

# Affordable Water Filtration Technology for Disinfection By-Product Control for Small Rural Communities by Using Carbon Extracted from Local Fly Ash

He Zhang, Tahir Husain

Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, NL, Canada

Email: he.zhang@mun.ca

**How to cite this paper:** Zhang, H. and Husain, T. (2021) Affordable Water Filtration Technology for Disinfection By-Product Control for Small Rural Communities by Using Carbon Extracted from Local Fly Ash. *Journal of Minerals and Materials Characterization and Engineering*, 9, 148-168.  
<https://doi.org/10.4236/jmmce.2021.92011>

**Received:** December 11, 2020

**Accepted:** March 13, 2021

**Published:** March 16, 2021

Copyright © 2021 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

## Abstract

The fly ash generated from local pulp and paper industries was transformed into activated carbon (AC) through physical activation process in a high temperature tube furnace in this study. Effects of two factors including activation temperature and activation time were investigated. Iodine number (IN), methylene blue value (MBV), and surface microstructure were all analyzed to assess the adsorption capacity of different carbon samples. The surface area of the carbon sample increased significantly from 486.44 m<sup>2</sup>/g to 847.26 m<sup>2</sup>/g before and after activation. The jar tests revealed that the use of 0.5 g (AC)/L (water) has the highest adsorption effectiveness. Meanwhile, the column filtration experiment indicated more than 60% of the organic matter can be removed by the carbon barrier within 2 hours filtration. The follow-up chlorination experiment illustrated that the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) could be considerably prevented after filtration. Above all, the cost-effective carbon filtration technology developed in this study can potentially be applied as a pre-treatment technology for intake source waters for local communities.

## Keywords

Activated Carbon Filtration, Column Washing, Drinking Water Treatment, Waste Management

## 1. Introduction

Chlorine has been commonly used as a disinfectant and oxidant in the world's drinking-water supply systems due to its characteristics and low cost. The

chlorination process not only removes odour, colour, and some unwanted metals but also kills disease-causing pathogens such as bacteria and viruses which commonly grow in water distribution systems. However, chlorine can react with natural organic matter (NOM) in drinking-water supply systems to produce compounds known as disinfection by-products (DBPs). NOM refers to a complex combination of organic compounds [1] [2] with varying molecular size and properties and different functional groups such as phenolic, hydroxylic, and carboxylic [3] [4]. NOM is derived from the decomposition of living organisms such as animals and plant residues [5] [6]. It can contain humic acids, fulvic acids, carbohydrates, carboxylic acids, proteins, lipids, amino acids, and polysaccharides, depending on the characteristics of the water basins [2] [3] [5]. Since their identification in 1970s, DBPs have been actively investigated. Significant research has been directed toward understanding their formation, occurrence, and the health effects of chronic exposure [7]. Research shows that there is an association between long-term exposure to high DBP levels and the increased incidence of liver, kidney, bladder, and colon cancers as well as other health impacts [8].

In Newfoundland and Labrador (NL) of Canada, over 90% of NL's water treatment plants use chlorine as the primary disinfectant. According to a comprehensive report prepared for water supply systems in NL, chlorinated water supply systems service approximately 98% of the provincial population [9]. Due to the potential carcinogenicity and other health impacts of DBPs, drinking-water regulations worldwide require regular monitoring of their concentrations in water supply systems. Among all the DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) have been identified as the largest two classes of DBPs detected on a weight basis in chlorinated drinking water, hence are considered in most studies. The statistics for THM and HAA analysis show that, as of September 2016, the averaged concentrations of THM in 136 of 497 of the province's water supplies exceed the guideline, and the HAA levels in 161 of 499 exceed the guideline [10].

Many NL communities with high THM and HAA levels in their water supplies are in rural areas with very low residential population. A recent study shows that small rural communities with a small population generally cannot afford the high cost of a comprehensive water treatment system and they also lack highly skilled, certified operators to maintain a residual level of chlorine and to address other technical challenges during the treatment process. Due to limited provincial resources, small rural communities are responsible for providing sustainable and safe drinking water to their residents at an affordable cost, but it is virtually impossible for them to meet such responsibilities [11]. Considering the above challenges and the financial constraints faced by these communities, an affordable and easy-to-operate filtration technology is needed to provide safe and sustainable drinking water to the residents of these communities.

Without comprising the microbiological quality of drinking water, proactive

actions should be taken to minimize the DBP concentrations caused by employing disinfectant. One effective strategy for controlling DBPs formation in drinking-water supplies is to remove its organic precursors [12]. Different water treatment processes have been researched and/or applied to remove NOM before it reacts with chlorine to form DBPs; these include a coagulation-based process, an oxidation process using ozonation, high pressure membrane filtration processes, and adsorption processes using activated carbon (AC) or various resins [13]. Some traditional water treatment methods showed low capability in NOM removal [14]. This leads to the necessity of equipping water treatment plants with additional treatment stages to decrease DBPs after chlorination [15] and reduce chlorine demand to prevent bacterial growth in pipelines [16]. Among these methods, enhanced coagulation and AC adsorption are the best available technologies for NOM removal [17]. AC has been used in many water treatment plants for organic matter removal due to its high affinity to organic matter even at low concentrations [18].

Commercial AC can be made from wood products, bituminous and lignite coal, coconut shells, and petroleum coke. These ACs have high removal efficiency, but due to the high cost of the raw materials, using AC filters manufactured from these materials in small communities is not economically feasible. This has led to the need to find a low-cost adsorbent by extracting unburned carbon from fly ash (FA). The application of activated carbon derived from fly ash can be utilized in both gas and water treatment for the adsorption of various contaminants including  $H_2S$  [19], copper and lead [20], selenium [21], as well as  $SO_2$  and  $NO_x$  [22]. This waste is abundant, with 10,000 metric tons being generated annually from local pulp and paper industry in NL [23]. The local pulp and paper industry utilizes a thermo-mechanical pulping process to produce approximate 700 tons of standard newsprint and other specialty newsprint grades per day. The pulp and paper manufacturing process is supported by steam generated from mill boilers. The main boiler burns a mixture of Bunker C fuel, waste oil fuel, and hog fuel. To control air emissions released to the atmospheres during the mill operation, the main boiler is equipped with emission control devices including mechanical dust collectors, low oxides of nitrogen ( $NO_x$ ) burners, and a wet scrubber. Each year, about 10,000 metric tons of fly ashes are generated from mill operation and disposed to landfills [24]. However, the leachate of landfill has turned into a potential threat to the surface and groundwater environment, and the landfill space is gradually becoming insufficient. Both these resulted in an increasing waste disposal cost. Hence, there is an urgent need for the local pulp and paper industry to seek sustainable waste management strategies to treat their fly ash waste. As their fly ash is rich in carbon [23], it is suitable to be converted into valuable product like AC. The finding of the study will not only contribute to the improvement of water quality in the source water pretreatment in local communities, but also benefit the local pulp and paper industry in reducing the amount of ashes ending up in landfill and thus save the

landfill space and associated disposal cost.

## 2. Methodology

### 2.1. Materials

Raw FA samples used in this research were collected from the main boiler of a local pulp and paper manufacturing company. The source water samples used in the jar tests and column filtration experiments were collected from a local community that highly concerns about the DBPs in their drinking water systems. Other materials and chemicals used in this research are: Nitric acid (HNO<sub>3</sub>, ACS reagent, 70%); Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, ACS reagent, 95.0% - 98.0%); Hydrochloric acid (HCl, ACS reagent, 37%); Iodine (USP, 99.8% - 100.5%); Potassium iodide (KI, anhydrous, free-flowing, Redi-Dri™, ACS reagent, ≥99%); Potassium iodate (KIO<sub>3</sub>, ACS reagent, 99.5%); Copper (II) sulfate (CuSO<sub>4</sub>, ReagentPlus®, ≥99%); Potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>, powder, ≥99.0%); Sodium phosphate dibasic (Na<sub>2</sub>HPO<sub>4</sub>, powder, ACS reagent, ≥99.0%); Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, ACS reagent, ≥99.0%); Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, ReagentPlus®, 99%); Methylene blue (powder, certified by the Biological Stain Commission); Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, ACS reagent, anhydrous, ≥99.5%); Sodium hypochlorite (NaClO, 5% usp solution, A&C Ltd., assay: 4.0% - 6.0%); potato starch (powder). All of them were purchased from Sigma-Aldrich Canada Co., ON, Canada.

### 2.2. Extraction, Activation and Characterization of Carbon Samples

The raw FA sample was firstly grinded into powder before characterization. The raw powder sample was then washed with 5% - 10% HNO<sub>3</sub> solution on a carbon to acid ratio of 1 g per 10 mL at 60°C for 2 hrs to recover unburnt carbon and remove impurities from the FA. After filtration, the particles were cleaned with distilled water for several times to eliminate any acid residue. At last, the filtered clean FA was dried at 110°C overnight before activation use. Characterization of particle size, pH, moisture, ash content, carbon content, Iodine number (IN), methylene blue value (MBV), and metal elements were conducted for both raw and clean FA samples.

Comparing with chemical activation, physical activation usually generates cleaner activated carbon (AC) products which are more suitable for water treatment technology development. Therefore, this study only focuses on physical activation of this wood-based fly ash. Iodine number, methylene blue value, scanning electron microscopy (SEM), as well as Brunauer, Emmett and Teller (BET) analyses were all used to assess the surface area and porosity development.

### 2.3. Effect of Activation Temperature

In this part, a programmable Lindberg/Blue M tube furnace was used for both carbonization and activation processes. The temperatures examined were 650°C,

700°C, 750°C, 800°C, 850°C and 900°C, respectively. In carbonization process, about 6 grams of the clean FA was firstly heated from room temperature to a desired temperature at a rate of 10°C/min under N<sub>2</sub> flow (75 cm<sup>3</sup>/min). Once reaching the desired temperature, the carbonization was continued for another hour. This was then followed by a 1-hour activation process under CO<sub>2</sub> flow (75 cm<sup>3</sup>/min) at the same temperature. The AC samples generated at different temperatures together with raw and clean FA samples were analyzed for loss of ignition, iodine number, and methylene blue value. The sample with high iodine number and methylene blue value was selected to evaluate the effect of activation time.

#### **2.4. Effect of Activation Time**

In this part of experiment, the clean FA sample was carbonized and activated under the selected activation temperature for 1 hour, 2 hours, and 3 hours, respectively. The AC samples generated in this part were analyzed for iodine number and methylene blue value. The one with high iodine number and methylene blue value was employed in the following water filtration experiments.

#### **2.5. Evaluation of Organic Matter Adsorption through Jar Test Experiments**

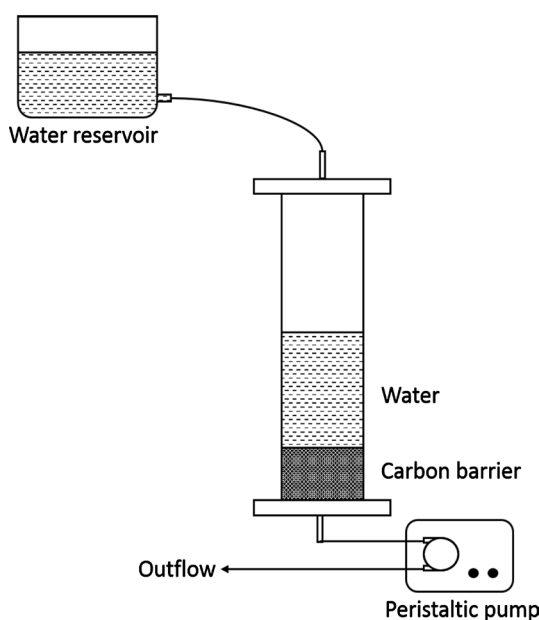
After evaluating the adsorption capacity of iodine and methylene blue by fly ash derived AC, real water samples were applied to further evaluate the adsorption of organic matter through batch test. The source water sample was collected from a local community that highly concerns about the DBPs in their drinking water systems. The natural organic matter in the source water was firstly characterized by measuring the total organic carbon (TOC). Other parameters of pH, alkalinity, color, turbidity, ultraviolet (UV) at the wavelength of 254 nm, and total dissolved solids (TDS) were also determined. Jar tests were conducted to evaluate the adsorption of organic matter by different AC doses and for different contact times. In this experiment, different amount of the AC sample was mixed with a series of 500 mL source water at ratios of 0.5 g/L, 1 g/L and 2 g/L. The mixtures were thoroughly mixed on magnetic stirrers for adsorption time of 15 mins, 30 mins and 60 mins, respectively. The mixtures were filtered by 0.45 µm membrane filters and the filtrates were analyzed for TOC and UV. Since natural organic matter is commonly measured as TOC, it is used to quantify the natural organic matter in the water samples. It is believed that some natural organic matter compounds have certain chemical structures that can absorb UV light especially at the wavelength of 254 nm [13] [25] [26]. Hence, UV<sub>254</sub> is also applied in the quantification of the natural organic matters. Besides AC dose and contact time, temperature and pH can have influences on the adsorption of organic matter as well. However, the adsorption tests in real cases were usually conducted at room temperature, and the pH of the source water does not have much fluctuation in different seasons. The effects of temperature and pH are therefore not considered in this study.

## 2.6. Development of Carbon Filtration Technology

A lab scale fixed bed carbon filtration system was developed. When the water enters the column, and passes through the carbon barrier, the natural organic matter in water can be adsorbed by the activated carbon so that the formation of DBPs can be avoided or mitigated. An acrylic glass column with 30 cm length and 40 mm diameter is made to implement the carbon filtration technology in the lab. In general, a 0.45  $\mu\text{m}$  membrane filter paper is placed at the bottom of the column and 5 g AC sample is then packed into the column. The column top part is connected to a water reservoir which contains water samples to be treated, and the water will pass through the column in a down flow mode. A peristaltic pump is connected at the column outflow to control the filtration speed. A sketch of the filtration system is displayed in **Figure 1**. A 24-hr column filtration test was conducted to evaluate the adsorption performance of the AC sample. The source water passed through the column in a down flow mode. The flow rate of this test was kept in the range of 6 to 8 mL/min and about 10 L in total of the source water has been filtered within the 24-hr period. In this study, the filtrate samples collected at the column outlet at the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, 6<sup>th</sup>, 12<sup>th</sup> and 24<sup>th</sup> hr were analyzed for both TOC and UV<sub>254</sub>.

## 2.7. Assessment of DBP Formation

In this part of study, the formation potential of two major groups of DBPs (THMs and HAAs) were examined for the local community and for both raw and filtered water samples. A sodium hypochlorite 5% usp solution (A & C Ltd., NaClO assay: 4.0% - 6.0%) was used as a disinfectant. Both raw and column filtered source-water samples were chlorinated by sodium hypochlorite and stored in a dark place for 24 hours. According to the Guidelines for Canadian Drinking



**Figure 1.** A sketch of carbon filtration system.

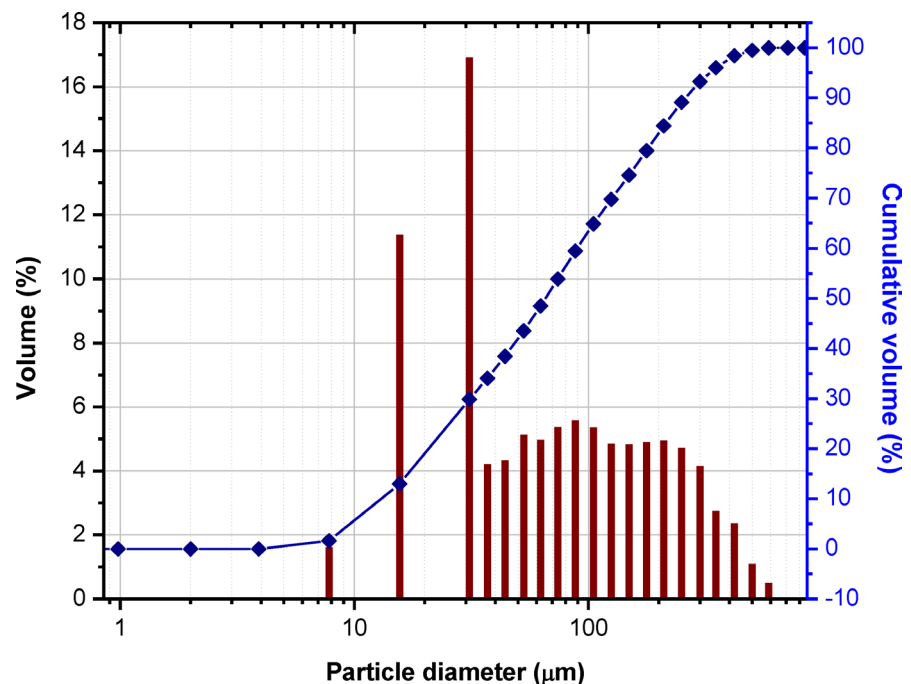
Water Quality (GCDWQ), free chlorine in the majority of drinking-water distribution systems is in the range of 0.04 mg/L to 2 mg/L [8]. To keep the concentration of free chlorine after 24 hours in the same range, different amounts of sodium hypochlorite solution were added to the water samples. The formation of THMs and HAAs was monitored after 1 hour, 4 hours, 12 hours, and 24 hours of chlorination. Meanwhile, the concentrations of four typical THM compounds—chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHClBr}_2$ ), and bromoform ( $\text{CHBr}_3$ )—and all nine HAA compounds, which are monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromoacetic acid (DBAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA), were analyzed.

### 3. Results and Discussion

#### 3.1. Characterization of Raw and Clean FA

The particle size of raw FA sample was analyzed. **Figure 2** shows the particle size distribution of the tested sample. From **Figure 2**, more than 25% of raw FA has the particle size of 15 to 31  $\mu\text{m}$ ; about 60% of it was evenly distributed in the range of 37 to 300  $\mu\text{m}$ ; the minimum and maximum particle sizes were 7.8 and 710  $\mu\text{m}$ , respectively.

The characteristics of pH, moisture content, ash content, carbon content, iodine number and methylene blue value for both raw and clean FA samples were examined. Results are shown in **Table 1**. Since the raw FA sample was cleaned



**Figure 2.** FA particle size distribution after grinding.

by  $\text{HNO}_3$  solution, the clean FA shows strong acidity while the raw FA is alkaline. The acids left in the FA samples could be removed in the following activation process. Most moisture and ash content were reduced after the cleaning process, which indicates the effectiveness of using nitric acid solution as cleaning reagent. Meanwhile, the reduction of ash content also resulted in the increase of carbon content of the FA sample, which would further benefit the activation process. The iodine number decreased, and the methylene blue value increased after cleaning, which means some impurities in the raw sample reacted with the iodine other than the methylene blue. Accordingly, it is very necessary to conduct the cleaning process before any further treatment so that the evaluation of the carbon adsorption capacity will be accurate.

The metal elements in FA were analyzed before and after the cleaning process, and results are shown in **Table 2**. The raw FA is rich in calcium, aluminum, iron and magnesium. After cleaning, about 44% of calcium was removed. The metal elements in FA were analyzed before and after the cleaning process, and results are shown in **Table 2**. The raw FA is rich in calcium, aluminum, iron and magnesium. After cleaning, about 44% of calcium was removed. Also, more than 60% of aluminum, and more than 70% of iron and magnesium were removed from the FA, which illustrates that the cleaning process is efficient in metal removal. Also, more than 60% of aluminum, and more than 70% of iron and magnesium were removed from the FA, which illustrates that the cleaning process is efficient in metal removal.

**Table 1.** Characterization of raw and clean FA samples.

Parameters	pH	Moisture/%	Ash content/%	Carbon content/%	IN/(mg/g)	MBV/(mg/g)
FA-Raw	11.44	1.67	14.04	78.68	444.56	57.42
FA-Clean	2.95	0.35	4.05	82.79	289.53	61.89

**Table 2.** Metal contents in FA before and after acid-washing.

Metal elements	Raw FA/ppm	FA after washing/ppm	Removal rate/%
Magnesium (Mg)	511.65	185.33	63.8
Aluminum (Al)	947.025	281.31	70.3
Iron (Fe)	784.202	175.19	77.7
Zinc (Zn)	11.724	9.07	22.6
Copper (Cu)	7.280	1.75	76.0
Lead (Pb)	2.252	0	100
Arsenic (As)	<LD		
Vanadium (V)	15.460	2.57	83.4
Nickel (Ni)	15.962	3.74	76.6
Calcium (Ca)	2656.356	1481.50	44.2



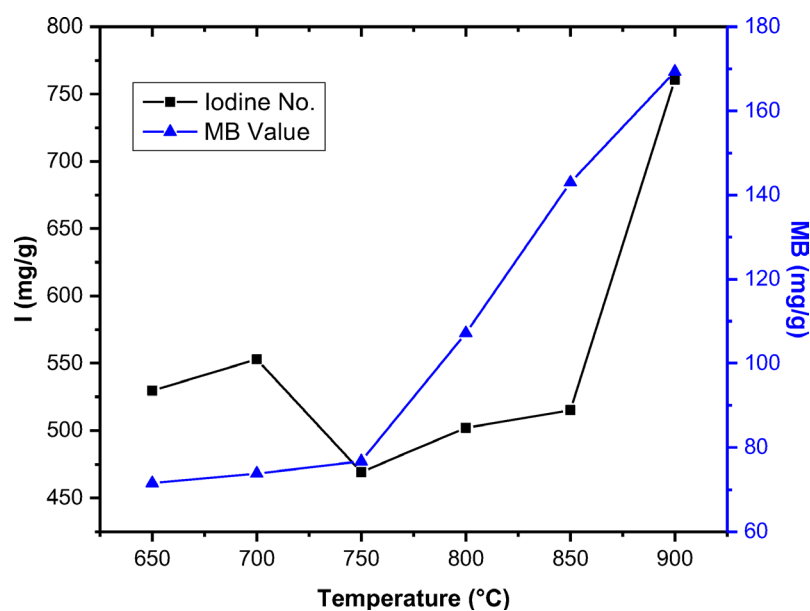
### 3.2. Effect of Activation Temperature

The fly ash derived activated carbon samples were evaluated by determining the loss of ignition, iodine number and methylene blue value. Results are shown in **Table 3**. Iodine number and methylene blue value are also shown in **Figure 3**. From **Table 3**, the loss of ignition basically increases when the activation temperature increases. The loss in the activation process is mainly due to the reaction between C and CO<sub>2</sub> [27]. When the activation temperature increases, the reaction will be accelerated, which will therefore result in a higher loss.

Iodine number and methylene blue value are two parameters that are commonly used to assess the performance of activated carbon. Iodine adsorption implies the micropore content of an AC sample, while the adsorption of methylene blue can give a hint about the mesopore structure [28]. From **Figure 3**, it is clearly that both iodine number and methylene blue value increase when the activation temperature increases. It illustrates that higher temperature results in higher level of micropore and mesopore development. However, the higher activation temperature applied, the higher ignition loss obtained. For the sample

**Table 3.** Characterization of FA and AC samples.

Samples	Loss of ignition/%	Iodine No./(mg/g)	Methylene blue value/(mg/g)
AC-650°C	7.79	529.66	71.57
AC-700°C	14.29	552.92	73.84
AC-750°C	13.70	469.26	76.7
AC-800°C	22.22	502	107.19
AC-850°C	36.84	515.16	142.98
AC-900°C	53.75	760.91	169.33



**Figure 3.** Iodine No. and MB value of carbon samples activated at different temperatures.

activated under 900°C, it has the most micropores and mesopores while the loss of ignition could be higher than fifty percent. It is not cost-effective to generate activated carbon with high energy consumption and loss of ignition. Comparing with activated carbon generated under 900°C, the one obtained at 850°C shows relative high level of micropore and mesopore, and relative low level of ignition loss. The 850°C is then selected to evaluate the effect of activation time.

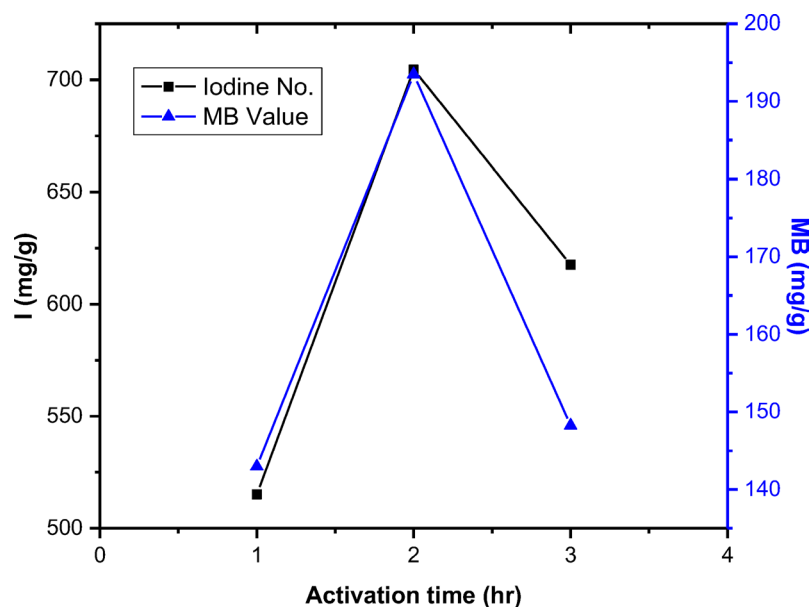
### 3.3. Effect of Activation Time

After testing different activation temperatures, different activation time periods were also examined. Results of iodine number and methylene blue value were shown in **Table 4** and **Figure 4**. The results of iodine number and methylene blue value illustrate that the sample being activated under 850°C for 2 hours has the most micropores and mesopores. It is hence selected to conduct the adsorption tests on real water samples.

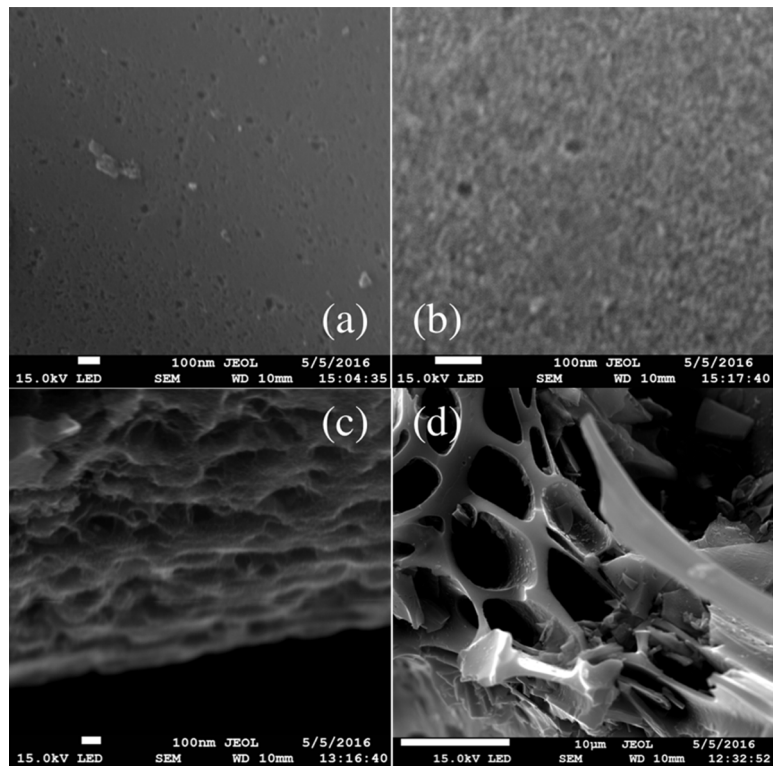
The surface microstructure images of FA-Clean and AC-850°C-2hr are observed by SEM and shown below. Comparing **Figure 5(a)** & **Figure 5(b)** with **Figure 5(c)** & **Figure 5(d)**, a dense porous structure was formed after activation, which is in accordance with the results of iodine and methylene blue tests. The BET surface area and porosity analysis were conducted to further assess how well the carbon has been activated. As listed in **Table 5**, there is a significant improvement

**Table 4.** Characterization of 850°C-activated AC samples.

Samples	Iodine No./(mg/g)	Methylene blue value/(mg/g)
AC-850°C-1 hr	515.16	142.98
AC-850°C-2 hr	704.53	193.47
AC-850°C-3 hr	617.63	148.24



**Figure 4.** Iodine No. and MB value of carbon samples activated with different time lengths.



**Figure 5.** SEM images of carbon particles: (a) & (b) before activation; (c) & (d) after activation.

**Table 5.** Surface area and pore volume of clean and activated carbon.

Samples	Surface area/(m <sup>2</sup> /g)	Micropore area/(m <sup>2</sup> /g)	Pore volume/(cm <sup>3</sup> /g)
FA-Clean	486.44	402.50	0.18
AC-850°C-2 hr	847.26	619.49	0.28

on surface area, micropore area and pore volume in the sample after activation. Nitrogen (N<sub>2</sub>) adsorption-desorption isotherm curves for both samples are also plotted in **Figure 6** and **Figure 7**, respectively. It is revealed that the adsorption rate of the carbon sample is highly improved after activation, which is also in accordance with the iodine and methylene blue test results.

### 3.4. Organic Matter Adsorption through Jar Test

The characteristics of the source water sample are listed in **Table 6**. The pH, turbidity and TDS of the analyzed source water are all within the GCDWQ. Only the level of color exceeds that in the guideline. Color is prevalent in natural source waters especially surface waters. The higher level of color indicates more organic matter in the water.

The adsorption capacity of fly ash derived AC was examined through batch tests. TOC removal and UV deduction were investigated and shown in **Figure 8** and **Figure 10**. As can be seen in **Figure 8**, 75% of TOC was removed after 60 mins adsorption at a dose of 0.5 g/L. The trend of TOC removal at dose of 1 g/L

is similar to that at 2 g/L from 15 mins to 60 mins. About 85% of TOC removal was found from 30 mins to 60 mins at both doses, which indicates that the maximum adsorption of TOC is around 85% and it can occur within 30 mins of

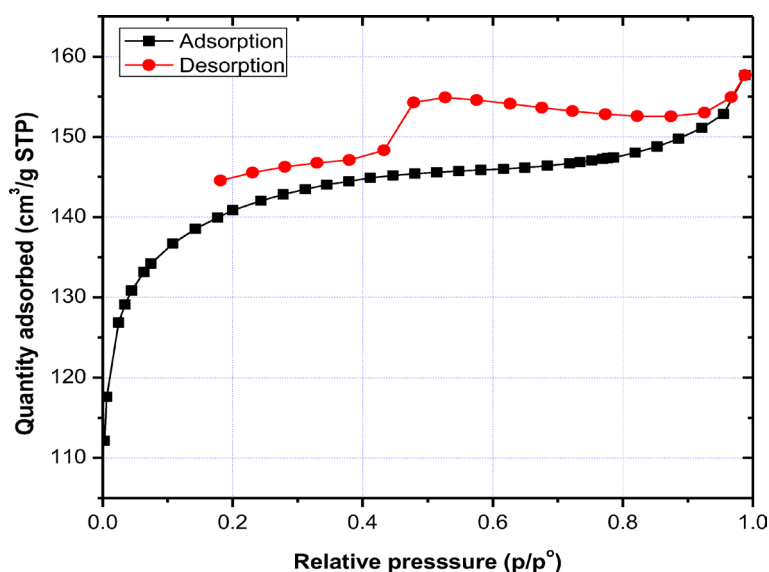


Figure 6. N<sub>2</sub> adsorption-desorption isotherm linear plot of FA-Clean.

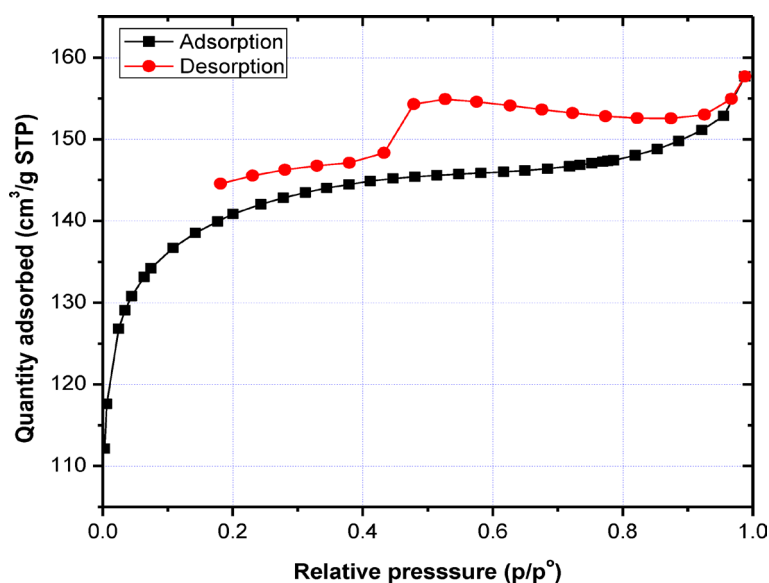


Figure 7. N<sub>2</sub> adsorption-desorption isotherm linear plot of AC-850°C-2 hr.

Table 6. Characteristics of community intake source water

Parameters	Alkalinity* (mg/L)	Color* (TCU)	pH	Turbidity (NYU)	UV <sub>254</sub> (A)	TDS* (mg/L)	TOC (mg/L)
Canadian Drinking Water Quality Guidelines	NA	15	6.5 - 8.5	1.0	NA	500	NA
Source water	7.00	31	6.67	0.24	0.271	21	8.472

(\*Source: Newfoundland and Labrador Water Resources Portal).

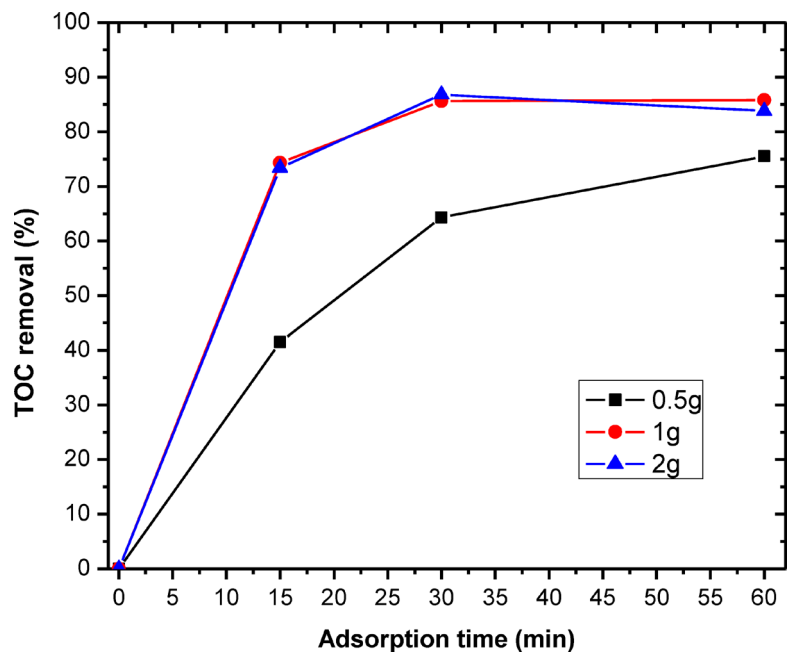


Figure 8. TOC adsorption kinetics by AC with different doses.

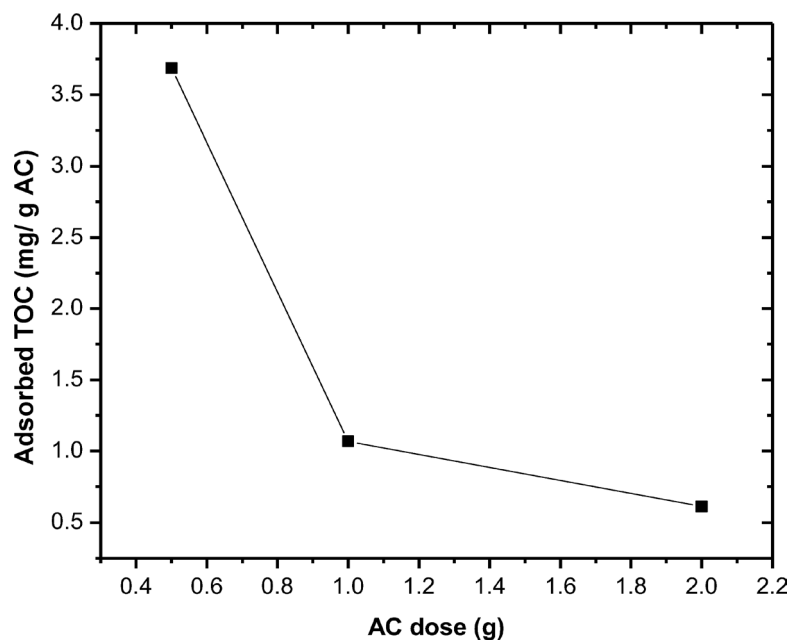
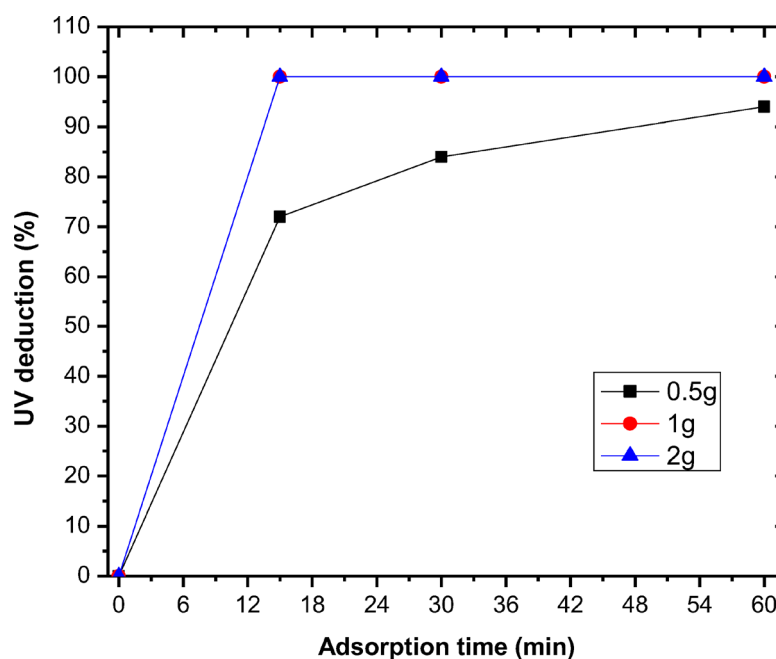


Figure 9. TOC adsorption isotherm by AC with different doses.

adsorption. As shown in **Figure 10**, a 72% of  $UV_{254}$  deduction was observed after 15 mins adsorption at the dose of 0.5 g/L, meanwhile a 95% of  $UV_{254}$  deduction was obtained after 60 mins at the same dose. For the doses of 1 g/L and 2 g/L, the  $UV_{254}$  was dramatically decreased to zero within 15 mins of adsorption, which illustrates the AC is extremely effective in  $UV_{254}$  deduction in the adsorption experiments. Comparing TOC removal with  $UV_{254}$  deduction at the carbon dose of 1 g/L with 15 mins adsorption time, 74% of TOC was while 100%  $UV_{254}$  deduction was detected. As stated earlier, both TOC and removed UV were commonly



**Figure 10.** UV deduction by AC with different doses.

used to quantify the organic matter. The difference in the TOC removal and UV deduction results implied that the composition of TOC was not only contributed by the UV-C absorptive organics (e.g., aquatic humic substances), some of its organic components might not be sensitive to the UV light [13] [29] [30]. From another point of view, the generated AC was more effective in the adsorption of light-sensitive organic matters. The same phenomenon was also discovered in the column experiment in the next section.

**Figure 9** displays the TOC adsorption isotherm by AC with different doses. From the isotherm, the adsorbed TOC by each gram of activated carbon is 3.7 mg/g, 1.1 mg/g and 0.6 mg/g for doses of 0.5 g/L, 1 g/L and 2 g/L, respectively. The use of 0.5 g (AC) /L (water) in the batch test has the highest adsorption effectiveness and the lowest cost of AC. This dose is thus determined to be appropriate in the following experiment.

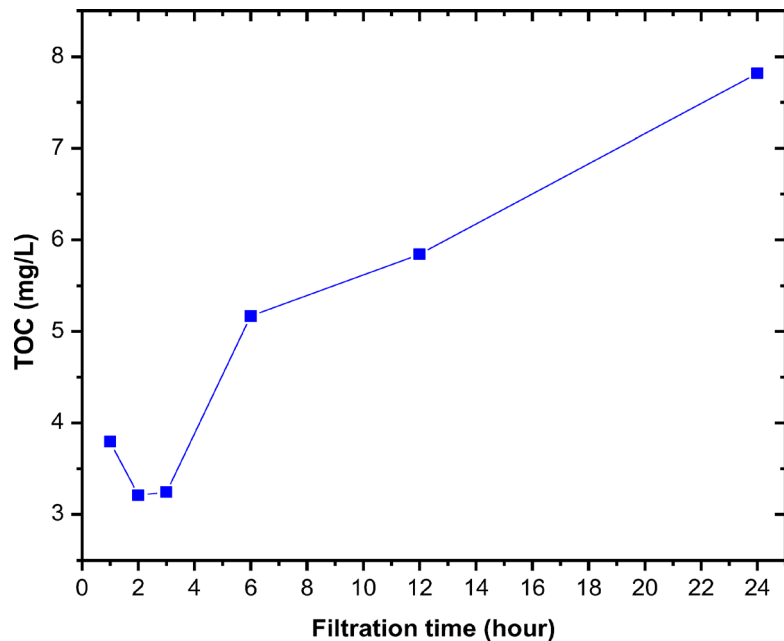
### 3.5. NOM Removal through Column Filtration

From **Figure 11**, the TOC of the column effluent samples decreases from 8.472 mg/L to 3.2 mg/L in the first two hours, and then increases to 7.8 mg/L at the twenty-fourth hour. The TOC in column effluent could have such a trend is mainly due to the unstable flow rate. Since the AC used in column test is in powder form, it can cause blocking problems sometime in the middle of the experiment. The flow rate is usually high in the beginning of the filtration, and it will gradually become slow. When the flow rate slows down, the contact time between carbon and water sample will be extended. Therefore, the TOC in the column effluent was decreasing in the first few hours.

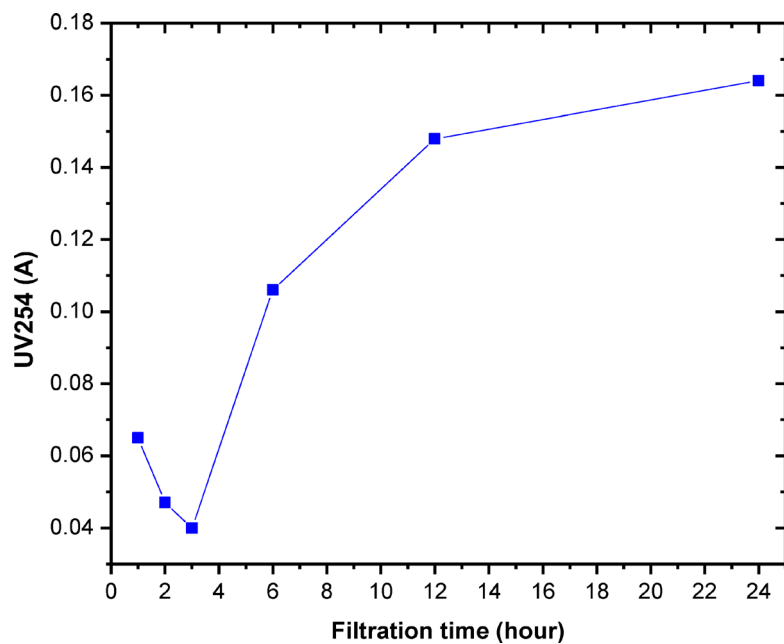
Comparing the original source water with the column effluent sample at the

end of the second hour, more than 60% of the organic matter has been adsorbed or removed by the carbon barrier. After 2 hours, the organic matter in the column effluent starts to increase but still below the original level, which implies that the adsorption rate of the carbon barrier is decreasing. After 24 hours, the TOC of the column effluent sample is close to 8 mg/L, which reveals that the carbon barrier becomes almost saturated.

From **Figure 12**, the result of  $UV_{254}$  has a similar trend as that of TOC, because of the blocking problem in the column. The  $UV_{254}$  of the column outflow



**Figure 11.** TOC concentration in column effluent within 24-hrs filtration.

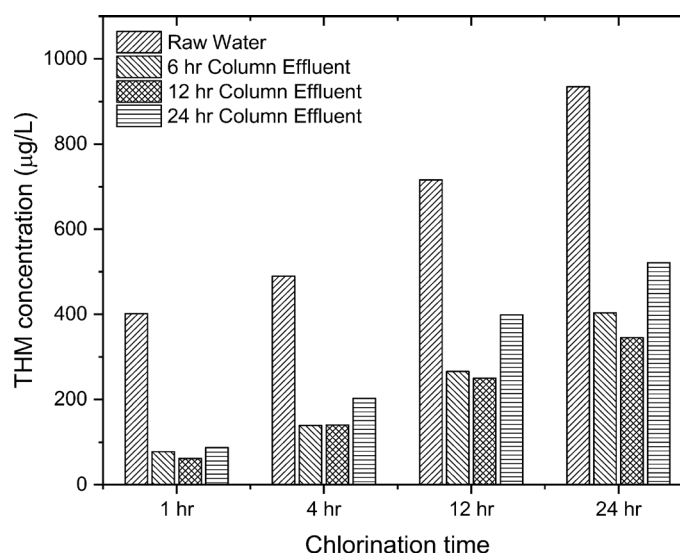


**Figure 12.**  $UV_{254}$  in column effluent within 24-hrs filtration.

sample decreases from 0.271 A to 0.04 A within three hours filtration, and then it increases to 0.164 A at the end of twenty-four hours. The TOC of the 24<sup>th</sup>-hour sample is about 92% of the original water sample, which indicates the carbon barrier is 92% saturated. However, the  $UV_{254}$  of the same sample is only 61% of the original water sample, which implies the carbon barrier is only 61% saturated. The big difference in the saturation degree from both results could possibly because some natural organic matters in the source water do not have UV-absorbing chemical structures. It also proves that the AC is more effective in adsorbing light sensitive organic matters. This phenomenon is also observed in the batch test, which may hint that the TOC results are more reliable than the UV results in this study.

### 3.6. Assessment of DBP Formation

**Figure 13** displays the total THM concentrations of both raw and column filtered water samples during chlorination; the total THM concentrations of all the samples increases as chlorination time increases. For the source water, the majority of THMs are formed within 12 hours of chlorination. For the column filtered water samples, THM concentrations gradually increase at relatively lower rates during the whole chlorination process. The source water has a THM concentration of 935  $\mu\text{g/L}$  after 24 hours, while the THM concentrations of the column 6-hour, 12-hour, and 24-hour effluent samples are about 404  $\mu\text{g/L}$ , 345  $\mu\text{g/L}$ , and 521  $\mu\text{g/L}$ , respectively. This indicates that column filtration is effective in NOM removal and can significantly reduce the amount of THM formed during chlorination. Among the column 6-hour, 12-hour, and 24-hour effluent samples, the 12-hour sample holds the lowest level of THM throughout chlorination; this implies that the 12-hour sample contains the least NOM. This is possibly due to the blocking problem that occurred in the middle of the column filtration, as blocking can lead to longer contact time between water and carbon



**Figure 13.** Total THMs of raw and column filtered samples during chlorination.



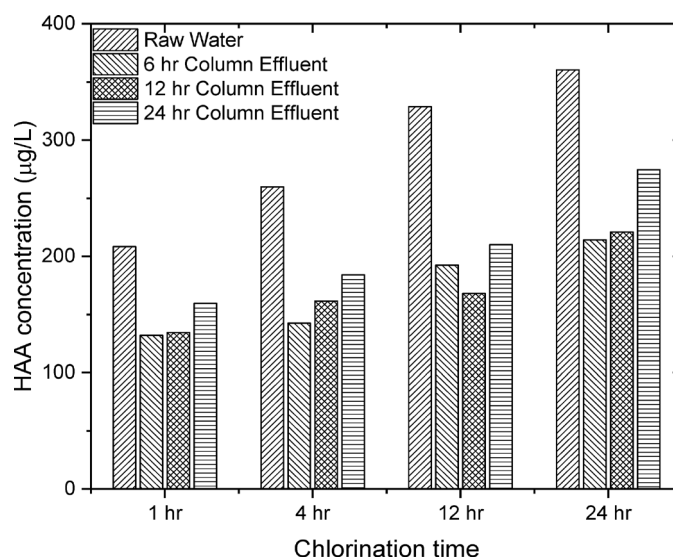
barrier and more NOM can be adsorbed. **Table 7** shows that chloroform plays a predominant part in the total THM concentrations. In comparing the source water and the column filtered water results, it is interesting to find that the bromine-containing THM compounds are only formed in the raw water but not in the effluent water samples during chlorination. **Figure 14** presents the total HAA concentrations of Sunnyside raw and column filtered water samples during different periods of chlorination. As with the THM results, the total HAA concentrations of all samples continuously increase within 24 hours. The raw water sample always shows a higher total HAA than that of column filtered effluent samples during chlorination; this proves that carbon filtration can prohibit

**Table 7.** Typical THM compounds in raw and chlorinated water samples (unit:  $\mu\text{g/L}$ ).

Samples	raw water				6 hr column effluent			
	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
$\text{CHCl}_3$	327.6	440.2	700.7	918.9	77.6	139.5	265.8	403.5
$\text{CHCl}_2\text{Br}$	35.2	20.9	15.0	16.2	0	0	0	0
$\text{CHClBr}_2$	18.4	9.1	0	0	0	0	0	0
$\text{CHBr}_3$	20.4	19.3	0	0	0	0	0	0
<b>Total THMs</b>	401.6	489.6	715.7	935.1	77.6	139.5	265.8	403.5

Samples	12 hr column effluent				24 hr column effluent			
	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
$\text{CHCl}_3$	61.9	140.3	249.9	345.2	87.5	202.5	398.7	521.4
$\text{CHCl}_2\text{Br}$	0	0	0	0	0	0	0	0
$\text{CHClBr}_2$	0	0	0	0	0	0	0	0
$\text{CHBr}_3$	0	0	0	0	0	0	0	0
<b>Total THMs</b>	61.9	140.3	249.9	345.2	87.5	202.5	398.7	521.4



**Figure 14.** Total HAAs of raw and column filtered samples during chlorination.

HAA formation. In a comparison of all the column filtered effluent samples, the HAA of 6-hour column effluent sample is close to that of the 12-hour column effluent sample, and they are slightly lower than the 24-hour column effluent sample. This reveals that the adsorption rate of the carbon barrier slowly decreases in the column filtration process. Even though carbon filtration can result in lower DBP concentrations, when both THM and HAA concentrations of the raw and column effluent water samples at the 24<sup>th</sup> hour of chlorination are considered, THM formation was prohibited at a higher degree than the HAA formation. Therefore, column filtration is more efficient in reducing THM formation potential than that of HAA. The concentrations of each of the nine HAA compounds for all chlorinated water samples are listed in **Table 8**, with DCAA exhibiting the highest concentration. TCAA is also an important component in total HAAs. The formation of BCAA, BDCAA, DBAA, CDBAA, and TBAA is very limited during chlorination for all samples. In some, such as source water,

**Table 8.** HAA compounds in raw and chlorinated water samples (unit: µg/L).

Samples	raw water				6 hr column effluent				
	Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
MCAA		36.8	9.9	7	10	10.3	0.0	0.0	0.0
MBAA		0	0	0	0	11.1	22.2	24.7	17.5
DCAA		127.3	200.9	274.8	281.5	76.3	88.7	126.1	154.3
TCAA		37.6	38.1	38.3	55.8	26.2	24.5	34.3	36.3
BCAA		0	0.3	1.1	1.5	1.1	1.3	1.9	2.3
BDCAA		0.5	0.7	0.8	1.1	0.7	0.7	0.8	1.0
DBAA		0	0	0	0	0.1	0.1	0.1	0.1
CDBAA		5.4	8.4	5.3	9.4	4.5	4.4	4.2	3.5
TBAA		0.6	1.5	1.4	1.1	1.6	1.0	1.5	1.6
<b>Total HAAs</b>		208.4	259.8	328.8	360.5	132.0	142.4	192.4	214.1
Samples	12 hr column effluent				24 hr column effluent				
	Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
MCAA		0.0	0.0	4.4	7.1	0.1	0.0	0.0	0.0
MBAA		14.8	23.6	1.4	17.8	6.4	14.9	0.2	4.9
DCAA		84.3	102.3	121.5	152.5	107.2	128.6	165.0	218.2
TCAA		28.7	27.5	32.4	35.2	35.1	32.2	38.1	42.6
BCAA		1.1	1.4	1.6	2.2	1.5	1.8	2.3	2.9
BDCAA		0.7	0.8	0.8	1.0	0.9	0.9	0.9	1.1
DBAA		0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1
CDBAA		5.0	4.6	4.2	3.5	6.4	5.9	5.7	4.6
TBAA		2.2	1.6	1.7	1.7	1.8	0.1	0.4	0.4
<b>Total HAAs</b>		134.4	161.5	168.1	221.0	159.5	184.1	210.1	274.5

the MCAA concentration decreases in the first 12 hours, but those of DCAA and TCAA increase. This phenomenon may suggest that MCAA is transformed into DCAA and/or TCAA during chlorination and indicate that more C-H bonds in acetic acid were substituted by Cl atoms and formed C-Cl bonds with the presence of free chlorine. A similar phenomenon found in other water samples demonstrates that a longer contact time can lead to a higher degree of chlorination.

#### 4. Conclusion

The fly ash derived AC has been proved to have high level of surface area and porosity which displays strong adsorption to iodine and methylene blue molecules. In jar tests, the AC demonstrated high adsorption efficiency for NOM while the efficiency reduced slightly in the column filtration due to the blocking issue. To overcome the blocking problem, a granular type of activated carbon is suggested in future study. In this study, TOC is identified as a more reliable NOM indicator than UV since the UV reading can only reflect the amount of light-sensitive organic matter. As the carbon barrier became gradually saturated, continuous filtration after 24 hours is therefore not suggested. The follow-up chlorination experiment on raw and column filtered water samples illustrates that the formation of THMs and HAAs can be considerably reduced after the water passed through the column. The cost-effective carbon filtration technology developed in this study can be potentially applied as a pre-treatment technology for intake source waters for local communities. Meanwhile, the generation of activated carbon from fly ash can benefit the local pulp and paper industries with their waste management.

#### Acknowledgements

The financial supports provided by the Harris Centre at Memorial University in the form of the Harris Centre MMSB Waste Management Applied Research Fund and the Natural Sciences and Engineering Research Council (NSERC) of Canada are highly appreciated.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

#### References

- [1] Leenheer, J.A. and Croué, J.P. (2003) Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environmental Science & Technology*, **37**, 18A-26A. <https://doi.org/10.1021/es032333c>
- [2] Cheng, W. Dastgheib, S.A. and Karanfi, T. (2005) Adsorption of Dissolved Natural Organic Matter by Modified Activated Carbons. *Water Research*, **39**, 2281-2290. <https://doi.org/10.1016/j.watres.2005.01.031>
- [3] Zularisama, A. Ismaila, A. and Salim, R. (2006) Behaviours of Natural Organic Matter in Membrane Filtration for Surface Water Treatment—A Review. *Desalina-*

- tion, **194**, 211-231. <https://doi.org/10.1016/j.desal.2005.10.030>
- [4] Thurman, E.M. (2012) Organic Geochemistry of Natural Waters. Vol. 2, Springer Science & Business Media, Berlin.
- [5] Schreiber, B. Brinkmann, T. and Schmalz, V. (2005) Adsorption of Dissolved Organic Matter onto Activated Carbon—The Influence of Temperature, Absorption Wavelength and Molecular Size. *Water Research*, **39**, 3449-3456. <https://doi.org/10.1016/j.watres.2005.05.050>
- [6] Frimmel, F.H. Abbt-Braun, G. Heumann, K.G. Hock, B. Lüdemann, H.D. and Spittler, M. (2008) Refractory Organic Substances in the Environment. John Wiley & Sons, Hoboken.
- [7] Richardson, S.D. Simmons, J.E. and Rice, G. (2002) Disinfection Byproducts: The Next Generation. *Environmental Science & Technology*, **36**, 98-205. <https://doi.org/10.1021/es022308r>
- [8] Health Canada (2017) Guidelines for Canadian Drinking Water Quality—Summary Table. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa.
- [9] DOE (2001) Source to Tap: Water Supplies in Newfoundland and Labrador. Department of Environment, Government of Newfoundland and Labrador.
- [10] ENVC (2017) Disinfection By-Products (DBPs). Department of Environment and Conservation, Government of Newfoundland and Labrador. <http://www.ecc.gov.nl.ca/waterres/quality/drinkingwater/DBPs.html>
- [11] Minnes, S., Vodden, K. and Team (2014) Exploring Solutions for Sustainable Rural Drinking Water Systems. Technical Report, Harris Centre, Memorial University, St. John's, 94.
- [12] World Health Organization (WHO) (2004) Environmental Health Criteria 216: Disinfectants and Disinfectant By-Products. International Programme on Chemical Safety. [http://www.who.int/ipcs/publications/ehc/ehc\\_216/en](http://www.who.int/ipcs/publications/ehc/ehc_216/en)
- [13] CBCL (2011) Study on Characteristics and Removal of Natural Organic Matter in Drinking Water Systems in Newfoundland and Labrador. Prepared by CBCL Limited for the Department of Environmental and Conservation, Water Management Division.
- [14] Xia, S. and Ni, M. (2015) Preparation of Poly(Vinylidene Fluoride) Membranes with Graphene Oxide Addition for Natural Organic Matter Removal. *Journal of Membrane Science*, **473**, 54-62. <https://doi.org/10.1016/j.memsci.2014.09.018>
- [15] Liua, P. Kellera, J. and Gernjak, W. (2016) Enhancing Zerovalent Iron Based Natural Organic Matter Removal by Mixing with Dispersed Carbon Cathodes. *Science of the Total Environment*, **550**, 95-102. <https://doi.org/10.1016/j.scitotenv.2016.01.067>
- [16] Chow, C.W., Fabris, R. and Drikas, M. (2004) A Rapid Fractionation Technique to Characterise Natural Organic Matter for the Optimisation of Water Treatment Processes. *Journal of Water Supply: Research and Technology*, **53**, 85-92. <https://doi.org/10.2166/aqua.2004.0008>
- [17] USEPA (2003) National Primary Drinking Water Regulations: Stage 2 Disinfectant and Disinfection Byproducts Rule: Proposed Rule, Federal Register, 49547-49681.
- [18] Babi, K.G., Koumenides, K.M., Nikolaou, A.D., Makri, C.A., Tzoumerkas, F.K. and Lekkas, T.D. (2007) Pilot Study of the Removal of THMs, HAAs and DOC from Drinking Water by GAC Adsorption. *Desalination*, **210**, 215-224. <https://doi.org/10.1016/j.desal.2006.05.046>
- [19] Aslam, Z., Shawabkeh, R.A., Hussein, I.A., Al-Baghli, N. and Eic, M. (2015) Synthe-

- sis of Activated Carbon from Oil Fly Ash for Removal of H<sub>2</sub>S from Gas Stream. *Applied Surface Science*, **327**, 107-115. <https://doi.org/10.1016/j.apsusc.2014.11.152>
- [20] Salehin, S., Aburizaiza, A.S. and Barakat, M.A. (2016) Activated Carbon from Residual Oil Fly Ash for Heavy Metals Removal from Aqueous Solution. *Desalination and Water Treatment*, **57**, 278-287. <https://doi.org/10.1080/19443994.2015.1006824>
- [21] Jegadeesan, G.B., Mondal, K. and Lalvani, S.B. (2015) Adsorption of Se (IV) and Se (VI) Using Copper-Impregnated Activated Carbon and Fly Ash-Extracted Char Carbon. *Water, Air, & Soil Pollution*, **226**, 234. <https://doi.org/10.1007/s11270-015-2520-5>
- [22] Davini, P. (2002) Flue Gas Treatment by Activated Carbon Obtained from Oil-Fired Fly Ash. *Carbon*, **40**, 1973-1979. [https://doi.org/10.1016/S0008-6223\(02\)00049-0](https://doi.org/10.1016/S0008-6223(02)00049-0)
- [23] Zhang, H., Husain, T. and Chen, Y. (2017) Corner Brook Pulp and Paper Mill Waste Management. The Harris Centre—RBC Water Research and Outreach Fund, Final Report. [https://www.mun.ca/harriscentre/reports/HUSAIN\\_WASTE\\_15\\_16.pdf](https://www.mun.ca/harriscentre/reports/HUSAIN_WASTE_15_16.pdf)
- [24] Department of Environment and Climate Change, Government of Newfoundland and Labrador (2017) Environment, Climate Change and Municipalities. [http://www.ecc.gov.nl.ca/env\\_protection/ics/pulp.html](http://www.ecc.gov.nl.ca/env_protection/ics/pulp.html)
- [25] Kornegay, B.H., Kornegay, K.J. and Torres, E. (2000) Natural Organic Matter in Drinking Water: Recommendations to Water Utilities. American Water Works Association,.
- [26] Krasner, S.W., Westerhoff, P., Chen, B.Y., Rittmann, B.E., Nam, S.N. and Amy, G. (2009) Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP Precursors in Effluent Organic Matter. *Environmental Science & Technology*, **43**, 2911-2918. <https://doi.org/10.1021/es802443t>
- [27] Chang, C.F., Chang, C.Y. and Tsai, W.T. (2000) Effects of Burn-Off and Activation Temperature on Preparation of Activated Carbon from Corn Cob Agrowaste by CO<sub>2</sub> and Steam. *Journal of Colloid and Interface Science*, **232**, 45-49. <https://doi.org/10.1006/jcis.2000.7171>
- [28] Itodo, A.U., Abdulrahman, F.W., Hassan, L.G., Maigandi, S.A. and Itodo, H.U. (2010) Application of Methylene Blue and Iodine Adsorption in the Measurement of Specific Surface Area by Four Acid and Salt Treated Activated Carbons. *New York Science Journal*, **3**, 25-33. <https://doi.org/10.4314/ijonas.v5i1.49921>
- [29] Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R. and Mopper, K. (2003) Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environmental Science & Technology*, **37**, 4702-4708. <https://doi.org/10.1021/es030360x>
- [30] Nkambule, T.I., Krause, R.W.M., Haarhoff, J. and Mamba, B.B. (2011) Treatability and Characterization of Natural Organic Matter (NOM) in South African Waters Using Newly Developed Methods. *Physics and Chemistry of the Earth, Parts A/B/C*, **36**, 1159-1166. <https://doi.org/10.1016/j.pce.2011.07.006>