Granulation of Powdered Activated Carbon Generated from Corner Brook Pulp and Paper Mill Ash Waste

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Executive Summary

Although chlorine is commonly used disinfectant in water treatment system to eradicate disease-causing pathogens but the residual chlorine in the water reacts with the natural organic matters (NOM) and produces compounds known as disinfection by-products (DBPs). There are hundreds of DBPs formed in the chlorinated water but trihalomethanes (THMs) and haloacetic acids (HAAs) are the two major groups of DBPs, which are currently being regulated by Health Canada.

In this study, the removal of NOM from surface water intake and reduction of THMs and HAAs in the water distribution system were investigated in the Pouch Cove community water system using granular activated carbon (GAC) developed from the Corner Brook Pulp and Paper (CBPP) fly ash. The clean carbon from CBPP was mixed with bitumen as binder and hexane as solvent which was calcinated and later activated to produce GAC. The GAC, thus developed, was used in the column tests to assess NOM removal efficiency in the intake source. Effects of binder to carbon ratio, calcination and steam activation temperature, temperature increasing rate, and steam activation time were studied to produce GAC with highest surface area, porosity, and hardness. Granules with 30:70 binder to carbon ratio, calcinated at 750°C, activated at 950°C for 3 hours with 15°C/min of heating rate were found to be the ideal conditions for GAC production for NOM removal more than 60%. Follow-up chlorination experiments illustrate that the formation of DBPs were significantly reduced in the water supply system. Used GAC were regenerated for reuse in the system. It is concluded that the regeneration at 916°C for 43 minutes under 350mL/min of steam would lead to optimum regeneration conditions. The findings of this study will help in developing GAC filtration technology to reduce DBPs and provide a simple, affordable, and safe drinking water to small communities in the province.

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1. Introduction

Activated carbon has been widely used as an effective adsorbent to remove odor, taste, toxic chemicals, organic carbons including natural organic matters, and unwanted contaminants (Kim, 2009). Activated carbon exists in two common forms, powder activated carbon (PAC) and granular activated carbon (GAC). Usually, PAC has a better pore structure and surface area than GAC but due to simplicity of GAC use, its regeneration potential, and its granular structure makes it more practical for NOM removal than PAC (GAN *et al.*, 2006).

1.1 Background Information

The Corner Brook Pulp and Paper (CBPP) Limited, which plays a vital role in the economy of the western Newfoundland, utilizes a thermal-mechanical pulping process to produce standard newsprint and other specialty newsprint grades. Approximately 700 metric tons of newsprint is produced per day using steam mainly from boiler No.7, which is operated by a mixture of bunker C fuel, waste oil fuel, and hog fuel. Approximately 10,000 metric tons of boiler ash and bottom ash are generated annually by the mill and disposed into the landfills (The Western Star, 2010). Since the ash is very rich with the unburned carbon 70-80% by weight (Zhang 2017a; Zhang, et al., 2017b; Shadbah etal, 2018; Taghizadehgan 2019), it is a good and economical source for activated carbon which once extracted from ash and cleaned can reduce the waste residue significantly for landfill disposal. The treatment of the ash during extraction of carbon will also detoxify the waste residue causing less impact on the groundwater and environment around the landfill.

Previous study mainly focused on the generation of activated carbon (AC) from CBPP ash through physical activation processes (Zhang 2017a; Zhang, et al., 2017b). The effects of different activation temperatures and different activation time lengths were investigated in the previous studies using powdered activated carbon (PAC) and found that the activated carbon (AC) generated from CBPP ash waste has a great potential to resolve the problem of disinfection-by-products (DBPs) in the drinking water systems in rural in the province (Shadbahr, et al., 2017, Zhang et al., 2017a; Zhang et al., 2017b). Although PAC has a good potential to remove NOM but it can only be employed in the static processes with no disturbance and once saturated with NOM, it should be removed and disposed without regeneration. Once applied in a filtration system, the PAC can cause blocking which will result in unstable water head pressures and inconsistent flow rates. Due to these reasons, PAC filtration technology is not common and it is not economically and technical feasible in the drinking water treatment systems. In order to improve the operational feasibility of this powder form of activated carbon from CBPP ash, a granular type of CBPP activated carbon derived from powdered form can last for a longer period and it can also be regenerated and reused.

1.2 Objectives and Scope of Work

The main objective of this study is to develop granular activated carbon from the current available powdered CBPP activated carbon to meet the practical application requirements and to benefit the local communities. Since CBPP fly ash contains more than 70% carbon by weight, the recovery of which from the ash will not only reduce the amount of waste disposal to the landfill but it will also convert waste materials into a valuable produc which has been found economically feasible and applicable in finding affordable and easy-to-install filtration technology for small community drinking water systems (Shadbahr et al., 2018, Zhang et al, 2017a, and Zhang et al, 2017b).

In this study, the parameters such as binder types and binder to AC ratio will be optimized in the granulation process. After granulation, the GAC will be further pyrolyzed under different temperatures and different pyrolysis time to induce the crosslinking reaction, improve surface area and enhance its porosity. The GAC with the largest surface area and porosity will be employed in the column filtration experiment.

Other objective of this study is to optimize the process of regeneration of the spent carbon for its reuse.

2. Experimental Setup

In this study we covered Pouch Cove water system for a detailed analysis. Pouch cove is a community with about 2,100 people in the community. It is located 27 km north of St. John's (Figure 1). The main intake source for the drinking water in this community is from North Three Island pond. The pond water pH before entering into the distribution systems is adjusted between 6.5 and 8.5 using soda ash and then chlorinated. Since there is no treatment to reduce NOM concentration in the raw water, DBPs in the chlorinated drinking water are high (average of 206µg/l of HAAs and 200 µg/l of THMs) while the Health Canada guideline is 80 µg/l for HAA and 100 µg/l for THM (Municipal Affairs and Environment-Government of Newfoundland and Labrador, 2018, March 13).

Figure 2-1: study area

Figure 2-2: North Three Island Pond, Pouch Cove

2.1 Water Characterization

Water samples from the lake were collected, transported to the lab, and stored in a refrigerator under 4℃. Bottles and lids used for water sampling were washed with detergent and rinsed with distilled water several times before collection. 100mg of ammonium chloride (NH_4Cl) per liter of water sample was added to remove residual chlorines (Kim *et al.*, 2003). For testing, the sampled water was filtered through 0.45 µm membrane filter to remove suspended organic carbons. Organic molecules remaining in the water after passing though the membrane is called dissolved organic matter (DOM) (Kolka *et al.*, 2008). Water samples were characterized for pH using pH meter, total organic carbon (TOC) using TOC analyser, and ultraviolet absorbance (UV_{254}) using Genesys 10S UV-Vis from Thermo-Scientific, and elemental analysis using ICP-MS.

2.2 Adsorbent Preparation

Corner Brook Pulp and Paper (CBPP) mill, located in the west coast of Newfoundland and Labrador, uses thermal and mechanical pulping process to produce 700 metric tons of newsprint per day. This mill produces around 10,000 metric tons of boiler ash and fly ash on yearly basis which is a valuable source for carbon (Levesque *et al.*, 2010). In this research, CBPP fly ash was used as the source of carbon to produce granular activated carbon.

2.2.1 Powder Activated Carbon Production

CBPP is a source of carbon with high carbon content. However, some impurities such as aluminum, magnesium, manganese, and calcium in low concentration exist in the source. The presence of impurities in the carbon is not desired in the preparation of activated carbon due to obstruction of pore development (Yeganeh *et al.*, 2006). The pretreatment of ash was therefore needed before activation.

Sieving and Pretreatment

Raw CBPP was sieved using a 30-mesh screen (U.S sieve series) to remove larger particles and then crushed in a Siebtecknik puck mill for 20 seconds. Grinded sample was then washed with 5% HNO_3 at the ratio of 10 mL of acid per g of carbon at 80°C for 2-3 hours to remove volatile organic compounds (VOCs) and other impurities. At the end, the sample was repeatedly washed with distilled water until reaching neutral pH value. The cleaned sample was then dried at110°C overnight. The obtained product is called washed CBPP in this study

CBPP Activation

In this study, two-steps process (carbonization and activation) for preparing activated carbon was used. Both carbonization and activation was carried out in a vertical programmable furnace (Carbolite Gero Manufacturer model) with high control accuracy to reach critical temperatures.

For pyrolysis, 15g of washed CBPP was placed in the furnace tube. The temperature was then increased to 850°C at a rate of 15°C/min and held for 1 hour. Nitrogen gas flow was passed through the furnace at 500cm^3/min to remove air in the tube and organic matters from the sample. Then nitrogen flow switched to CO_2 and steam at the rate of 500cm^3/min for 2 hours to develop pore structure and carbon burn off. Carbo was weighed once tube cooled down to room temperature. The product of activation thus obtained is called PAC in this study.

Carbon burn off was calculated according to Equation 2-1.

$$\textbf{Burn off (\%)}=\frac{w_1-w_2}{w_1}\times 100 \qquad \textit{Equation 2-1}$$

Where W_1 is the weight of washed CBPP before activation; and W_2= weight of PAC

2.2.2 Granular Activated Carbon Production

Raw CBPP, washed CBPP, and PAC were used to develop granular activated carbon. Five different binders including Carboxymethyl Cellulose (CMC), polyvinyl alcohol (PVA), Calcium sulfate (CS), sodium carboxymethyl cellulose (S-CMC) and bitumen are commonly used to produce GAC. Mixing PAC with binders did not require heat treatment while using raw and washed CBPP, additional calcination step was needed (Machnikowski et al., 2010).

CMC, PVA, CS, and S-CMC were mixed with PAC, raw, and washed CBPP at the binder to carbon ratio of 10:90, 20:80, and 30:70. Then water was added to the mixture until a homogeneous paste was produced. The paste was then put in an extruder with 3mm diameter and extrudates were cut to 5-7 mm long. The extrudates were put in oven (105°C) to dry overnight. In case of using bitumen as a binder, hexane was used as the solvent and extrudates were put under the fume hood to dry.

Calcination and activation temperature, time, and heating rate will impact the chemical nature of the binder and quality of the produced GAC (Rubio et al., 1999). Besides these factors, amount of binder would affect hardness and compressive resistance of the granules as well as its surface area and adsorption capacity. To study such effects, the different binder to carbon ratio were considered in this study (Rubio et al., 1999). Moreover, steam temperature was considered as another factor to obtain high quality and efficient granular adsorbent. The range and variations for each factor is summarized in Table 2-1.

Table 2-1: Variables and their ranges for granulation study

Variable	Range
Activation and calcination temperature	750,850,950°C
Activation time	1, 2,3 hrs
Heating rate	5,10,15°C/min
Binder to carbon ratio	10:90,20:80,30:70
Steam temperature	60,70,80°C

2.3 Adsorbent Characterization

Activated carbon is one of the most effective filtration media with high surface area and porosity to remove impurities from water. Source of raw carbon has a significant role in the characterization of final product (DeSilva, 2000). To assess the removal of impurities and get clean carbon of acceptable quality, different characterization tests were conducted on raw and washed CBPP, PAC, and GAC which are summarized below:

2.3.1 pH

ASTM D338-05 method was used to determine the pH of raw and washed CBPP, and PAC. For this, 10.0 g of sample on a dry basis was used and 100mL of boiled water was added to the carbon. The solution was boiled for 4minutes and filtered. The filtrate was cooled to 50°C and pH was determined using a pH meter (Mettler Toledo, Education series EL20).

2.3.2 Moisture Content

Moisture content of raw CBPP was determined using ASTM D2867-09 standard method. According to the method, first a dried crucible with lid was weighed. Then, 1-2g of carbon was put into the crucible in such a way that its depth should not exceed 1.25cm and then the filled crucible with lid was weighed and put in the oven with 110°C for 3 hours. After cooling down in a desiccator, the dried sample, crucible and lid was weighed. The moisture content had been calculated by Equation 2-2.

$$\textbf{Moisture content, wt\%} = \frac{(C-D)}{(C-B)} \times 100 \qquad \textit{Equation 2-2}$$

where,

C = weight of crucible + cover + original sample
B = weight of crucible + cover; and
D = weight of crucible + cover + dried sample

2.3.3 Ash Content

ASTM D2866-11 describes a procedure to determine the ash content of activated carbon. According to this method, an empty crucible was heated in a furnace at 650̊C for an hour to remove all impurities. After cooling down, around 2g of dried raw CBPP, washed CBPP, and PAC samples were put in the crucible and burned in a furnace at 650°C for 16 hours. After cooling down in a desiccator, crucible with the ash was weighed and the ash content was calculated using the Equation 2-3.

$$\textbf{Ash content, wt\%}= \frac{(D-B)}{(C-B)}\times 100 \qquad \textit{Equation 2-3}$$

where,

B= weight of dried crucible
C= weight of crucible + original sample
D= weight of crucible + ash

2.3.4 Iodine Number

The amount of iodine adsorbed by 1g of carbon is called iodine number. This number gives a rough estimate on the micro-porosity of the carbon. To determine iodine number using ASTM D4607-11, the required amount of carbon (raw CBPP, washed CBPP, PAC, and GAC) was weighed; in case of testing GAC, representative sample was grinded until 95% of the sample passed through 100-mesh screen (U.S. sieve series). Then, 10mL of 5% HCl was added and the solution was boiled for 30s. In the next step, 15mL of iodine solution was added to the mixture and stirred for 15 minutes at 200rpm. At the end, the solution was filtered and 10mL of the filtrate was titrated with Sodium thiosulfate. Starch is the indicator for the titration. Iodine number is then calculated using Equation 2-4.

$$\textbf{IN}= \frac{[(C_0\times V_0)-(C_1\times V_1\times DF)}{M_C}\times 126.9 \qquad \textit{Equation 2-4}$$

where,

IN = Iodine number, mg/(g of carbon)
C_0 = Concentration of iodine solution, 0.1N
V_0 = Initial volume of iodine solution, 15mL
C_1 = Concentration of sodium thiosulfate, 0.1N
V_1 = Volume of sodium thiosulfate used for titration, mL
D_F = Dilution factor, 15/10
M_C = Weight of carbon, g

2.3.5 Methylene Blue Number

Methylene blue which is an organic dye is used to determine mesoporosity of the activated carbon... The activated carbon with methylene blue adsorption over 200mg/g is considered as an excellent meso-porous carbon (Yan *et al.*, 2009).

In this study, GB/T 7702.6 (2008) method is used to determine the methylene blue number (MBN). 15-20mL of methylene blue stock solution was added to 0.1g±0.001 of raw CBPP, washed CBPP and PAC and grinded GAC. The mixture was shaken at 150rpm for 30 minutes and then filtered using 10μm filter paper. The filtrate was diluted for 200-500 times and the adsorption was determined using UV spectrophotometer at 665nm.

2.3.6 Elemental Analysis

In order to determine the concentration of major elements in the raw and washed CBPP, PAC, and GAC, elemental analysis was performed. Microwave-assisted acid digestion followed by ICP-MS was used to trace elements concentrations, specifically heavy metals. For this, ICP-MS, model ELAN DRC II of Perkin Elmer manufacturer, was used.

2.3.7 Hardness

Although there are several methods to determine the hardness for GAC but for this study, Ball Pan Hardness Method (ASTM D3802-16) was used. To determine the hardness number, 2g of 40-mesh screened GAC was put in a beaker and 10 glass marbles (15mm diameter, 5g each) was added. The beaker was capped with an aluminum foil and stirred at 200rpm for 20minutes. The obtained material was sieved using the same mesh-screen and the retained material was weighed and hardness number was calculated using Equation 2-5 below (Ahmedna *et al.*, 1997).

$$\mathbf{Hardness} = \frac{(\textit{weight of carbon retained on the mesh-screen})}{\textit{initial sample weight}} \times \mathbf{100} \qquad \textit{Equation 2-5}$$

2.3.8 BET surface area and pore size distribution

The surface area and pore size distribution are two important properties of the adsorbent (Brunauer-Emmett-Teller, 1938). Pore size distribution determines size and shape of a given pollutant which can be adsorbed by the activated carbon (Pelekani & Snoeyink, 2000). Brunauer-Emmett-Teller (BET) surface area and porosity of PAC and GAC were measured by N_2 adsorption at 77K using 3Flex Surface Characterization Analyzer from Micromeritics Instrument Corporation. Equation 2-6 to Equation 2-10 are used to determine the surface area in m^2/g.

$$\frac{1}{v(\frac{P_0}{P}-1)} = \frac{1}{v_m c} + (\frac{c-1}{v_m c} \times \frac{P}{P_0}) \qquad \textit{Equation 2-6}$$

$$v_m = \frac{1}{S+1} \qquad \textit{Equation 2-7}$$

$$c = a + \frac{S}{I} \qquad \textit{Equation 2-8}$$

$$SA_{BET} = \frac{v_m N A_{(N)}}{v} \qquad \textit{Equation 2-9}$$

$$S_{BET} = \frac{SA_{BET}}{a} \qquad \textit{Equation 2-10}$$

Where:

v = volume of adsorbed N_2 gas at standard temperature and pressure (STP)
P and P_0 = the equilibrium and saturation pressures of the adsorbate
v_m = volume of gas required to form one monolayer (STP)
c = BET constant related to energy of adsorption
N = Avogadro’s number (6.02E+23)
$A_{(N)}$ = cross section of N_2 (0.162 nm^2)
SA_{BET} = total BET surface area (m^2)
a = mass of adsorbent (g)
S_{BET} = specific BET surface area (m^2/g)

By plotting $1 / v\ [(P_0 / P) - 1]$ on the y-axis and P/P_0 on the x-axis in the range of $0.05<P/P_0<0.35$, the BET surface was calculated. The slope (S) and the y-intercept (I) of the plot were used to calculate v_m and the BET constant (Mofarrah, 2014).

3. Experimental Techniques

3.1 Experimental Design

Column test experiment was designed using a column with a diameter of 2.5cm and height of 15cm. A scheme of experimental setup is shown in Figure 3-1. Column test was conducted using 5cm (8g), 9cm (12g), and 12cm (17g) of the column filled with produced GAC to study the effect of packing height. A flow of 6mL/min of water samples passed through the column using a peristaltic pump (FisherScientific ,Variable-Flow Peristaltic Pumps). Treated water was collected from the column and analyzed for concentration of NOM using TOC and UV analyzer. Table 3-1 shows time and amount of treated water for sample collection.

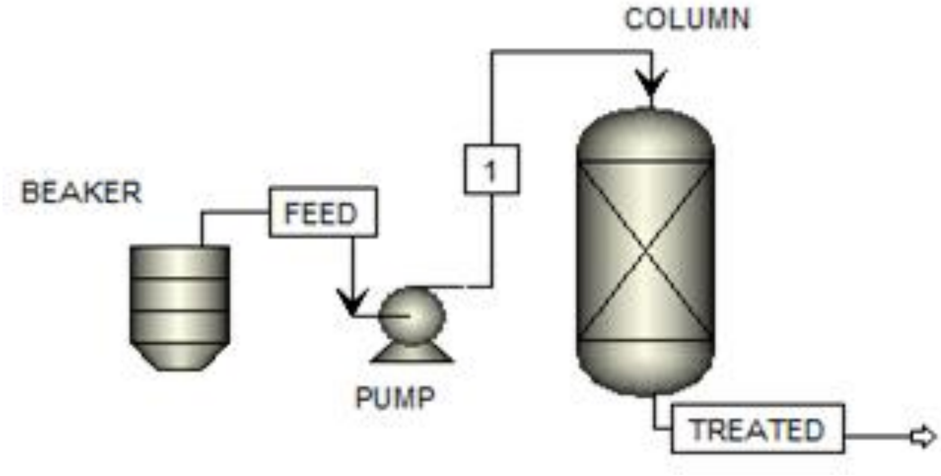

Figure 3-1: Experimental setup for column test

Table 3-1: Sample collection from column test

Time (min)	Treated water (mL)	Time (min)	Treated water (mL)
2	12	720	4320
15	90	900	5400
60	360	1240	7440
90	540	1575	9450
120	720	1800	10,800
180	1080	2040	12,400
360	2160	2220	13,320
480	2880	2340	14,040
660	3960	2507	15,040

Chlorination

In this study, sample collected from column tests were chlorinated for different contact times to determine the formation potential of THMs and HAAs. The residual chlorine was maintained between 0.04-2.0 mg/L in the distribution system according to Canadian guidelines (Health Canada, 1996). Table 3-2 shows the time and amount of treated water for chlorination. THMs and HAAs generated during chlorination process were analyzed by liquid-liquid extraction, followed by a GC (HP-6890) coupled with a μ-ECD detector.

Table 3-2: Sample collection for chlorination

Time (min)	Treated water (mL)	Chlorination contact time (hr)
60	360	1,8,36
180	1080	1,8,36
480	2880	1,8,36
1300	7800	1,8,36
1800	10,800	1,8,36

Extraction Method

To extract HAAs from chlorinated sample, procedure developed by Domino et al. (2003) were employed. In order to extract THMs from chlorinated sample, US EPA (1995) protocol was used.

Regeneration

Time of contact, temperature, and the amount of steam and CO_2 are three major variables considered to optimize regeneration of spent carbon in this study. By changing these three variables in the ranged listed in Table 3-3, the response in the change of MB number, IN number, and hardness of regenerated samples were recorded and the combination giving maximum MB, IN and hardness was used as a guideline to optimize regeneration of the spent carbon.

Table 3-3: Factors and levels of experiment

Variable	Lower level	Upper level
A: time (minute)	30	120
B: Temperature (°C)	650	950
C: steam and CO_2 flow (mL/min)	200	500

4. GAC Production

Except bitumen, none of the other binders were able to produce cohesive granules. Mixing bitumen with PAC produced fragile and fragment GACs. In addition, granules produced by using raw CBPP mixed with bitumen produced really hard calcinated granules, however, activating the resulted granules produced high content of ash and soft granules.

In the following section, characterization of granules produced from mixing bitumen with washed CBPP is reported.

4.1 GAC Production by Washed CBPP and Bitumen

Bitumen is a black and highly viscous form of petroleum. To use this viscous and sticky binder, various studies used heating of bitumen at 140°C to soften the bitumen (Ahmedna et al., 2000, Pendyal et al., 1999a, Pendyal et al., 1999b). In order to avoid the emission of harmful vapors from heated bitumen, it was dissolved in hexane and mixed with the carbon. Effects of calcination and activation temperature, activation time, heating rate, amount of binder, and steam temperature were studied to determine optimum condition for GAC production. This section covers the findings to determine the optimum conditions to make granulated carbon using bitumen as a binder.

4.1.1 Calcination Temperature

To determine the effective calcination temperature, granules with different binder to carbon ratio by weight (10:19, 20:80, and 30:70) were produced. Each sample was calcinated at three different temperature (750, 850, and 950°C) with 15°C /min for 1 hour. Each case is characterized for burn-off, MB adsorption and Iodine number tests. Results for characterizations listed in Table 4-1 are summarized below:

- Burn-off rate: As listed in Table 4-1, by increasing binder-to-carbon ratio the burn-off will increase at a given temperature. However, increasing the temperature for each binder-to-carbon ratio, has no specific effect on the burn-off rate indicating that the binders and carbons are bonded at 750°C.

- MB Adsorption: Calcinated granules have been grinded for MB tests. It is obvious that by increasing temperature, the opening of the pores increased which led to increasing MB adsorption values.
- Iodine number: The increase in the temperature will decrease iodine number for binder to carbon ratios of 30:70 and 20:80 and has no specific effect on the binder which has carbon ratio of 10:90. This shows that the calcination temperature of 750°C is the ideal temperature for calcination. A decrease in the Iodine number may be due to pore widening from micropores to mesopores.

Table 4-1: Characterization for the effect of calcination temperature on different carbon-to-binder ratios

Temperature (°C)	Ratio	Burn-off (%)	MB (mg/g)	IN (mg/g)
750	10:90	14.56	12.49	988.35
850	10:90	14.25	15.55	987.33
950	10:90	14.28	17.35	987.21
750	20:80	21.76	7.64	969.93
850	20:80	20.55	12.5	934.07
950	20:80	21.97	16.28	921.32
750	30:70	27.75	5.98	953.45
850	30:70	27.14	8.12	900.09
950	30:70	27.28	14.12	898.7

4.1.2 Activation Temperature

To determine the best temperature for activation, CO_2 activation at 750, 850, and 950°C for 2 hours for binder to carbon ratios of 10:90, 20:80, and 30:70 has been considered. In this case, the calcinated granules at 750°C for 1 hour at 15°C /min temperature increase was used. Burn-off rate, MB adsorption, Iodine number, and hardness tests were considered as characterization tests. The results are listed in Table 4-2 with the findings as follows:

- Burn-off rate: Table 4-2 shows that increasing the activation temperature will increase the burn-off rate and carbon loss.
- Methylene Blue (MB) Adsorption: Increasing the temperature from 750°C to 850°C does not show any significant increase in MB adsorption values. However, at 950°C, MB adsorption increases to a higher level showing a better activation at 950°C.
- Iodine number (IN): increasing activation temperature from 750°C to 850°C will lead to a better porosity development with higher iodine number. However, above 850°C, iodine number decreases due to micro-pores widening to produce more

mesopores with a significant increase in the MB adsorption values. Moreover, lower binder to carbon ratio gives high MB number. It is important to mention that although the decrease in the IN above 850°C can be considered as a negative for activation but iodine adsorption is still high (above 1000mg/g) at higher temperature.

- Hardness: Higher porosity will lead to lower hardness, especially, for lower binder to carbon ratio. It is obvious that increasing the activation temperature for binder to carbon ratio of 10:90 and 20:80 will lead to extremely soft granules.

The experimental runs conclude that the calcination at 750°C, activation at 950°C, and binder to carbon ratio of 30:70 are the optimized conditions for the granulation.

Table 4-2: Characterization for the effect of activation temperature on different carbon-to-binder ratios

Temperature(°C)	Ratio	Burn-off (%)	MB (mg/g)	IN (mg/g)	Hardness (%)
750	10	6.47	17.36	1014.73	0.51
850	10	7.7	18.35	1004.82	0
950	10	8.59	60.55	990.22	0
750	20	5.17	9.82	1006.78	61.38
850	20	7.057	17.29	1061.13	18.44
950	20	7.98	55.15	1045.22	11.26
750	30	3.94	10.33	988.35	88.14
850	30	6.71	16.22	1064.78	86.6
950	30	7.67	49.26	1041.64	85.35

Calcination temperature increasing rate

In the previous section, it is concluded that the calcination at 750°C is the optimum temperature and binder to carbon ratio of 30:70 as optimum ratio. In order to determine the best temperature increasing rate for calcination, 30% binder and calcination at 750°C with temperature increasing rate of 5°C/min, 10°C/min and 15°C/min were tested and the findings are summarized in Table 4-3..

It is obvious from the Table that at a at slower temperature increase rate, the burn-off rate and Iodine number will decrease but MB adsorption will increase and more mesopores will be formed. However, the increase in the MB is not very significant. Therefore, the calcination should be done at 750°C with 15°C/min temperature increase.

Table 4-3: Characterization for the effect of activation temperature increasing rate on 30% binder granules

Temperature increasing rate(°C/min)	Burn-off	MB (mg/g)	IN (mg/g)
15	27.75	5.98	953.45
10	25.37	10.34	944.95
5	24.98	11.42	943.97

Activation temperature

The calcinated granules at 750°C with 15°C/min heating rate, and binder to carbon ratio as 30:70 are the optimal values for calcination while the activation temperature of 950°C is considered as the most effective temperature for activation. The findings on activation temperature increasing rate are presented in Table 4-4.

Based on the analysis, it is clear that by decreasing the temperature increasing rate, it will result in a better MB and Iodine adsorption values. However, the hardness will decrease to near 80%. Although there are no well-defined guidelines on the limit for GAC's hardness, for this study a hardness below 85%, is considered to be soft.

Table 4-4: Characterization for the effect of activation temperature increasing rate on 30% binder granules

Temperature increasing rate (°C/min)	Burn-off (%)	MB (mg/g)	IN (mg/g)	Hardness (%)
15	7.67	49.26	1041.64	85.35
10	8.76	50.8	1050.59	85.60
5	8.9	55.15	1094.29	81.63

4.1.3 Steam Activation, Steam Temperature

By finding the optimum calcination temperature, calcination temperature increasing rate, binder to carbon ratio, activation temperature, and activation temperature increasing rate, the effect of steam activation has been tested. One important factor in the steam activation is the steam temperature. For this, 30% calcinated granules were activated at 950°C with the steam temperature of 60, 70, and 80°C. The results are summarized in Table 4-5 with the main findings as follows:

- Burn-off rate: The burn-off rate increases with the increasing temperature with higher carbon loss although it helps in producing GAC with higher porosity and better adsorbent.
- MB adsorption: by increasing the steam temperature, more mesopores are formed with a better adsorbent.
- Iodine number: Increasing the steam temperature from 60°C to 80°C, will cause widening of the pores and forming new micro-pores.
- Hardness: A better result in the steam activation at 80°C is achieved. Although high burn-off rate is observed, the pores are well formed in the GAC while developed GAC has relatively high hardness.

Based on the experimental runs covering various ranges, it is concluded that the activation temperature at 950°C and keeping the steam temperature at 80°C are the optimized conditions for GAC activation.

Table 4-5: Effect of steam temperature on GAC's characterizations

Steam temperature (°C)	Burn-off (%)	MB (mg/g)	IN (mg/g)	Hardness (%)
60	7.83	31.86	1245.86	89.29
70	10.26	51.4	1259.98	86.68
80	21.1	220.15	1332.68	86.59

Steam Activation time

To determine the effect of activation time on GAC production, 30% granules were calcinated at 750°C with 15°C/min for 1 hour. Then, steam activation at 950°C with 15°C /min and the steam at a temperature of 80°C was used for 1,2, and 3 hours. The results are listed in Table 4-6. It is concluded that increasing the time from 1 hour to 3 hours will result in improved MB and IN with acceptable hardness. Therefore, 3 hours of activation was chosen to produce GAC.

Table 4-6: Effect of activation time on GAC's characterizations

activation time (hr)	Burn-off (%)	MB (mg/g)	IN (mg/g)	Hardness (%)
1	12.33	77.97	1295.68	87.09
2	21.1	220.15	1332.68	86.59
3	23.44	240.71	1420.56	84.94

In conclusion, to produce ideal GAC, 30:70 binder to carbon ratio of granules should be calcinated at 750°C with 15°C/min of heating rate for 1 hour. The calcinated granules should then be activated at 950°C with 15°C/min using steam at 80°C for 3 hours.

4.2 Elemental Analysis for produced GAC

Table 4-7 shows metal concentration in PAC and GAC. The result for tracing different elements in raw CBPP is also reported again for comparison purposes. Based on the results, it is observed that during cleaning and production of PAC, all the elements were removed considerably from raw CBPP. However, high concentration of Vanadium and Nickle in produced GAC in comparison with raw CBPP and PAC which may be due to untreated bitumen as a binder.

Table 4-7: Elemental analysis for PAC and GAC

Elements	Raw CBPP (ppm)	PAC (ppm)	GAC (ppm)	Elements	Raw CBPP (ppm)	PAC (ppm)	GAC (ppm)
Li	4.64	0.78	0.54	Cu	29.58	17.98	11.31
Be	0.053	0.017	0.006	Zn	74.10	1.74	0.42
B	26.20	6.69	0.84	As	0.93	0.19	0.16
Mg	2550.57	1154.15	841.88	Rb	23.128	1.68	0.64
Al	2220.38	709.33	274.31	Sr	92.74	26.34	19.22
P	1465.21	214.37	193.35	Mo	3.91	4.26	2.88
Ca	25432.69	3794.94	3182.35	Ag	0.07	0.01	0.01
Ti	155.37	98.08	35.41	Cd	0.31	0.019	0.02
V	6.85	2.7	48.6	Cs	0.12	0.02	0.018
Cr	14.86	10.83	8.58	Ba	116.65	27.55	0.74
Mn	3471.06	791.63	625.05	La	2.54	0.45	0.2
Fe	2185.04	1217.69	993.77	Ce	2.57	0.79	0.36
Co	12.42	0.77	0.93	Pb	4.048	0.14	0.059
Ni	8.36	5.01	19.3	U	0.17	0.11	0.056

4.3 BET Surface Area and Pore Size Distribution of GAC

Nitrogen adsorption and desorption into GAC at 77K resulted in isotherm curves and pore size distribution of GAC that are shown in Figure 4.1 and Figure 4.2 respectively. Isotherm for GAC is a combination of type I and type IV isotherms according to IUPAC classifications which is attributed to an adsorbent with both micropores mesopores. Applying Equation 2-6 to Equation 2-10, obtained that the BET surface area of GAC is 588m^2/g. Also, micro-pore volume and meso-pore volume are 0.276, 0.017 cm^3/g, respectively.

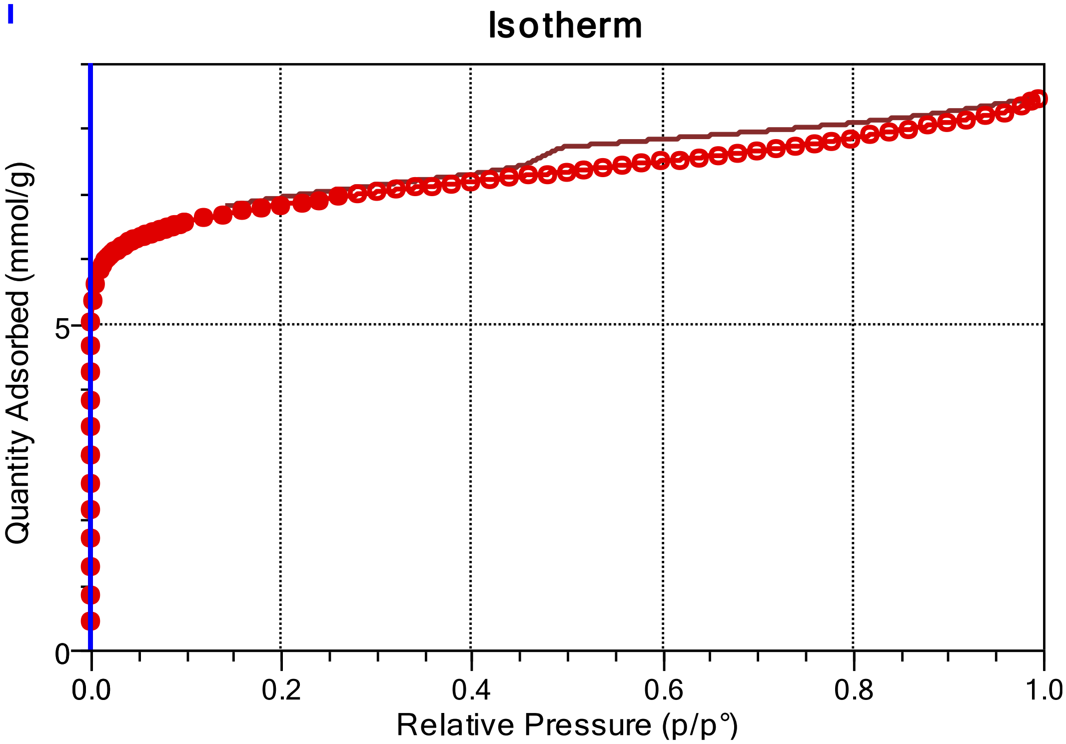

Figure 4-1: Isotherm plot of GAC

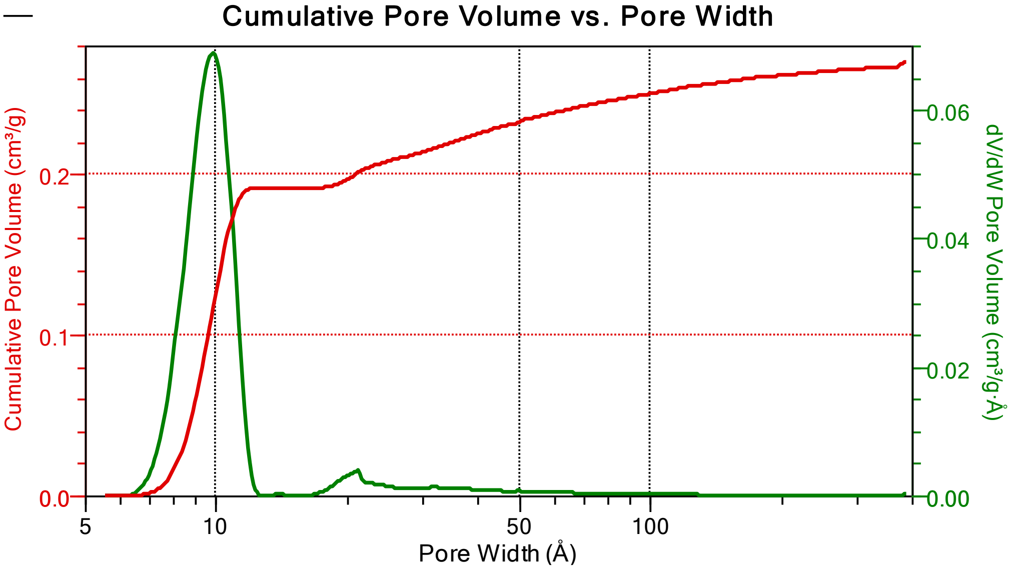

Figure 4-2: Pore Size Distribution for GAC

5. Results and Discussion

5.1 Breakthrough Curves

A breakthrough curve in an adsorption system is a curve of adsorptive concentration versus time (McCabe et al., 1993). Breakthrough curve for NOM adsorption using GAC was developed for bed length of 5, 9, and 12cm as shown in Figure 5-1(a). It is obvious from the plot that by increasing the length of bed from 5cm by using 8g of GAC to 12cm using 17g of GAC, the adsorption at the beginning and required time for saturation has increased. The breakthrough curves using UV analyzer is provided in Figure 5-1(b) which also shows a similar trend.

5.2 Elemental Analysis for Treated water

Elemental analysis of raw and treated water is reported in Table 5-1. According to the Canadian guideline, the concentration of most of the elements are lower than the maximum allowable concentrations in drinking water (Water & Organization, 2000).

5.3 Chlorination

NOM and their characterization in water before adding disinfectant and contact time between NOM and disinfectant have significant effect on the DBP formation. In this study, treated water collected from column test at 60, 180, 480, 1300, and 1800 minutes were chlorinated for 1 hour, 8 hours, and 36 hours contact time to determine the formation potential of THMs and HAAs in the chlorinated water. Chlorination dose was controlled so the concentration of residual chlorine in the distribution system was maintained in the range of 0.04-2.0 mg/l, as per Canadian guidelines (Health Canada, 1996). Table 5-2 shows the time and amount of treated water for sample collection. TOC level of the treated sample is also shown in the Table.

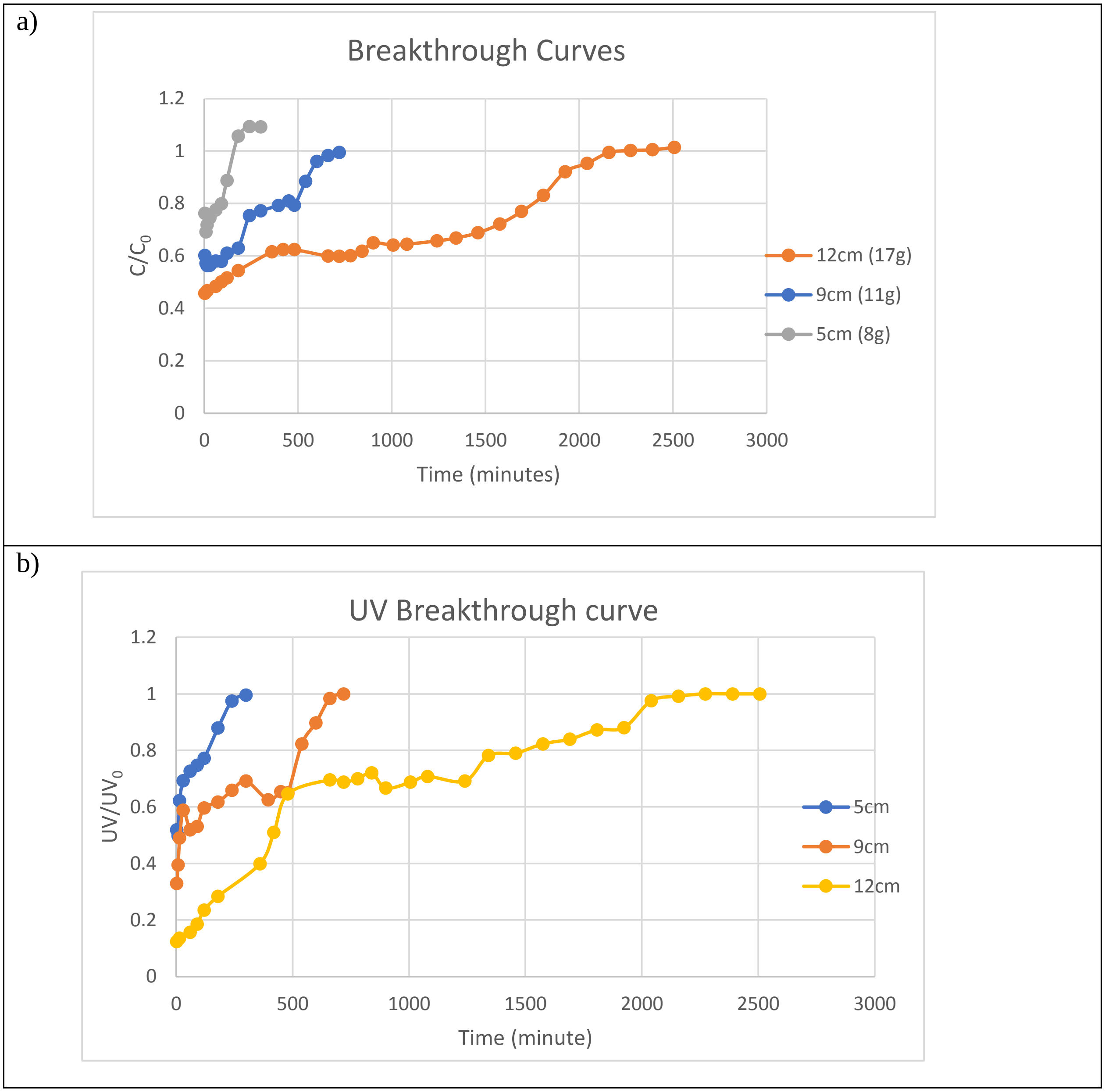

Figure 5-1: Breakthrough Cuves for NOM adsorption a)Concentration b)UV

Table 5-1: Elemental analysis for treated water

Element	Raw water (ppb)	Treated water (ppb)	Maximum allowable concentration (ppm)	Detection limit (DL) (ppb)
Cl	11161	10557	2.0	1,043
Ca	2060	7037	-	45
Cr	< DL	0.193	0.05	0.138
Mn	2.82	6.94	-	0.031
Fe	154	115	-	7.2785
Co	0.027	0.012	-	0.011
Cu	1.41	0.851	-	0.1005
As	< DL	0.214	0.01	0.16
Br	54.8	30.5	-	5.4043
Cd	< DL	0.02	0.005	0.0094
Pb	0.08	0.1	0.01	0.0175

Table 5-2: Sample collection for chlorination

Time (min)	Treated water (mL)	TOC level (mg/L)
60	360	3.631
180	1080	4.087
480	2880	4.689
1300	7800	5.02
1800	10,800	6.24

There are hundreds of DBPs formed in the water due to reaction of NOM with the residual chlorine. However, two groups of DBPs, Trihalomethanes (THMs) and Haloacetic acids (HAAs), have attracted attention due to high formation potential. In the following sections, the effect of NOM removal on the THM and HAA formation will be discussed.

5.3.1 THMs Analysis after Chlorination

The THM group includes four compounds: Chloroform (CHCl3), Bromodichloromethane (CHCl2Br), Dibromochloromethane (CHClBr2), and Bromoform (CHBr3). Figure 5-2 and Table 5-3 show the results for the total THM formation and concentration of the individual compounds, respectively. Figure 5-2 displays the total THM concentrations in raw and treated water during chlorination. As shown in Figure 5-2, the total THM level is increasing with the chlorination contact time. In raw water, 40% of all THMs are formed within the first hour of chlorination. THM level gradually increases in treated water and at slower increasing rate than in the raw water. Raw water has a THM concentration of 2270 ppb after 36-hr of chlorination, while the THM concentrations of 36-hr chlorination for the filtered water through column taken after 60, 180, 480, 1330, and 1800 minutes are 852 ppb, 868 ppb, 1059 ppb, 1120 ppb, and 1132 ppb, respectively. Comparing these values to THM levels in the raw water clearly shows that the column filtration is effective and can significantly reduce THMs levels in Pouch Cove drinking water (more than 50% reduction). From Table 5-3, it is clear that the chloroform (CHCl3) is a dominant compound in total THM concentration. Moreover, comparing Dibromochloromethane (CHClBr2), and Bromoform (CHBr3) concentration in raw and treated water, it is obvious these compounds are only forming in raw water and that the potential for the formation of these compounds is completely eliminated after filtration.

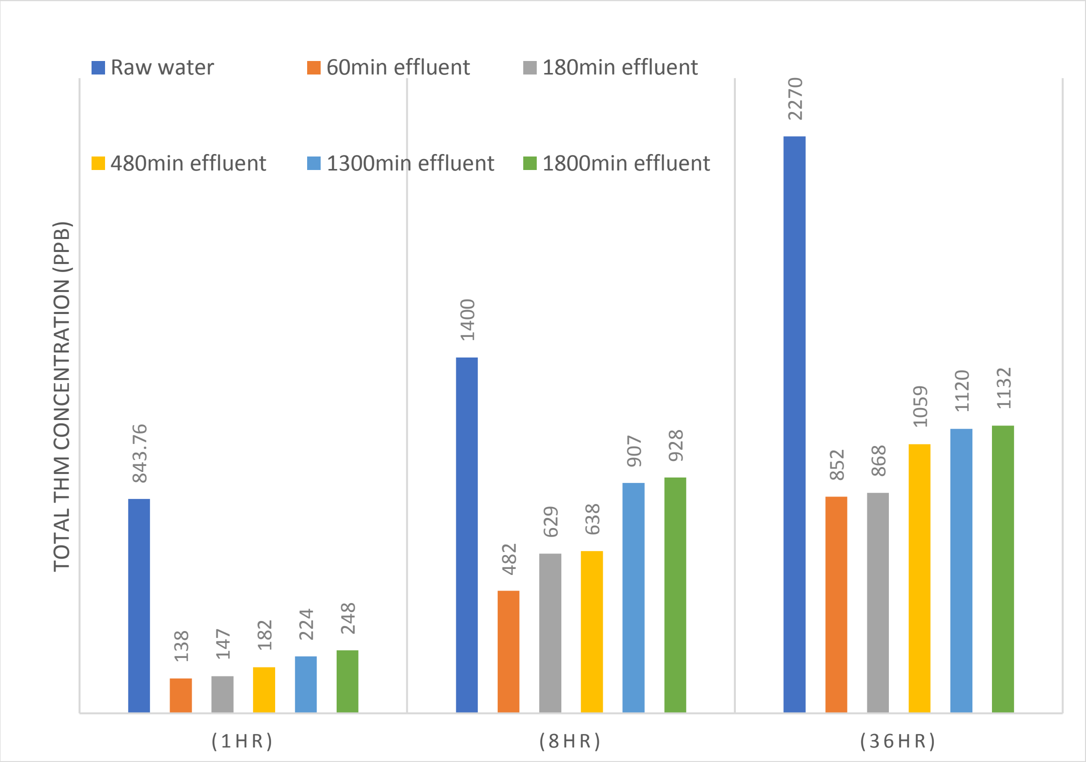

Figure 5-2: Total THMs in raw and column samples during chlorination

Table 5-3:THM compounds in raw and treated water

THMs	Raw Water (ppb)			50min effluent (ppb)			180min effluent (ppb)		
Chlorination time (hr)	1	8	36	1	8	36	1	8	36
$CHCl_3$	780.82	1350.3	2148.3	119.5	420.7	774.7	130.9	552.9	776.2
$CHCl_2Br$	46.78	29.2	84.1	18.1	61.1	77.5	15.7	75.6	91.7
$CHClBr_2$	3.20	5.5	12.6	0	0	0	0	0	0
$CHBr_3$	12.96	15	25	0	0	0	0	0	0
Total THMs	843.76	1400	2270	137.6	481.8	852.2	146.6	628.5	867.9
	480min effluent (ppb)			1300min effluent (ppb)			1800min effluent (ppb)		
Chlorination time (hr)	1	8	36	1	8	36	1	8	36
$CHCl_3$	149.33	577.3	955.52	193.1	825.6	1028	206.5	821.4	1047.4
$CHCl_2Br$	32.64	60.64	103.28	30.7	81.1	92.0	41.5	106.4	84.4
$CHClBr_2$	0	0	0	0	0	0	0	0	0
$CHBr_3$	0	0	0	0	0	0	0	0	0
Total THMs	181.97	637.94	1058.8	223.8	906.7	1120	248	927.8	1131.8

5.3.2 HAAs Analysis after Chlorination

The HAA group includes nine compounds which are Monochloroacetic acid (MCAA), Monobromoacetic acid (MBAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Bromochloroacetic acid (BCAA), Bromodichloroacetic acid (BDCAA), Dibromoacetic acid (DBAA), Dibromochloroacetic acid (DBCAA), and Tribromoacetic acid (TBAA).

Figure 5-3 and Table 5-4 show the results for total HAAs formation and concentration of individual compound.

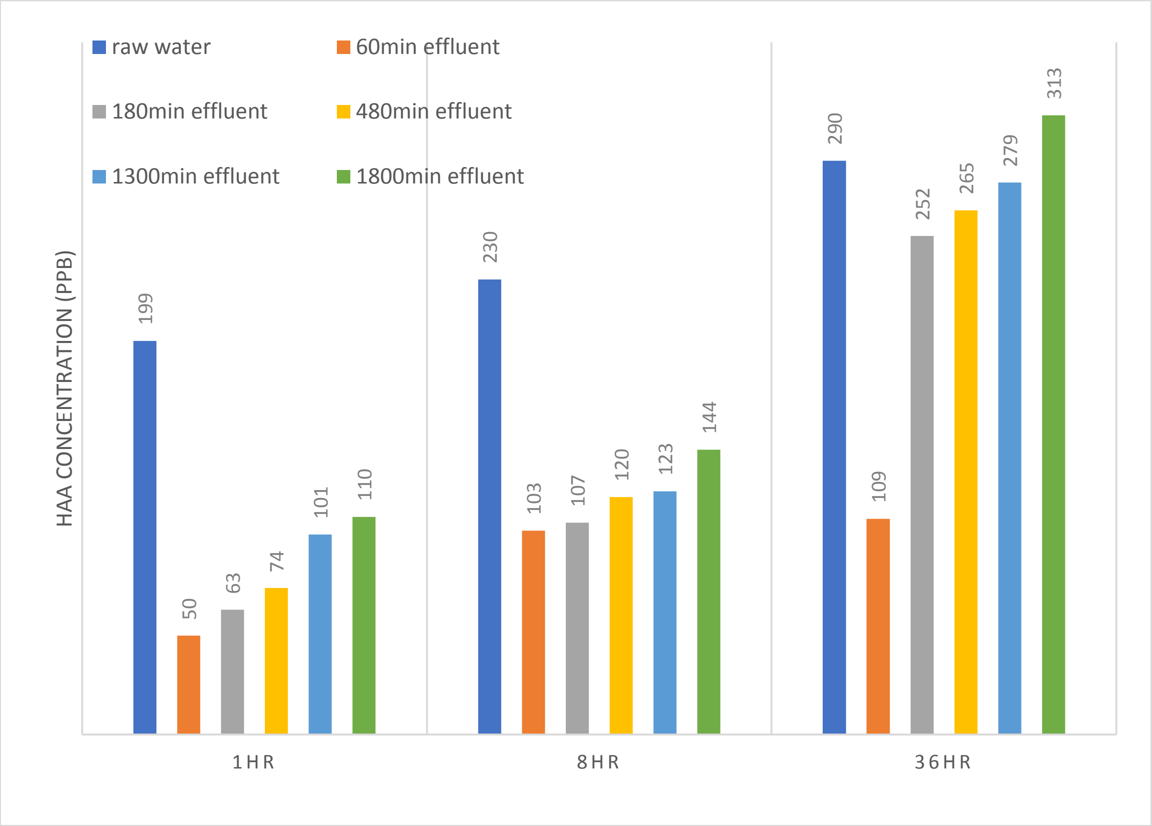

Figure 5-3: Total HAAs in raw and column samples during chlorination

Table 5-4: HAA compounds in raw and treated water

HAAs	Raw water (ppb)			60min effluent (ppb)			180min effluent (ppb)		
Chlorination time (hr)	1	8	36	1	8	36	1	8	36
MCAA	0.05	0.05	0.05	0	0	0	0	0	77.17
MBAA	1.68	2.86	3.2	0	0	0	0	0	0.05
DCAA	147.9	175.5	227.1	18.40	58.06	58.75	26.78	61.39	112.67
TCAA	32.7	33.59	35.03	10.97	16.12	29.54	10.92	17.74	36.10
BCAA	9.54	10.01	13.7	6.57	10.04	8.84	8.22	10.56	16.37
BDCAA	0.95	0.9	0.9	1.15	1.29	1.81	1.0793	1.3625	2.61
DBAA	0	0	0	0	2.56	2.55	4.31	0	2.89
CDBAA	6.6	7	9	12.87	14.99	7.31	12.06	15.56	4.62
TBAA	0	0	0	0	0	0	0	0	0
Total HAAs	199.42	229.91	289.98	49.96	103.06	108.8	63.38	106.61	252.48
	48 min effluent (ppb)			1300min effluent (ppb)			1800min effluent (ppb)		
Chlorination time (hr)	1	8	36	1	8	36	1	8	36
MCAA	0	0	5.19	0	0	0	0	0	75.05
MBAA	0	0	1.36	0	0	0	0	0	2.389
DCAA	33.06	66.08	150.27	52.2	66.91	161.9	58.9	86.21	144.45
TCAA	12.9	25.2	77.96	20.58	21.95	85.44	30.62	28.82	60.55
BCAA	9.05	11	17.64	11.01	11.03	19.01	8.8	13.56	17.93
BDCAA	1.16	1.92	4.37	1.61	1.67	4.76	1.61	1.8977	3.76
DBAA	5.32	2.59	2.75	2.58	2.71	2.83	2.55	2.67	3.04
CDBAA	12.63	13.24	5.49	13.17	18.39	4.89	7.68	10.77	5.88
TBAA	0	0	0	0	0	0	0	0	0
Total HAAs	74.12	120.03	265.03	101.15	122.66	278.83	110.16	143.93	313.05

Figure 5-3 shows the total HAA concentration of raw and filtered water for different period of chlorination. Similar to THM results, the HAA concentration in all samples is increasing by increasing the chlorination contact time. Except for 36-hr of chlorination for 1800minute in the filtered sample, HAA concentrations in all samples are lower than in the raw water samples which conclude that the developed GAC filtration has the ability to remove precursor causing formation of HAAs in the water. All column filtered samples show that at the beginning of the filtration, fresh GAC outperforms in the reduction of HAAs compared to the regenerated carbon.

In addition, considering the fact that using GAC for water treatment would result in lower concentration of DBPs. Comparing the results of HAA removal with the THM, that the developed GAC is more effective to reduce formation of THMs than HAAs.

The concentration of each compounds of HAA compounds is listed in Table 5-4. For all chlorinated samples, DCAA is the dominant compound among all HAA compounds. TCAA and

BCAA are also dominant after DCAA in the total HAAs. The concentration of BDCAA, DBAA, CDBAA, and TBAA during chlorination process are very limited in both raw and treated water. In some treated samples, the concentration of MCAA is decreasing for 1hour and 8-hour of chlorination while after 36-hour of chlorination, the concentration of MCAA is even higher than in the raw samples. This may be due to leaching of substances from adsorbent into the water.

5.4 GAC Regeneration

The effects of regeneration temperature, time, and steam flow on regeneration efficiency were studied and 13 different experiments were conducted for the ranges as listed Table 5-5. For each experiment, spent GACs loaded with adsorbed NOM were washed with deionized water several times to remove impurities. The washed spent GAC were dried in oven at 105°C. The regeneration process was carried out by placing the 2g of spent GAC in tubular furnace. The target temperature as listed in Table 5-5 was set along with the target nitrogen flow. Upon reaching the designed temperature, nitrogen was replaced with CO_2 and steam at the designed flow rate.

Table 5-5 lists the results of MB, IN, and hardness of regenerated GAC at different temperature, time, and gas flow. Three responses have been considered to determine the optimum condition in which the MB, IN, and hardness of regenerated GAC are at the maximum level. Increasing regeneration temperature, time, and gas flow would increase the MB adsorption and decrease the hardness. This matter is due to pore widening and reactivation. However, for IN adsorption, increasing the temperature and gas flow would reduce MB due to pore widening from micropores to mesopores.

Table 5-5: Results of thermal regeneration

Time (min)	Temperature (°C)	Flow (mL/min)	Response 1: MB	Response 2: IN	Response 3: Hardness
75	800	350	219	1224	81
30	800	350	209	1195	91
120	800	350	301	1223	78
45	690	250	196	1157	92
75	800	200	243	1103	85
75	800	350	252	1212	85
75	800	500	282	1217	80
75	950	350	346	1208	79
75	650	350	174	1156	92
75	800	350	245	1227	84
105	690	450	244	1214	82
105	905	250	265	1140	83
45	905	450	315	1211	83

5.4.1 Regeneration Optimization

Response surface methodology was used to optimize parameters. As listed in Table 5-6, the optimum condition of GAC regeneration were estimated as 916°C for 43 minutes under 350mL/min of steam (Taghizadehgan, 2019). The findings of this study will help in the pilot scale study to remove NOM and thus provide affordable and safe drinking water in small communities in the province

Table 5-6: Optimum condition for GAC regeneration

Time (min)	Temperature (°C)	Flow (mL/min)	MB (mg/g)	IN (mg/g)	Hardness (%)
43	916	350	287	1215	85

. The results on regenerated breakthrough on NOM adsorption using regenerated GAC are plotted in Figure 5-4.

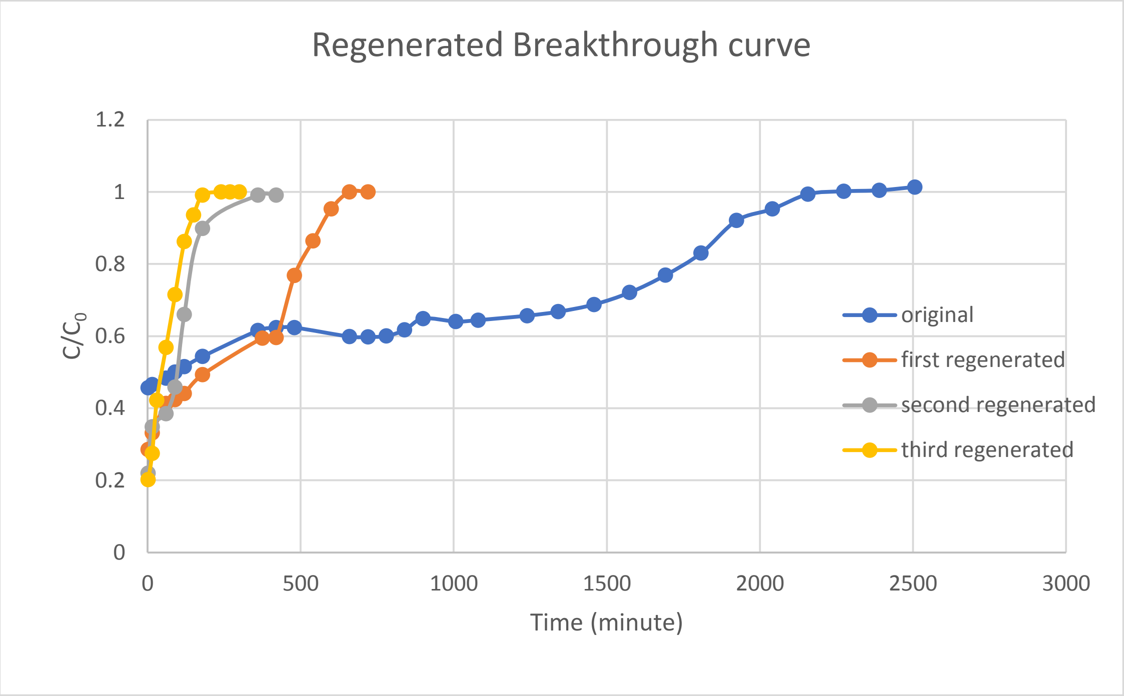

Figure 5-4: Breakthrough Cuves for NOM adsorption using regenerated GAC

Comparing the results for NOM adsorption using regenerated GAC and comparing MB and IN of original GAC and regenerated GAC, the higher NOM adsorption in the beginning and fast saturation of regenerated GAC was observed. By increasing time, flow rate, and temperature of regeneration, the hardness for regenerated GAC decreased.

6. Conclusions and Recommendations

GAC was produced using a mixture of hexane, washed CBPP, and bitumen. Produced extrudes at different binder to carbon ratio were calcinated and activated at different temperature, temperature increasing rate, and activation time to determine the ideal condition for granulation. Different parameters including MB, IN, and hardness were investigated to determine the efficiency of GAC to remove NOM.

The following conclusions are drawn from this study:

1. The extrudes of 30:70 binder to carbon ratio calcinated at 750°C for 1hr, activated at 950°C with 80°C steam for 3 hours under 15°C/min heating rate were found optimum. The MB, IN, and hardness of optimized GAC were approximately 241mg/g, 1420 mg/g, and 85%, respectively.
2. The study shows that the produced GAC has high potential for efficient removal of NOM from raw water from Pouch Cove intake source. The packed column of 12cm height and 2.5cm diameter of GAC removes more than 60% of NOM from water for over 36 hours (i.e., 17 liters of raw water).
3. Chlorination was carried out for both filtered and raw water for 1 hour, 8 hourd, and 36 hours of contact time. The analysis shows that the chlorination of filtered water for 36 hours contact time has 80% lower THMs concentration than in the unfiltered water.
4. Used GAC in column test were regenerated under different temperature (650-950°C), time (30-120minutes), and steam flow rate (200-500 cm^3/min). The analysis shows that the regeneration for 43 minutes at 916°C under 350 cm^3/min of steam flow rate was ideal condition and regenerated GAC studied up to 3 cycles was effective to remove NOM for about 12hours (i.e., 4.5liter of water).

The following recommendations are made to improve effectiveness of GAC in water supply systems:

1. The analysis on NOM adsorption and reduction of DBPs in the drinking water reported in this study is based on only one community. To generalize effectiveness of GAC to remove

different types of NOM, more communities covering seasonal variations in NOM and DBP reduction should be investigated.

2. Only one kind of binder which is bitumen was investigated. It is however proposed that the future studies should cover various available binders in the market
3. Test runs with two adsorption columns in series should be considered in future to further improve the NOM removal and thus reducing the THMs and HAAs in the drinking water to meet Health Canada guidelines.

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