples. For chlorination, aqueous sodium hypochlorite was used. The THM formation in both the filtered and raw water was studied with contact times of 4, 12, 18, and 24 hours. After that, water samples were analyzed for THM, as shown in Table 3.9: the levels of chloroform and BDCM were significantly lower in the filtered water than in the raw water for the same contact time. The other two compounds, DBCM and bromoform, showed no significant changes.

Table 3.9 Pouch Cove THMs filtered and raw water data

Pouch Cove Raw Water	Dose mg/l	Contact time (hrs)	Filtration time (hrs)	Chloroform	DCBM	DBCM	Bromoform	RTHMs	FTTHMs	EPA TTHMs	Canadian TTHMs
	8	4	0	144.38	55.30	36.1022	22.18	257.97		80	100
	8	12	0	155.60.	55.85	36.48	22.25	270.20		80	100
	8	18	0	179.39	60.089	36.28	22.17.	297.94		80	100
	8	24	0	165.22	57.083	36.09	22.16	280.57		80	100
Pouch Cove Filtered Water	8	4	4	28.44	29.07	35.12	22.25		114.90	80	100
	8	12	16	27.91	28.78	34.95	22.23		113.88	80	100
	8	18	74	44.47	42.44	39.61	22.13		148.6677	80	100
	8	24	125	52.88	43.61	39.32	22.23		158.06	80	100

As shown in Figure 3.5, the individual concentration of THM compounds such as chloroform, BDCM, DBCM, and bromoform were very high; these gradually decreased in the raw water with different contact times.

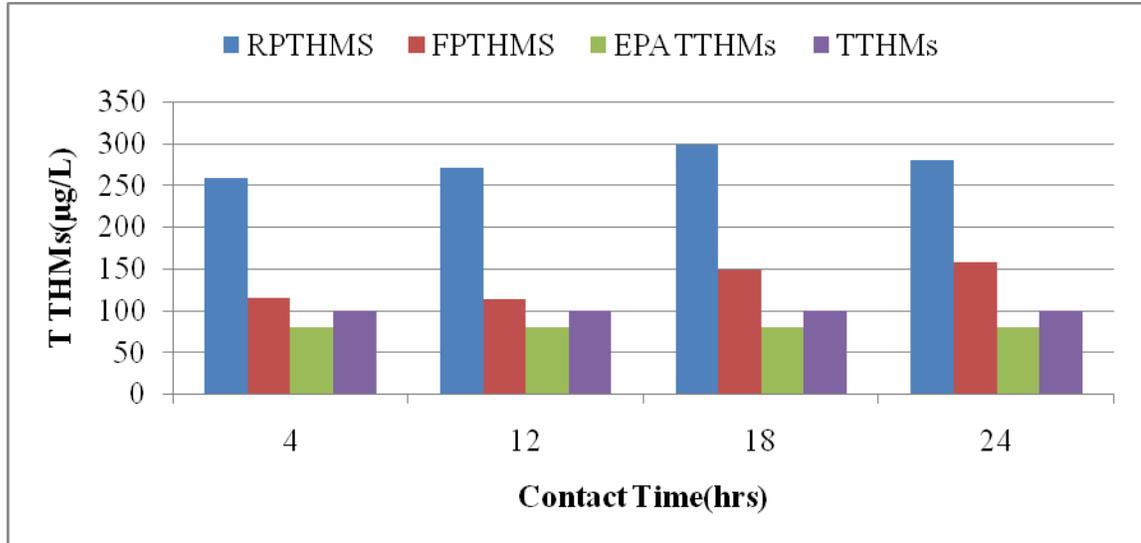


Figure 3.5 Total THMs in raw and filtered water with different contact times in Pouch Cove

As shown in Figure 3.5, filtered water with a low TOC level has significantly lower THM compounds than raw water.

3.7.1 HAAs after chlorination of Pouch Cove raw and filtered water with different contact times

After analyzing the sample for HAAs, as shown in Table 3.10, the concentration of all nine HAAs except BCAA were very low in the filtered water compared to their concentrations in the raw water.

Table 3.10 Individual HAAs in raw and filtered water – Pouch Cove intake source

	Dose mg/L	Contact time (hrs)	Filtration Time (hrs)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	PRTHAA	PFTHAA
Pouch Cove Raw Water	8	4	0	0	0	14.27	13.87	140.12	0	23.79	0	0	192.0683	0
	8	12	0	0	0	15.81	11.5	176.15	0	22.34	0	0	225.8292	0
	8	24	0	0	0	8.61	10.86	189.94	0	22.36	0	0	231.7967	0
Pouch Cove Filtered Water	8	4	4	0	0	0	0	11.33	0	0	0	0	0	11.33
	8	12	16	0	0	0.75	0	13.78	0	19.77	0	0	0	34.31
	8	24	154	0	0	1.38	12.36	17.04	0	21.09	0	0	0	39.52

As shown in Figure 3.6, only DCAA, TCAA, BCAA, and DBAA compounds show high levels in the raw water after chlorination, and the concentration of these compounds increased gradually with contact time after chlorination.

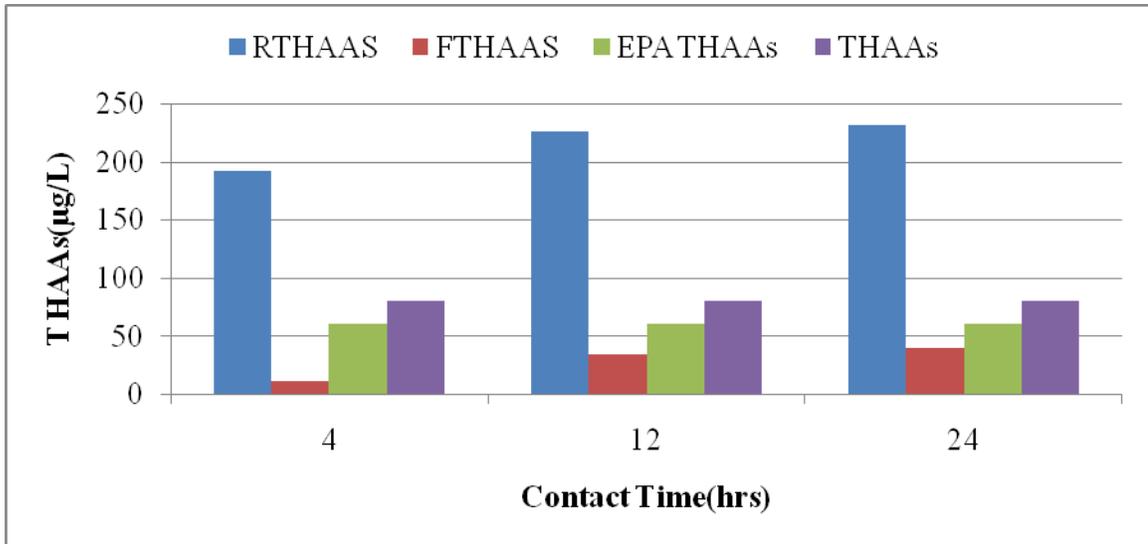


Figure 3.6 Individual HAAs in raw and filtered water with different contact times in Pouch Cove

3.8 THM analysis after chlorination of Torbay raw and filtered water with different contact times

As shown in Table 3.11, in the chlorinated raw water all four THM compounds were higher than in the treated water with a low TOC value. This pattern is almost the same as that in the Pouch Cove community water system. Chloroform and BDCM concentrations significantly decreased in the treated water. The other two compounds in THM group, DBCM and bromoform, do not show any significant changes in both treated and raw water.

Table 3.11 Individual THM compounds in raw and filtered water in Torbay intake source

Raw Water Torbay	Dose (mg/L)		Filtered Water Timing (hrs)	Chloroform	BDCM	DBCm	Bromoform	RTTHMs	FTTHMs	EPA TTHMs	TTHMs
Raw Water Torbay	8	4	0	56.97	72.95	35.31	22.91	188.15	0	80	100
	8	12	0	625.50	67.008	34.73	22.54	749.79	0	80	100
	8	18	0	468.05	76.73	34.97	22.26	602.03	0	80	100
	8	24	0	624.56	62.78	34.43	22.21	743.99	0	80	100
Filtered Water Torbay	8	4	4	27.02	27.60	36.08	22.18		112.90	80	100
	8	12	16	34.65	34.26	36.80	22.12		127.84	80	100
	8	18	74	257.93	67.84	35.52	22.05		383.37	80	100
	8	24	120	304.14	72.79	35.45	22.08		434.48	80	100

As shown in Figure 3.7, the THM in the filtered water (FTTHMs) is much lower than in the THMs in the raw water (RTTHMs).

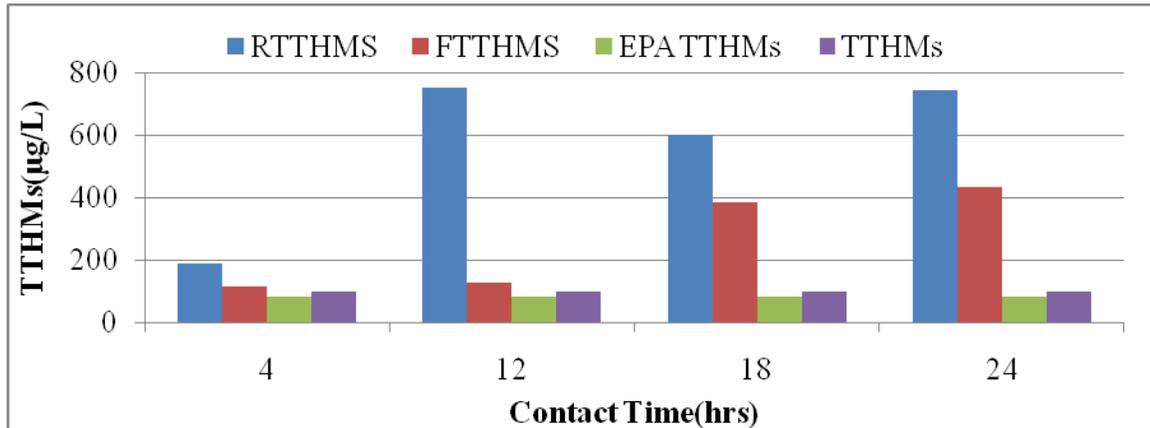


Figure 3.7 Individual THMs in raw and filtered water with different contact times in Torbay

As shown in Table 3.12 and Figure 3.8, the concentrations of DCAA, TCAA, BCAA, and DBAA were higher in the raw water, but after filtration the total HAA was considerably reduced.

Table 3.12 Individual HAAs in raw and filtered water – Torbay intake water system

	Dose mg/L	Contact Time (hrs)	Filtered Water (hrs)	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	TRHAA	TFHAAs
Raw Water Torbay	8	4	0	0	0	7.08	13.58	82.08	0	24.73	0	0	127.47	0
	8	24	0	0	0	5.81	12.61	65.98	0	22.40	0	0	106.81	0
Filtered Water Torbay	8	4	4	0	0	0	0	11.56	0	0	0	0	0	11.56
	8	24	120	0	0	16.21	17.46	83.05	0	23.46	0	0	0	140.20

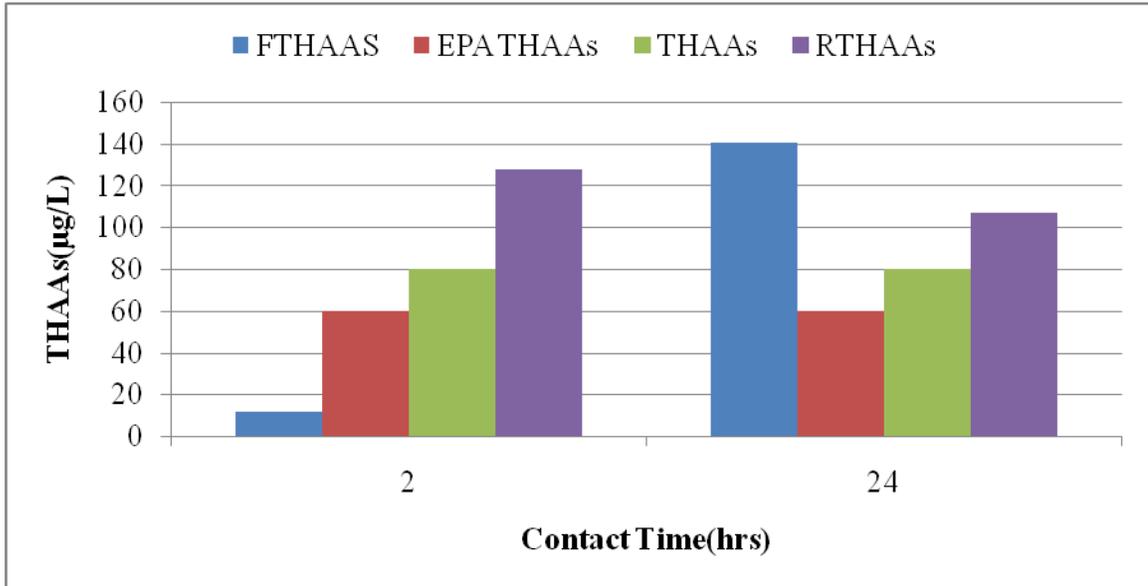


Figure 3.8 Formation of HAAs in raw and filtered water with different contact times in Torbay

CHAPTER 4 CONCLUSIONS AND RECOMMENDATION

Although there are different types of treatment methods, including membrane filtration, coagulation, reverse osmosis, and other adsorption processes, available to reduce THMs and HAAs in drinking-water systems, most of them require trained personnel to operate and maintain the system and a high capital investment. For these reasons, it is not feasible to install such systems in small communities. The main objective of this research was to identify a cost-effective adsorbent that would remove DBPs and their precursors. The adsorbent developed from ash residues can be easily installed and operated at a very low incremental cost. In this research, the extracted adsorbent was tested with a series of experiments using raw and treated water from the community of Pouch Cove near St. John's. The results show a significant removal of DBPs and their precursors. This research also shows that the developed product can be used as an effective and inexpensive filtration media to reduce THMs and HAAs in the water supply system. This adsorbent also has the potential to provide safe drinking water to rural communities.

4.1 Conclusions

The following main conclusions were drawn from this research.

1. For Pouch Cove tap water, more than 50% of the THMs were removed with a continuous run for 48 hours.
2. The extracted clean carbon removed more than 95% of the HAAs from the Pouch Cove tap water for a continuous filtration for seven hours.
3. The TOC concentration in the Pouch Cove raw water was 13.64 mg/L. After 150 hours of filtration, the TOC was less than 5.56 mg/L. After up to 15 hours of filtration, the reduction was more than 85%.
4. There was also a considerable reduction in turbidity and UV absorbance, which indicates an overall improvement in the quality of the water in both communities.
5. To assess the formation of THMs and HAAs in the raw water in the communities of Pouch Cove and Torbay with different TOC values, the raw water and the filtered water were chlorinated with a fixed amount of chlorine, keeping the same contact times for both waters. The formation of THMs in the Pouch Cove water showed that chloroform and BDCM levels were 144.45 and 55.33 µg/L respectively in the raw water for a four-hour contact time, while filtered water had only 28.44 and 29.07 µg/L chloroform and BDCM; this showed a significant decrease in DBP formation in the treated water.
6. HAA compounds, such as DCAA, TCAA, BCAA, and DBAA, were 14.27, 13.87, 140.1, and 23.79µg/L respectively in the raw water at a four-hour contact time. These compounds were completely eliminated in the filtered water.

4.2 Recommendations

Although the adsorbent used for this research has the potential to remove DBPs from drinking-water supply systems, the results reported here is based on limited data and requires an in-depth investigation before it can be used as a filtration media. Some of the limitations highlighted in this section with a summary for future research are as follows:

1. Our analysis is based on a limited number of samples. In order to better understand the variation of THMs and HAAs in tap water, more samples should be collected and analyzed and cover different seasons and times, including weekends and weekdays. Sample collection should also be done at different locations in the water distribution systems and records should be maintained on the type of pipe materials and the size of the pipes at the point of sampling.
2. It is recommended that the adsorption capacity be improved by activation and micro-sieving of the extracted carbon and by using different physical and activation processes. Further research work on the preparation of activated carbon with chemical impregnation and homogenization is recommended.
3. Regeneration and backwashing of the adsorbent was not conducted in this research. It would be useful to develop the feasibility of regeneration of the adsorbent.
4. Since TOC values were performed only in the summer months, more samples should be collected and analyzed covering temperature ranges in different seasons and hydrologic variations.

5. Residual chlorine in the tap water should be maintained at a level that does not cause any microbial growth and, at the same time, the levels should not be too high. In this research, a limited number of samples were chlorinated to study the potential formation of THMs and HAAs with different contact times. It is suggested that a detailed scientific investigation be conducted on the measurement of residual chlorine in the treated water with a better control of its level with different contact times of up to three to four days.

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