

SAFE DRINKING WATER SUPPLY FOR SMALL & RURAL COMMUNITIES IN NL WITH A CASE STUDY OF POUCH COVE

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APRIL 2016

Acknowledgements

The support provided by the Harris Centre at Memorial University in the form of the Harris Centre RBC Water Research and Outreach Fund is highly appreciated. Appreciation is also extended to the Water Resources Management Division of the Department of Environment and Conservation for providing technical support and arranging for water samples from the water supply system in Pouch Cove for this project.

Executive Summary

Chlorine is the most common disinfectant used in the province of Newfoundland and Labrador. However, in the presence of natural organic matter (NOM) in drinking-water sources, disinfection by-products (DBPs) are formed when chlorine is used to treat drinking water. The two largest groups of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), are frequently studied by researchers because of their toxicity and high levels in drinking water.

In 1998 Newfoundland and Labrador began monitoring THMs and HAAs and it was found that several water utilities had THMs and HAAs above the specified Canadian guidelines, mostly in small, rural drinking-water systems. Pouch Cove was selected for this study as elevated levels of THMs and HAAs were found in their drinking-water system.

This study focused on the development of a simple and affordable filtration technology. A passive carbon barrier was studied in the lab to remove NOM, commonly measured as total organic carbon (TOC), before chlorination. The carbon barrier was made from extracted unburned carbon from oil fly ash (OFA), which is abundant within Canada and abroad. The passive nature of this barrier makes it easy to operate and its extremely low cost makes the system affordable for small communities. The OFA samples used for this study were obtained from the Rabigh power plant in Saudi Arabia, which currently generates about 60 tons of OFA daily and currently being disposed into landfills.

Since raw OFA contains organic and inorganic impurities, study samples were cleaned and treated through one of two processes, acid leaching or NaOH modification, followed by physical activation. Activated carbon (AC) samples were then applied to reduce the TOC and UV in the Pouch Cove drinking-water samples. In this adsorption treatment, a Split Plot design was employed to investigate the effects of different factors (pH, temperature, carbon dosage, sample volume, and contact/adsorption time), as well as the interaction effects among these factors. The results indicate that pH, temperature, carbon dosage, and sample volume are significant factors in designing a filtration technology. The optimal condition for TOC and UV reduction is a low temperature and a low pH. When the temperature is over 35°C, or the pH is greater than 8, no reduction was observed. The overall TOC removal by activated OFA is relatively low; the maximum removal rate can reach 66% within 30 minutes. Compared with NaOH-modified AC, acid-leached AC is a better adsorbent to achieve TOC and UV reduction.

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1 Background Information

1.1 Current drinking-water-quality status in Newfoundland and Labrador

Microorganisms and chemicals in drinking water are difficult to remove through conventional water-treatment methods. To eradicate microorganisms, chlorine is commonly used as an effective disinfectant. In the presence of natural organic matters (NOM) in the water (USEPA, 2009), the residual chlorine reacts with DOC and forms disinfection by-products (DBPs) in the drinking water which are now recognized as being potentially hazardous to human health under long-term exposure scenarios. Therefore, more attention in recent years has been on how to reduce DBPs in the drinking water in those communities where a complete treatment system, using advanced treatment technologies, is cost-prohibitive.

In Canada, most water-treatment plants use chlorine for both primary and secondary disinfection purposes. The evaluation results of the 2001–2004 Drinking Water Surveillance Program (DWSP) showed that 165 of 179 (92%) treatment plants in Ontario use chlorine as their primary disinfectant. In the province of Newfoundland and Labrador (NL), over 90% of the treatment plants use chlorine as the primary disinfectant. Although the provincial government has taken actions to improve drinking-water quality with measures such as source-water protection and operators' education (e.g., the source-to-tap program (DOEC, 2001), several communities still have DBP concentrations exceeding the drinking-water-quality guidelines (DOEC, 2014a).

NOM, as a precursor that causes the formation of DBPs in drinking-water systems, is commonly measured as total organic carbon (TOC). It is added to natural water bodies by natural processes such as soil chemical reactions, hydrological processes, organic materials, and a complex mixture of aromatic and aliphatic hydrocarbons (Leenheer and Croue, 2003). In general, NOM can be classified into two groups: the first is dominated by humic substances, which are hydrophobic in character and contain mostly humic and fulvic acids; the second consists mainly of non-humic substances and is a combination of organic compounds such as hydrophilic acids, proteins, amino acids, and carbohydrates.

Research team in the Faculty of Engineering and Applied Science began assessing the levels of DBPs in small community drinking-water systems in 1997. The early work was mainly based on sampling and analyzing THMs in drinking-water systems and assessing the risk to consumers in selected communities (i.e., St. John's, Clarenville, and Shoal Harbour) in the province (Kar, 2000; Sadiq et al., 2002; Chowdhury and Husain, 2005). The study showed high levels of THMs in Shoal Harbour and Clarenville, but since St. John's has a large system, the level of THMs in St. John's was found to be low. In order to find corrective measures to reduce THMs, this work was later extended to studying the mechanism of formation of THMs and HAAs in drinking water by concentrating on five communities (i.e., Keels, Clarenville, Ferryland, Bonavista, and Burin) (Boyalla, 2004; Boyalla et al., 2006; Boyalla et al., 2009) and predictive models were developed (Husain et al., 2009). These studies indicated that the formation of DBPs is mainly due to the presence of DBP precursors, which is mainly high-level natural organic matter (NOM) represented by the total organic carbon (TOC). The study showed that an effective way to reduce THMs and HAAs in the drinking water is to remove NOM before chlorination.

As the reaction between NOM and residual chlorine can cause the formation of more than 600 forms of DBPs in a water-supply system, it is difficult to monitor all of them. Recent literature has focused on two groups, trihalomethanes (THMs) and haloacetic acids (HAAs), which form the largest class of DBPs in chlorinated drinking-water systems. Chloroform (CHCl_3), bromodichloromethane (BDCM) or CHBrCl_2 , chlorodibromomethane (CDBM) or CHBr_2Cl , and bromoform (CHBr_3) are compounds within the THM group. The sum of their concentrations, known as total trihalomethane (TTHM), should not exceed $100 \mu\text{g/l}$ (Health Canada, 2012). There are nine compounds within the HAA group: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and tribromoacetic acid (TBAA); and three mixed chloro- and bromo- acetic acids: bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and bromochloro acetic acid (BCAA). The total combined concentration of the five most prevalent HAAs (MCAA, DCAA, TCAA, MBAA, and DBAA), known as HAA_5 , should not exceed $80 \mu\text{g/l}$ (Health Canada, 2012). In NL, especially in rural areas, the THM and HAA concentrations are much higher than the Canadian drinking-water-quality guidelines of $100 \mu\text{g/L}$ and $80 \mu\text{g/L}$, respectively (Health Canada, 2012). Out of approximately 480 sampled public

water-supply systems in the province, 134 displayed high levels of THMs, according to the Guidelines for Canadian Drinking Water Quality (GCDWQ) (DOEC, 2014b). Compared to the USEPA standard, however, approximately 159 out of 473 sampled public water-supply systems in NL display high levels of HAAs (DOEC, 2014c). This illustrates that approximately one-third of the public water supplies cannot provide safe, potable water. When this is considered in conjunction with the summer of 2013 drinking-water-quality index, it can be inferred that the majority of these exceedances occur in small, rural drinking-water systems, usually in combination with other parameter exceedances, particularly colour (DOEC, 2009).

As mentioned earlier, DBPs form mainly by the reaction between NOM and disinfectant like chlorine, but their formation is also affected by pH, water temperature, and seasonal variations (Ahmad, 2013). For instance, in winter their level is relatively lower than in other seasons. This can also be understood in terms of lower temperatures, as microorganism activity in the source water is reduced, and, therefore, less organic matter exists in the water. Since a large percentage of NL communities generally use surface pond water as their drinking-water source, DBPs are monitored regularly by the Water Resources Management Division of the Department of Environment and Conservation (WRMD-DOEC).

Surface water, such as rivers, ponds, and lakes, is often surrounded by bushes and exposed without any protection. When it rains, these ponds can be contaminated by sediments and organic matter in the soil; hence, the water in these rivers, ponds, and lakes is generally considered to contain more organic matter than groundwater. This organic matter is usually considered a major source of DBPs (Kar, 2000). According to the 2013 annual report (DOEC, 2014a) of the Government of NL's Department of Environment and Conservation (DOEC), NOM concentration in the province's drinking water was as high as 11 mg/L. Additionally, mostly water reaches the supply system through the distribution pipes, is stored in water supply tanks, and distributed to the household units. It is important to estimate the duration that the water stays in these distribution pipes before it reaches consumers (Baribeau et al., 2004; Dion-fortier et al., 2009). Research has shown an increase in THM concentration with time in storage tanks and pipe systems (Weinberg et al., 2006; Dion-fortier et al., 2009). As the water remains in the pipelines in off hours, that is, midnight to morning, this allows extra reaction time between

the free NOM and free residual chlorine, causing an increased concentration of DBPs in the water-supply system (Ahmad, 2013; Sadiq and Rodriguez, 2004).

1.2 Health impacts of long-term exposure

Of all possible DBPs, chlorinated and brominated (e.g., chloroform and bromoform) DBPs are considered the major sources of risk to human health. Some compounds, such as THMs and HAAs, are harmful to human health and have been shown to be carcinogenic, mutagenic, and/or teratogenic in animal studies (Clifford et al., 1999); their elevated levels in drinking water will have long-term health effects on consumers.

Boiling tap water significantly reduces THMs. As the boiling time increases, THM concentration is reduced by almost 90%, but boiling does not significantly affect the removal of HAAs. After boiling water for 1, 2, and 5 minutes, the total THMs can be reduced by 75%, 84%, and 97% respectively, compared to total HAAs, which are reduced only by 17%, 22%, and 23% respectively (Kranser et al., 2005).

1.3 Small community challenges in drinking-water treatment

The sparse geographical distribution of small communities in NL combined with community populations of generally fewer than 1,000 people does not lend itself to easy solutions to drinking-water-quality issues. These communities simply do not have access to the same resources (human or financial) as larger communities do. They have a lower median household income and fewer businesses and industry; this results in a lower tax base. Populations in most small communities in Newfoundland and Labrador are aging and declining in size. These factors make it more difficult for them to afford the infrastructure and qualified operators necessary to provide high-quality drinking water to their populations if water-quality issues arise (DOEC, 2009).

Small communities with very high THM and HAA levels in their drinking water do not have proper water treatment in place and insufficient protection for their water sources. Water treatment facilities in these communities are equipped only with a pre-screen, such as a grate, to remove large pieces of matter, supplemented by a chlorine disinfection system, with no

coagulation as pre-treatment or any kind of filtration for NOM removal. Pouch Cove does not have a water treatment plant and it relies solely on the chlorination of intake water and pH adjustments. Currently, chlorine disinfection is a preferred and economical choice for small communities like Pouch Cove.

1.4 Application of activated carbon for the removal of natural organic matter

The best available technologies to reduce NOM as identified by USEPA (2003) are enhanced coagulation and activated carbon (AC). The effectiveness of these methods, however, depends on pH, alkalinity, the dosage of coagulant and/or AC, and humic and non-humic NOM fractions in the water (Uyak et al., 2006). Coagulation effectively removes humic substances and high molecular organic matter; carbon adsorption removes non-humic substances with low molecular weight, colour, and taste and odour-causing substances (Amy et al., 1992). AC, due to its high affinity to remove organic matter even at low concentrations, has been used in many water-treatment plants (Graese et al., 1987; Black et al., 1996; Babi et al., 2007). The Cincinnati Water Works, one of the world's largest granular activated carbon (GAC) filter systems for removing TOC, has an on-site GAC regeneration facility (Rodriguez-Reinoso, 1997). A thermal reactivation study of spent GAC from this plant shows that the reactivated GAC has a comparable removal efficiency of TOC even after six cycles of use (Moore et al., 2001).

Although some of the commercially available AC, made from petroleum coke, bituminous and lignite coal, wood products, and coconut shells, show a high potential for removing DBPs and its precursors, due to the high cost of the raw materials the AC manufactured from these materials is not economical and affordable in small communities (Streat et al., 1995). This has led to the need to find a low-cost adsorbent by extracting unburned carbon from oily fly ash (OFA). This waste is abundant, with millions of tons being generated annually from the burning of heavy fuel oil (HFO). Only a small portion of OFA is reused for productive purposes; most is dumped into landfills (Shackelford, 2000). As reported in the literature, about 3 kilograms of ash residue is generated by burning 1000 liters of HFO (Tsai and Tsai, 1997); approximately 90% of this ash passes through the flue gas stream, which is collected by air pollution control devices such as electrostatic precipitators (ESP) or cyclones (Hsieh and Tsai, 2003). On average, 50-60 tons of

OFA is generated daily from a 2300 MW HFO-operated power plant (Wayne and Turner, 2009; Hsieh and Tsai, 2003).

Millions of tons of OFA are generated yearly worldwide but very little is reused. The current practice, dumping OFA into landfills or waste containment facilities, causes potential environmental hazards (Fernandez et al., 2003; Mohapatra and Rao, 2001; Shackelford, 2000). Due to its low density (0.25 g/cm^3) and fine particulate size (average diameter 40-60 μm), OFA tends to travel long distances and can adversely impact plants, animals, and human health. Extracting carbon from OFA will not only minimize hazards but it will also significantly reduce its original volume.

Mofarrah et al. (2012) investigated the beneficial uses of OFA as a stabilizer or fill material by mixing it with cement. Since OFA contains 70-85% unburned carbon, it has a high potential as an adsorbent. Recent studies show that OFA can remove phenols, methylene blue, lead, and chromium VI from wastewater streams by up to 92% (Mofarrah et al. 2013, Mofarrah et al., 2014, Mofarrah, 2014). OFA also has a high affinity for removing TOC from intake water sources in Pouch Cove and other communities with high levels of THMs and HAAs in their drinking-water supply systems (Husain et al., 2012).

The extracted carbon from OFA has shown promising results in reducing TOCs from the water-supply systems of two communities (i.e., Pouch Cove and Torbay) near St. John's (Ahmad, 2013). In the Pouch Cove system, the TOC level of 13.64 mg/l was reduced by more than 70% by the clean carbon. There was also a considerable improvement in turbidity reduction in the filtered water. Although these results are promising, they are based on only a few non-activated samples. Through an activation process, the surface area and pore size will be increased considerably. In this way, AC could be generated.

AC has been applied as a filtration material in water-supply systems for many years. It has effectively removed toxic chemicals, gases, and unwanted contaminants from water sources. The adsorption ability of AC varies with its porous structure. A good AC should have high porosity, increased surface area, suitable pore distribution, and high mechanical strength. In previous

studies, AC has mostly been used to remove NOM, TOC, DOC, taste, odour, micro pollutants, and heavy metals (Kim, 2009).

1.5 Objective and scope of work

The main objective of this study was to assess the performance of adsorbents to be introduced as a passive carbon barrier in small water-supply systems to remove NOM from intake water before chlorination. A carbon barrier was made from extracted unburned carbon from OFA. Past studies show that it is an excellent adsorbent for removing colour and organic matter (Ahmad, 2013; Mofarrah and Husain, 2012; Mofarrah et al., 2013a & b). The passive nature of this barrier makes it easy to operate and the extremely low cost makes the water system affordable for small communities.

This study focuses mainly on THM and HAA DBPs, as applied to the Pouch Cove drinking-water system. The preliminary study showed that the TOC level in the Pouch Cove water is relatively high, 9-12 mg/l in the intake water source, and, as a result, the THMs and HAAs are relatively high (Ahmad, 2013). This study, therefore, has the following objectives:

- Improve the adsorbent through different activation process;
- Assess TOC reduction with changing environmental and hydrological conditions;
- Study the formation potential of THMs and HAAs in this system; and
- Optimize the design parameters of the filtration technology for a pilot scale study.

The findings of this study will help in selecting and developing a simple and affordable filtration technology for rural communities in the province where chlorination is used as the main disinfectant.

2 Characterization of Carbon

Since the carbon used for this research is mainly extracted from OFA, the raw material was characterized to assess the impurities and their removal efficiency by different methods. The extracted carbon of acceptable quality was later activated. The section briefly covers the characterization and activation of OFA.

2.1 Methodology

The physical and chemical characterization of raw materials and extracted carbon is briefly discussed in the following sections.

2.1.1 pH

A pH meter was used to test the pH values of the OFA samples following the ASTM method. Four grams of OFA sample was added to 50 ml boiling deionized water and kept boiling on the heating plate for 4 minutes; the sample was then cooled to the ambient temperature.

2.1.2 Moisture content

Moisture content was determined by following the ASTM method. A crucible was placed in a muffle furnace at 650°C for 1 hour, then cooled in a desiccator, and the crucible weighed and the weight recorded. Weigh 2 ± 0.1 g of OFA sample in the crucible and place in a conventional oven at $110 \pm 5^\circ\text{C}$ for overnight. Weigh the crucible and sample together until there is no changes of weight. Then the moisture content can be calculated as

$$M\% = \frac{W_{raw} - W_{dry}}{W_{raw}} \times 100\%$$

in which,

M%: moisture content in w/w%

W_{raw} : the weight of raw sample

W_{dry} : the weight of the sample after drying

2.1.3 Ash content

The OFA sample was first dried at $110 \pm 5^\circ\text{C}$ in a conventional oven to remove the moisture. A crucible was burned in a muffle furnace at 650°C for 1 hour, cooled to the ambient temperature

in a desiccator, and then weighed. The dried sample was then weighed and transferred to a crucible and placed in a muffle furnace at 650°C for 16 hours. The ash content can be calculated as

$$M\% = \frac{W_{dry} - W_{ash}}{W_{dry}} \times 100\%$$

in which,

M%: ash content in w/w%

W_{dry} : the weight of dried sample

W_{ash} : the weight of ash after burning

2.1.4 Density

The OFA sample was weighed (about 5 g), transferred to a 25 ml cylinder, and the volume recorded. Knock the cylinder lightly on the table surface to make the OFA sample firm and without any space. Calculate the true density of sample by the following relationship:

$$\rho = \frac{w}{v_{firm}}$$

Where ρ = density, w = weight of the sample, , and v_{firm} =volume of firm sample.

2.1.5 Metal content

The concentration of trace and major metals was analyzed by an Inductively Coupled Plasma – Mass Spectrometer (ICP-MS).

2.1.6 SEM analysis

Surface morphology and point elemental analysis was analyzed by scanning electron microscopy (SEM) (Phenom Pro). A sticky pad was placed on a pin and a thin layer of OFA sample was spread on the pad and homogenized by spraying compressed air to remove additional layers of sample. Then the pin is transferred to the sample holder, which is inserted into the instrument for analysis.

2.1.7 BET surface area and pore volume

The BET surface area and porosity of OFA samples were measured by N₂ adsorption at 77K using an automated adsorption apparatus BEL SOPR-MAX, BEL Japan Inc. The surface area

(m²/g) was measured from the adsorption isotherm by the Brunauer, Emmett and Teller (BET) equation (Equations 3-6 to 3-10), using the relative pressure range of 0.05-0.35, considering that the area of the N₂ molecule is 0.162 nm² at 77K (Rodriguez-Reinoso, 1997). The total pore volume, V_T, was obtained from the N₂ adsorption isotherm at p/p₀ = 0.99.

$$\frac{1}{v\left(\frac{P_o}{P}-1\right)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{p_o}\right) \quad (2-1)$$

$$v_m = \frac{1}{S+I} \quad (2-2)$$

$$c = 1 + \frac{S}{I} \quad (2-3)$$

$$SA_{BET} = \frac{(v_m NA_{(N)})}{v} \quad (2-4)$$

$$S_{BET} = \frac{SA_{BET}}{a} \quad (2-5)$$

where, v = volume of adsorbed N₂ gas at standard temperature and pressure (STP), P and P_0 are the equilibrium and saturation pressures of the adsorbate, v_m = volume of gas (STP) required to form one monolayer, c = BET constant related to energy of adsorption, N = Avogadro's number (6.02E+23), $A_{(N)}$ = cross section of N₂ (0.162 nm²), SA_{BET} = total BET surface area (m²), S_{BET} = specific BET surface area (m²/g), a = mass of adsorbent (in g). The BET surface was calculated from the BET equation 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 slope (S) and the y-intercept (I) of the plot were used to calculate v_m and the BET constant c .

One important index of the capability of physical absorption is the specific surface area. A higher surface area indicates better adsorption capability. A nitrogen (N_2) adsorption isotherm curve is one of the most commonly used methods for surface area analysis. Industrially, an iodine test is the general method to determine the surface area of AC. A methylene blue test is utilized to analyze the mesopore volume of AC. In this study, a TriStar II Plus micrometric analyzer was utilized to analyze the surface area and the pore distribution of the OFA samples. These samples were first heated at 120°C for 2 hours for the degassing procedure. Then 500 mg of sample were weighed and analyzed under different pressure levels.

2.2 Results and discussion

2.2.1 Characterization

Two samples of OFA, labelled OFA-1 and OFA-2, were obtained from a power plant that burned HFO and crude oil. These samples were obtained from two different stages of power plant development (OFA-1 from an old unit; OFA-2 from a newly installed unit) with different combustion efficiency and particle collection devices installed. The results of the characterization of these samples are summarized in Table 2-1. Both OFA samples are highly acidic and have entirely different pH values than the coal fly ash (CFA) and wood ash (WA). Generally, the pH values of CFA and WA is from 8 to 12, which is highly alkaline; OFA-1 and OFA-2 have pH values of 2.3 and 1.9 respectively, which is acidic. The direct disposal of OFA into the landfill could possibly cause metal leaching into the soil and further contaminate the groundwater. The moisture content in these two OFA samples is relatively low: 1.4% and 1.8%. The ash content of OFA-2 is much higher (21.65%) than that of OFA-1 (0.91%). The unburned carbon in OFA-1 is about 90%; in OFA-2 it is only 55% by weight. The high ash content is an indication of a high concentration of heavy metals and other impurities (see Table 2-2): the metal content in OFA-2 is much higher than in OFA-1. The concentration of vanadium (V) in OFA-2 is 20 times higher than in OFA-1: 17,085 mg/kg or 1.71% by weight, which is higher than in the ores being processed for V recovery. If an ore has 0.5% or more V by weight, it is considered to be economical to process and recover (Kerr, 2013). A high concentration of Ni is also found in OFA-2. The British Geological Survey illustrates that if Ni in the ore is 0.2% to 3% it is economical to process (Survey, 2008). Since the Ni level in OFA-2 is 8182 mg/kg, which is equivalent to 0.8% by weight, it is economical to recover Ni from the OFA-2 samples.

Table 2-1 Characterization of OFA

	pH	Moisture content (%)	Ash content (%)	Density (g/cm ³)	Mean particle size (μm)	Total carbon content (%)
OFA-1	2.3	1.4	0.91	0.31	108	90
OFA-2	1.9	1.98	21.65	0.35	135	55

Table 2-2 Trace and heavy metals of OFA-1 and OFA-2

Sample	OFA-1	OFA-2
Unit	mg/Kg	
Mg	2,125	15,266
Ca	964	2,418
V	717	17,085
Ni	417	8,182
Fe	795	6,742
S	10,147	55,015
Cr	5	33
Al	542	2,085

X-ray Diffraction Analysis

The X-ray Diffraction (XRD) results are shown in Figure 2-1 and 3.3. Due to the high component of carbon, a huge graphite peak can be found at $2\theta=26^\circ$ of all the XRD patterns of OFA samples. XRD patterns of OFA-2 indicate that there is no difference in the crystal phases but there are some differences of intensity. The highest intensity of graphite was obtained from acid-recovered carbon; the lowest was from the raw sample. This could be because acid leaching and crushing can break the metal carbon bond.

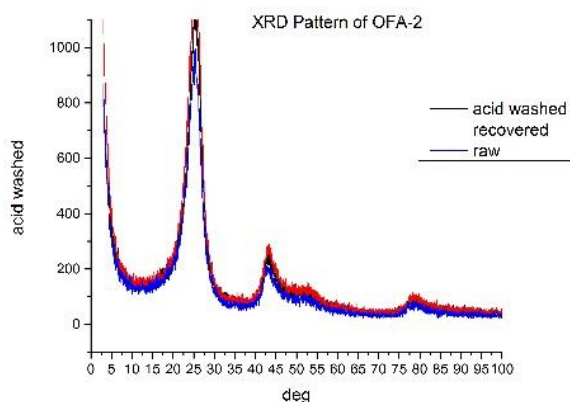


Figure 2-1 XRD pattern of OFA-2

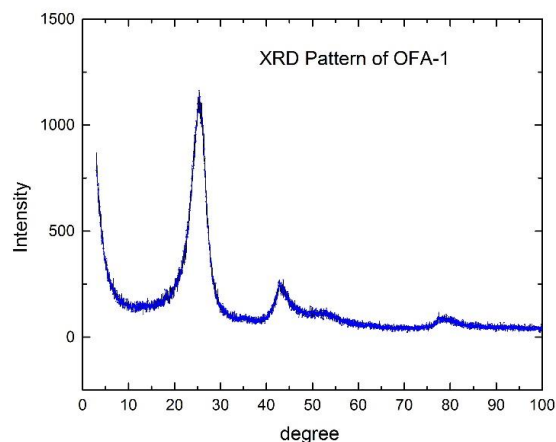


Figure 2-2 XRD pattern of OFA-1

2.2.2 Surface area

Raw, acid-washed, and activated samples were analyzed for BET surface area (Brunauer, Emmett, and Teller, 1938); the results are listed in Table 2-3. Due to high impurities, the surface area of the raw material is relatively low ($2 \text{ m}^2/\text{g}$). After acid leaching, the surface area increased to $12 \text{ m}^2/\text{g}$; after physical activation, it increased to only $20 \text{ m}^2/\text{g}$. Although the OFA samples after activation have 10-fold increase in surface area relative to the raw materials, but compared with commercial AC, which usually has a surface area in the range of 800 to $1000 \text{ m}^2/\text{g}$, the surface area of activated OFA is still very low.

The results of pore volume and pore size indicated that none of the OFA samples has

micropores. This could be due to the horizontal fixed heating tube used for OFA activation. As the OFA placed in this tube cannot be rotated, there is not enough contact area for the OFA samples. Only the upper layer is in contact with the CO₂; Ammonia hydroxide (NH₄OH) and sodium hydroxide (NaOH) were utilized as chemical activation reagents. The results show that there is no improvement of surface area with the NH₄OH-modified OFA: from 12 m²/g to 13 m²/g. Similarly, the NaOH-aided physical activation did not improve the surface area, but morphological differences can be detected by SEM analysis (Figure 2-1).

Table 2-3 BET surface area of OFA-2 and crushed OFA-1

Sample	BET surface area (m ² /g)	Pore volume cm ³ /g	
		Micro pores	
Raw	2	ND	
Acid washed	12	ND	
Activated	20	ND	
Crushed activated	17	ND	
Ammonia modified	13	ND	

2.2.3 SEM analysis

Figure 2-3 (a-d) show the SEM images of the OFA-1 and OFA-2 samples. Figure 2-3a demonstrates the microstructure morphology in the raw OFA-1; Figure 2-3b shows the microstructures in the OFA-2 sample. Although a similar type of sponge structure was found in both the OFA-1 and the OFA-2 samples, large amounts of metal oxides and sulfur were detected on the surface of the OFA-2 sample. This finding is consistent with the metal concentration analysis discussed earlier.

Figure 2-3 (c, d) show the microstructure of the AC from OFA-2 by NaOH and physical activation respectively. In the NaOH-activated OFA-2 samples, some metal oxides and some free metal oxides are still attached to the particle surface. Mesopores and macropores were developed after activation by NaOH. Metal oxides and free oxides can rarely be found in the physical activated sample and more carbon was burned off. The pore size in the physical activation

sample is larger than in the sample that underwent chemical activation by NaOH.

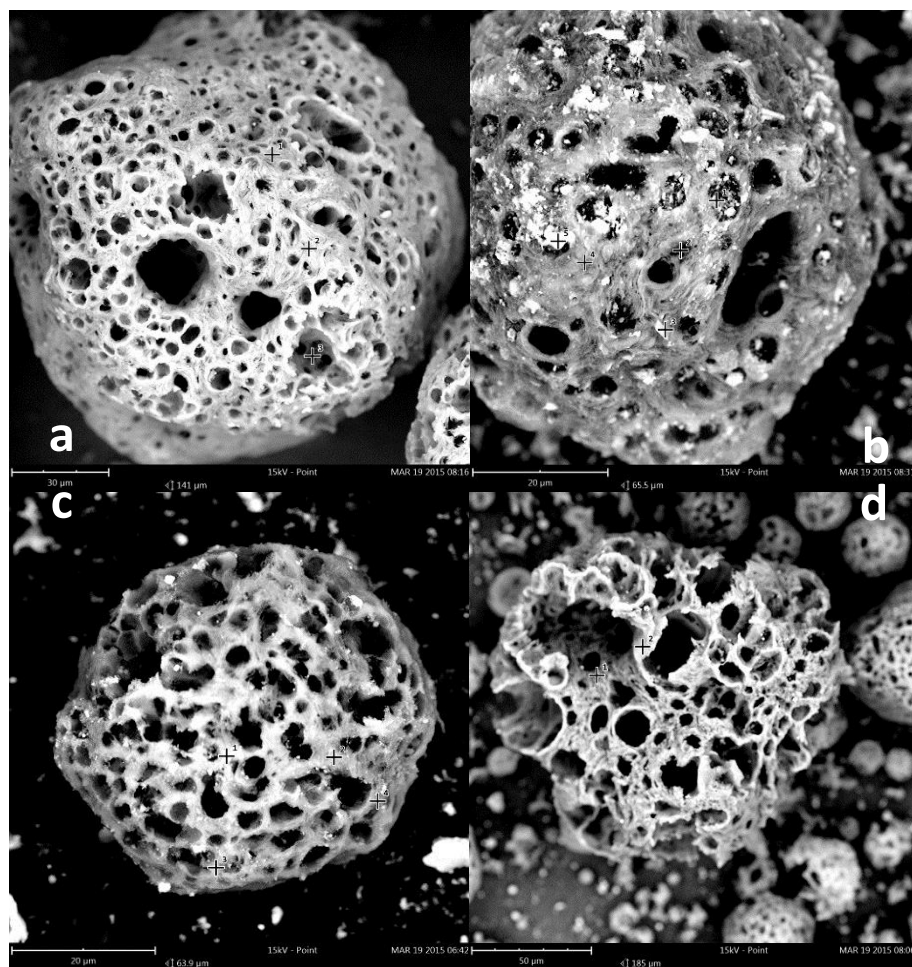


Figure 2-3 SEM analysis of OFA samples (a) Raw OFA-1; (b) Raw OFA-2; (c) AC-NaOH; and (d) AC-Physical activation

2.3 Economic carbon recovery by recycling acid solutions

Carbon recovery technology varies due to the different characteristics of each OFA sample. CFA has a high pH, high sulfate (SO_4^{2-}) and calcium (Ca), and extremely fine particle sizes. OFA samples are highly acidic, and almost no silicon (Si) exists in the matrices. The effective treatment methods for extracting carbon from OFA samples are acid leaching, washing with hot water, and NaOH leaching. Acid leaching will equally dissolve most of the metals into solution; NaOH will be more specific for certain metals, such as molybdenum (Mo) and V. Because of the low pH values of the OFA samples, adding fresh water can also help in leaching metals from them. Single-stage acid washing was applied in this study.

Ten grams of OFA sample were weighed and transferred to a 500 ml beaker, 60 ml of 1.5 N H_2SO_4 was added to the beaker, and then the beaker was placed on a hot plate for 1 to 4 hours to leach the metals. Acid recycling was applied to perform a cost-effective metal leaching procedure. Parallel experiments were run to compare both the recycling performance of OFA-1 and OFA-2. Two groups of experiments were performed under the same conditions. One group of samples was covered by watch glasses; the other group was connected to a reflux condenser tube with anhydrous calcium chloride (CaCl_2) to prevent acid evaporation. Two samples, each 10 g were placed in a 500 ml glass beakers, and mixed with 60 ml 1.5N H_2SO_4 at 80°C and stirred on a hot plate with a magnetic stirrer. Once sample was stirred for 1 while other for 4 hours. After filtration, the acid solutions were measured in a 100 ml cylinder and the remaining volumes recorded. The collected acid was reused for fresh sample leaching with fresh acid added to make up the total acid volume to 60 ml. Residual acid volumes were recorded every time. OFA samples were washed with 500 ml of deionized water to remove the acid and impurities. The cycles were repeated for five times to leach OFA-1 and 11 times for OFA-2.

Figures 2-5 and 2-6 compare the results of reused acid on OFA-1 leaching times of 1 and 4 hours Ni, V, and Zn accumulate in the acid solution, metal removal rate is relatively stable, and after three reuses of acid, longer leaching time results in a better leaching. The removal rate of V ranged from 83.3% to 93.2%; the removal rate of Ni reached 75% to 81.5%. The highest removal rates occurred with 4 hour leaching trials.

Figure 2-6 shows the recycling of acid and fresh water in the leaching of the OFA-2 sample. The highest V removal rate of 91.7% occurred in the first washing. From the second to the tenth recycling of the same water, the concentration of V was very stable, around 2200 ppm. Fresh acid leaching of Ni reached 76.6% removal, remaining stable at 75% from the second to the tenth recycling. The preliminary analysis shows that the recycling and reuse of acid with supplementary fresh acid can achieve results close to those with fresh acid. Due to its high initial concentration and high leachability of V and Ni and relatively low carbon content, OFA-2 could be a valuable resource for metal recovery.

Ognyanova et al. (2009) studied metal extraction from spent catalysts. Besides roasting samples to recover metal oxides, the optimum leaching condition was confirmed for metal extraction from complex matrices of metals. The optimum condition for V extraction was 0.6 M H₂SO₄ in the presence of oxygen for 6 hours. Ni can be extracted by 1 M H₂SO₄ for 30 minutes. Statistical analysis shows that H₂SO₄ concentration will not affect the leaching efficiency, but contact time has a positive effect on V leaching and very little effect on Ni leaching. High acid to solid ratio may have a negative effect on metal leaching; however, more in-depth study needs to be conducted (Ognyanova et al., 2009).

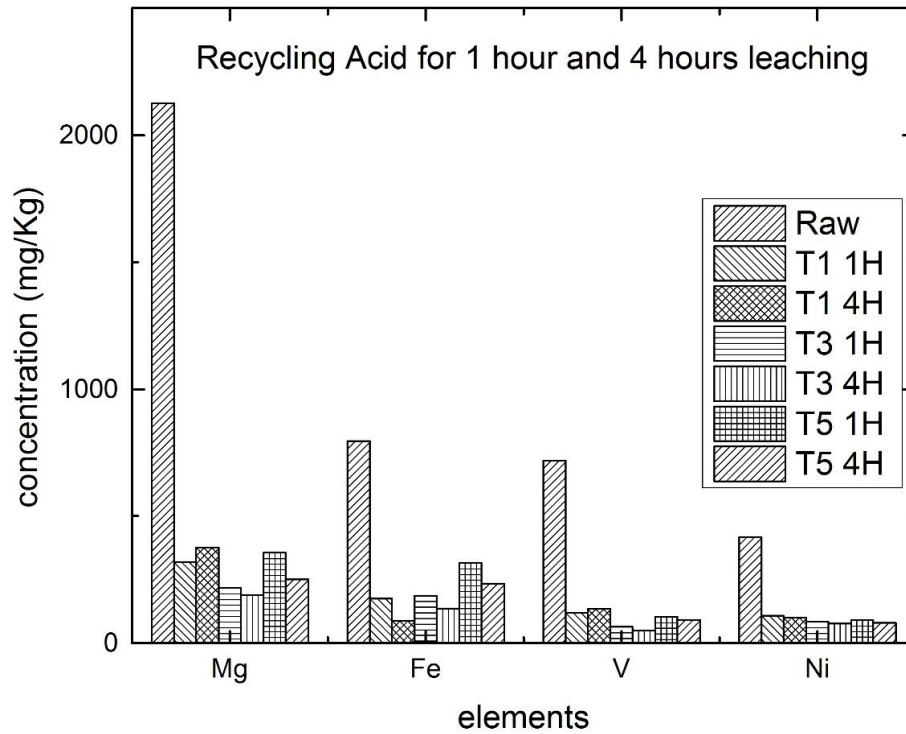


Figure 2-4 1 hour and 4 hour leaching efficiency of OFA-1

Where,

Raw is the concentration of metals in OFA-1 as received; T1 1H and T1 4H are first leaching with fresh acid leaching for 1 and 4 hours; T3 1H and T3 4H are the third leaching using recycled acid with supplementary fresh acid; T5 1H and T5 4H are the fifth leaching using recycled acid with the supplement of fresh acid.

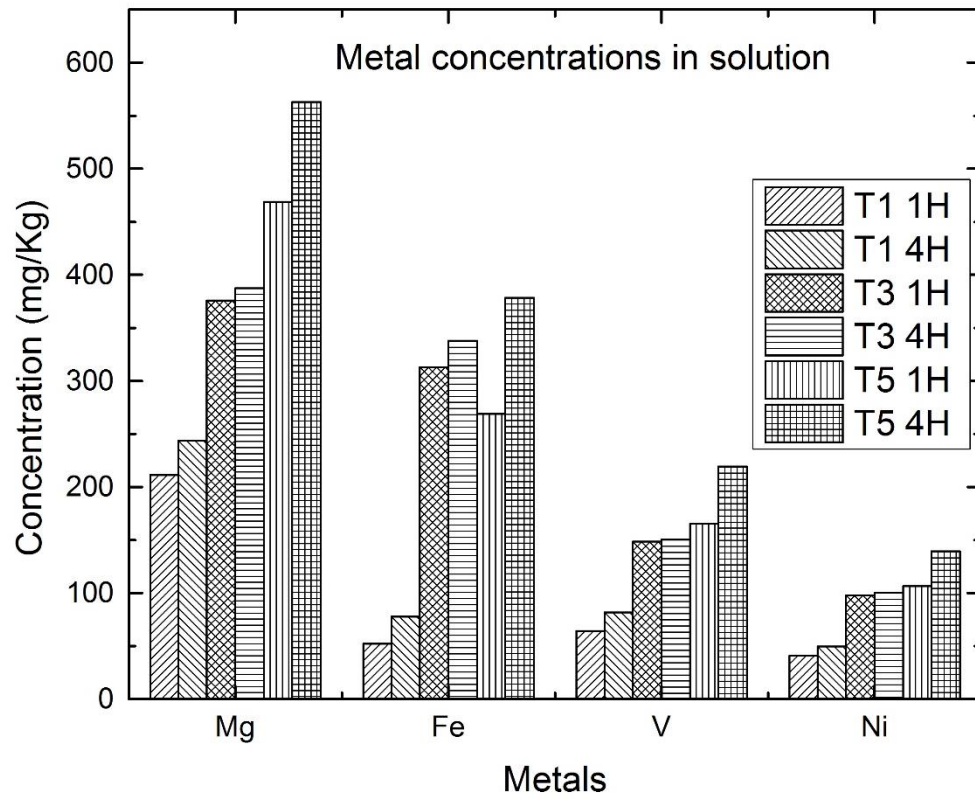


Figure 2-5 Leachable metals in acid of OFA-1

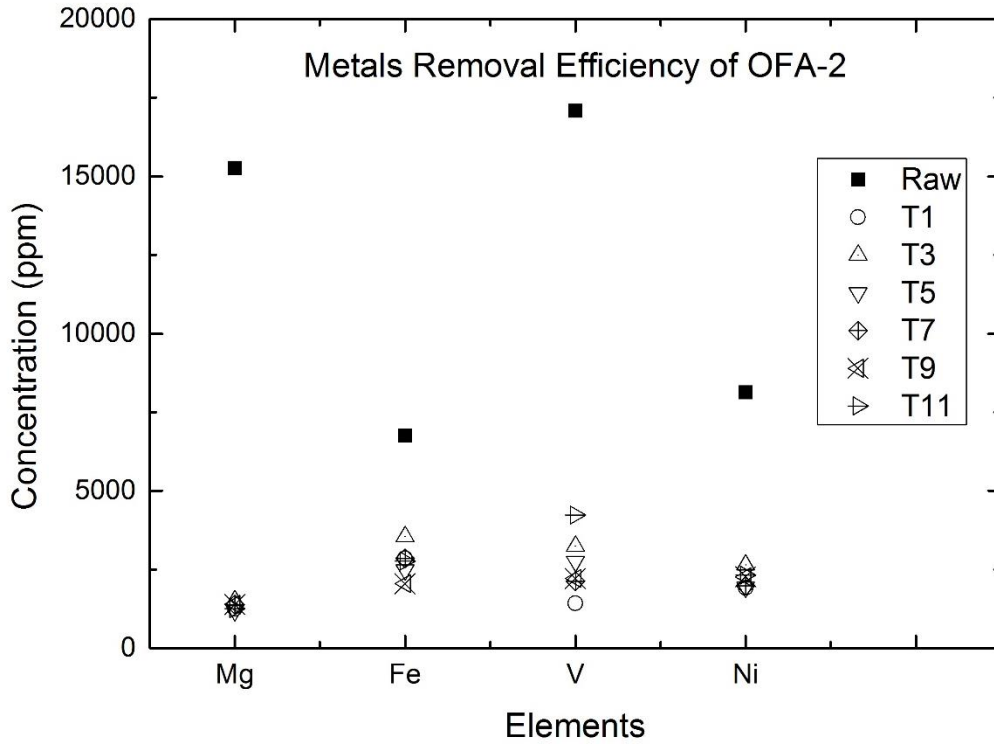


Figure 2-6 Metal leaching efficiency of OFA-2

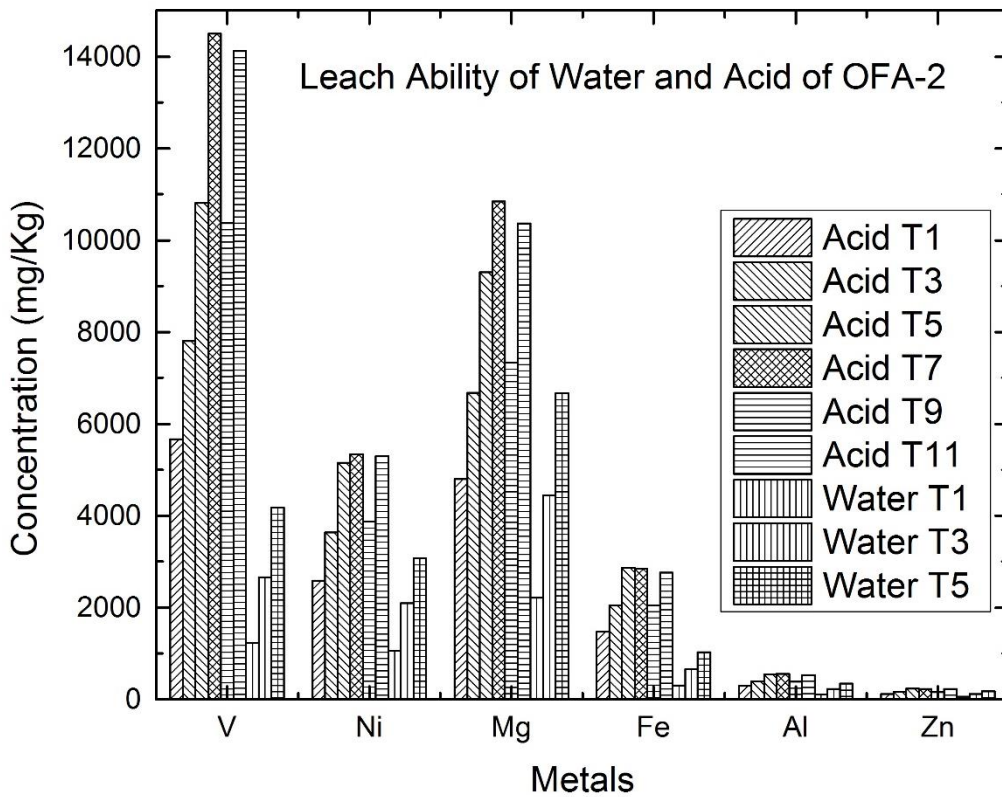


Figure 2-7 Metal leachability of water and acid of OFA-2

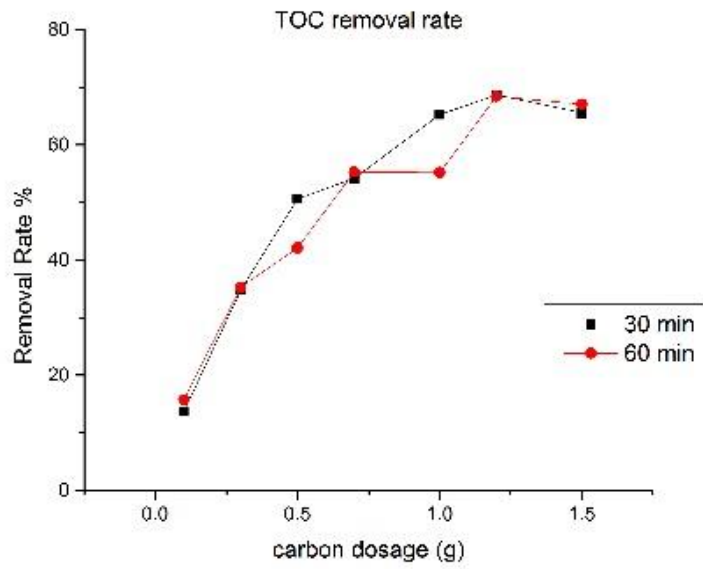
3 Batch Test and DBP Formation Potential

3.1 Batch test

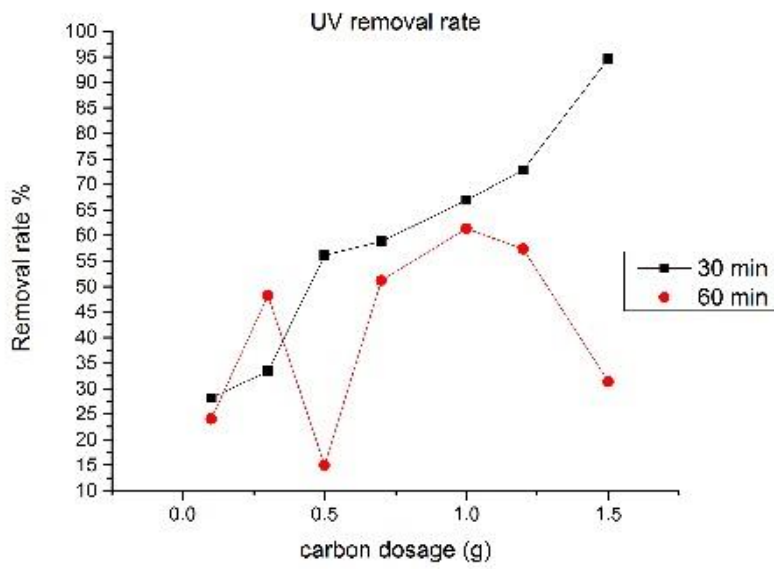
A batch test was conducted to develop the relationship between TOC removal rate and changes in UV_{254} values with parameters such as contact time and carbon dosage. For this, 100 ml of the water sample was added to a 250 conical flask; carbon dosages of 100, 300, 500, 700, 1000, 1200, and 1500 mg were added to the sample water. The flasks were placed on a mechanical shaker at 120 rpm for 30, 60, 120, 240, 360, and 1440 minutes to mix the carbon and water. After shaking, all samples were filtered by 0.45 μm filter paper to remove the fine particles. Filtered water samples were analyzed by a TOC analyzer and UV-Vis (HP 8452 UV-Vis analyzer). The results of the batch tests are listed in Table 3-1. To study the removal efficiency of TOC and UV_{254} with the contact times, these values were plotted against carbon dosages as shown in Figure 3-1.

Table 3-1 Result of batch test

Carbon dosage (mg)	Contact time											
	minutes											
	30		60		120		240		360		1440	
	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC	UV_{254}	TOC
0	0.32	8.895										
100	0.23	7.68	0.24	7.497	0.22	7.217	0.24	7.443	0.22	7.463	0.22	7.621
300	0.21	5.803	0.17	5.76	0.15	5.352						
500	0.14	4.394	0.27	5.152								
700	0.13	4.076	0.16	3.977								
1000	0.11	3.092	0.12	3.988								
1200	0.087	2.788	0.14	2.811								
1500	0.017	3.066	0.22	2.933								

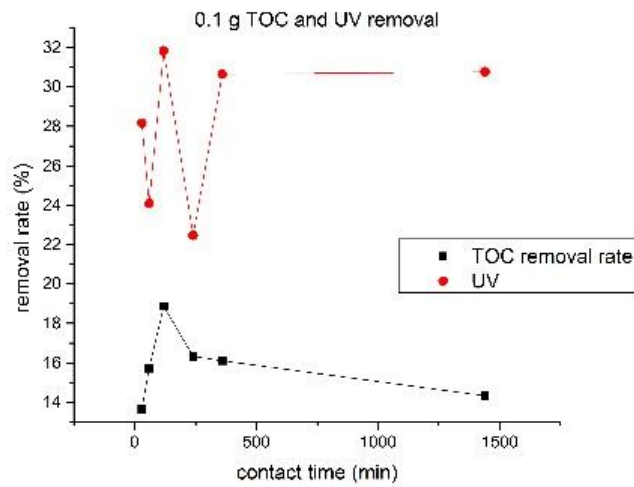


(a)

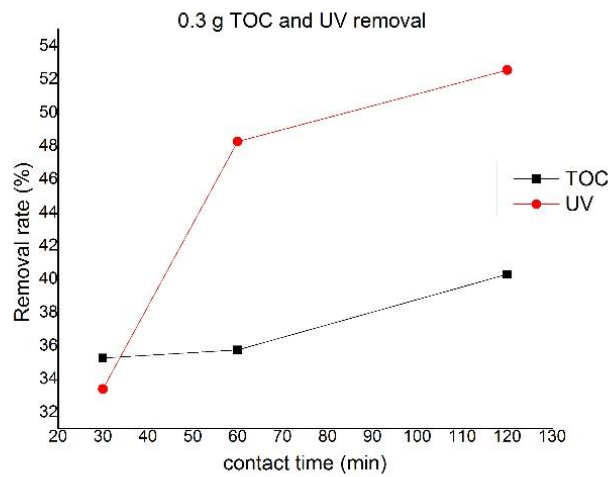


(b)

Figure 3-1 TOC and UV removal by carbon dosage



(a)



(b)

Figure 3-2 OFA-2AC TOC and UV adsorption by time

The TOC removal plots show that the removal rate with a carbon dosage of OFA-2 from 100 mg to 1200 mg and 30- and 60-minute contact times, there is an increasing tendency of the removal rate, while at a 1500 mg dosage point, an inflection point appeared, and both the 30- and 60-minute adsorption rates are lower than for the 1200 mg dosage. When 1200 mg of OFA-2AC were added to raw water, it can achieve maximum absorbance within 30 minutes. When 100 mg of OFA-2 AC was mixed with the raw water, the UV₂₅₄ adsorption rate from 30 minutes to 24 hours ranged from 0.22 to 0.24, which indicates that 100 mg of OFA-2AC can reach saturation within 30 minutes. No matter how long it mixed with the water, no more organic matter can be removed. Similar to UV adsorption, the TOC removal rate using 100 mg of OFA-2AC for

different contact times ranged from 13.66% to 18.86%. The dosage of 300 mg of OFA-2AC showed the highest, 40% removal of TOC at 120 minutes and 52% removal of UV₂₅₄ at the same time period. Figure 3-1 shows that the highest TOC removal rate can be achieved at a 30-minute contact time by using 1200 mg of OFA-2AC.

3.2 DBP formation potential

Different dosages of chlorine were applied to the filtered water as disinfectant and after 1-hour contact time with residual chlorine, the HAAs and THMs were analyzed in the chlorinated water.

The results are listed in

Table 3-2. As shown in the table, with the same amount of TOC different concentrations of chlorine will significantly affect THM formation. As listed in

Table 3-2, 100 mg of AC was mixed with the raw water and chlorinated at different chlorine doses. The TTHM concentration of the less chlorinated sample was only one-third that of the high-level chlorination. The results show that, after chlorination, raw water had the highest TTHMs and THAAs. Compared with the tap water collected from the Pouch Cove community, both concentrations are very close. Variation may be due to the seasonal change and different collection times (Ahmad, 2013). A comparative assessment was conducted with different levels of free chlorine dosage added to the filtered water, as listed in

Table 3-2 and Table 3-3. The results show a relatively stable concentration of BDCM and DBCM irrespective of the dosage of free chlorine added. The formation of chloroform, generally considered the main compound in the THM group, is significantly affected by chlorine dosage. The HAA formation potential listed in Table 3-3 indicates that raw water has a high potential to form high levels of TCAA.

Table 3-2 THMs after different chlorination dosages

Water sample	Free chlorine	Chloroform µg/L	BDCM µg/L	DBCM µg/L	Bromoform µg/L	TTHM µg/L
Filtered water	0.04	95	12	7	ND	114
Filtered water	1.35	300	13	7	ND	320
Raw water	7	330	11	7	ND	348
Tap water ^a		219	27.5	19.9	22.3	288.7

a. Source: Ahmad (2013)

Table 3-3 HAAs after different chlorination dosages

	Free chlorine	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA
	mg/L	Unit: µg/L									
Tap water*		0	0	163.7	7.1	233.9	0	25.3	0	20.5	450.5
Raw water	0.05	0	0	346.9	108.3	18.2	0	0	0	0	473.4
Filtered water	0.15	0	0	73.4	8.6	8.2	0	0	0	0	90.2
Filtered water	1.35	0	0	139.3	11.3	9.7	0	0	0	0	160.3

a. Source: Ahmad (2013)

4 Optimization of TOC Removal Condition

4.1 Design of the experiment

A widespread principle of experiment design is to only change one factor and keep all other factors fixed at one time: this is also known as the One Fact at a Time (OFAT) approach. However, use of this approach will be very time consuming and cost intensive for projects with a limited budget and limited study time.

4.1.1 Determination of factor levels

Through a literature review, five main parameter effects, including pH (A), temperature (B), carbon dosage (C), sample volume (D), and contact time (E), were selected for this study. Several runs of pre-tests were performed to determine the range of factors. Since temperature is difficult to change, a two-level factorial split plot design was chosen to model the experiment. The design is listed in Table 4-1.

Table 4-1 Factors and levels of the experiment

Factors	Unit	Low level in actual value	High level in actual level
A: pH		2	8
B: Temperature	°C	25	35
C: Carbon dosage	mg	50	100
D: Sample volume	ml	50	100
E: Contact time	hrs	0.5	4

4.1.2 Material and method

Water samples were collected from the Pouch Cove water system. This pond is used as the source water for local residents of the community. Sample water was immediately transported to the laboratory and refrigerated at 4°C. For pH adjustment, 1N HCl and 1N NaOH were prepared from concentrated HCl and NaOH (Sigma Aldrich, Canada). Modified fly ash was prepared by

acid washing and physical activation at 800°C of the fly ash collected from a local power plant. Samples were dried for 24 hours before use. A mechanical shaker was used for experiments at 25°C and a heating plate with a magnetic stirrer for heating the sample to 35°C and stirring the water sample to adequately mix it with the absorbent. UV_{254} of raw water samples from Pouch Cove intake source analyzed by HP UV-Vis 8453 at 254 nm is 0.365 cm^{-1} .

Modified fly ash samples were mixed with water samples in Erlenmeyer flasks at designed values. The mixed samples were reacted at different temperatures and contact times to determine the removal rate. A heating plate was adjusted to 35-40°C to maintain the sample temperature around 35°C and a shaker was used at room temperature. Treated samples were passed through a 0.45 μm vacuum filtration to remove fine particles and microorganisms before the UV and TOC analysis. UV_{254} was determined at wavelength of 254 nm.

4.2 Results and discussion

Table 4-2 lists all experiment results at different condition combinations.

Table 4-2 Results of the experiment

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Response 1	Response 2
Run	A: Temperature	B: Carbon dosage	C: Water volume	D: pH	E: Contact time	UV	TOC
	°C	mg	mL		hour	cm ⁻¹	ppm
1	35	100	100	8	4	0.336	10.1
2	35	100	50	8	0.5	0.256	10.4
3	35	50	100	2	4	0.139	5.412
4	35	50	50	8	4	0.32	10.96
5	35	50	100	8	0.5	0.411	11.2
6	35	50	50	2	0.5	0.121	5.054
7	35	100	50	2	4	0.07	3.824
8	35	100	100	2	0.5	0.164	5.355
9	35	100	50	2	4	0.07	3.602
10	35	50	100	8	0.5	0.352	12.34
11	35	100	50	8	0.5	0.29	12.33
12	35	100	100	2	0.5	0.137	5.348
13	35	100	100	8	4	0.302	11.44
14	35	50	50	2	0.5	0.127	5.032
15	35	50	100	2	4	0.189	7.357
16	35	50	50	8	4	0.3	12.95
17	25	50	50	2	4	0.116	5.852
18	25	100	50	8	4	0.259	8.23
19	25	50	100	8	4	0.366	10.36
20	25	50	50	8	0.5	0.355	9.81
21	25	100	50	2	0.5	0.06	3.532
22	25	100	100	2	4	0.122	6.19
23	25	50	100	2	0.5	0.134	6.455
24	25	100	100	8	0.5	0.341	9.7
25	25	100	100	8	0.5	0.312	9.69
26	25	100	50	8	4	0.221	11.79
27	25	100	50	2	0.5	0.031	3.522
28	25	50	50	2	4	0.087	5.305
29	25	50	100	2	0.5	0.153	7.015
30	25	50	50	8	0.5	0.296	9.8
31	25	100	100	2	4	0.118	6.064
32	25	50	100	8	4	0.322	9.91

The analysis indicates that carbon dosage, water volume, and pH are significant factors in removing TOC. Another OFAT experiment specifically examined the effect of temperature during the procedure. The results, listed in Table 4-3, indicate that raising the temperature significantly reduces the absorbance efficiency.

Table 4-3 Effect of temperature

Temperature	pH	Carbon dosage	Water volume	Contact time	UV ₂₅₄	TOC
°C		mg	ml	hour	cm ⁻¹	mg/L
25	6.7	100	100	1	0.268	8.474
35	6.7	100	100	1	0.36	11

4.3 Validation of model

Four different conditions were chosen to validate the model. The actual values and predicted 95% confidence intervals (CI) are listed in Table 4-4:

Table 4-4 Validation of the model

Temperature	Carbon dosage	Water volume	pH	Contact time	UV	Predicted
25	60	80	6.5	0.5	0.268	(0.239, 0.339)
30	70	55	4	1	0.135	(0.113, 0.223)
25	80	50	3	1	0.133	(0.073, 0.163)
30	90	60	7	2	0.255	(0.194, 0.304)

The results of the chosen conditions to validate the model indicate that the UV reduction is stable and can fall into the predicted 95% CIs. Most of the validation experiment results are very close to the mean of the predicted points. This model is relatively accurate and can be applied to real experiment prediction. However, in real cases, adjusting the pH to a very low value is not reasonable, but adjusting the carbon dosage and water volume to the optimal condition could achieve the highest UV₂₅₄ and TOC absorbance.

5 CONCLUSIONS AND RECOMMENDATIONS

The following main conclusions are drawn from this research:

- 1) Acid recycling can effectively reduce the cost of extracting clean carbon from OFA.
- 2) Acid leaching and physical activation of an OFA sample has the potential to improve its surface area. At present, 20 m²/g of surface area using physical activation and 13 m²/g surface area using NH₄·OH modified activation is achieved which is very low. It may mainly be due to uneven heat distribution in the horizontal furnace with no rotary tube. A rotary furnace can improve carbon activation by providing better contact and better temperature distribution.
- 3) Chemical activation can develop more mesopores than the acid and physical activation.
- 4) The efficiency of the activated OFA sample to adsorb TOC is relatively low; 1.2 g dosage of carbon reduces a 66% TOC in the raw water. A longer contact time does not affect TOC and UV reduction significantly.
- 5) The optimal condition of TOC and UV reduction is found at a low temperature and low pH; when the temperature is over 35°C, or the pH is greater than 8, no significant reduction in TOC and UV occurs.
- 6) Acid-leached OFA is a better absorbent of TOC and UV than alkaline-modified OFA.

The following recommendations are made from this study:

- 1) More in-depth research is needed on the optimization of carbon recovery and metal extraction.
- 2) Since OFA-2 has a high level metal content, it is recommended to develop an economically feasible leaching and metal recovering process.
- 3) More activation technologies should be studied to improve surface area and micropore development in the extracted clean carbon from OFA.
- 4) A comprehensive leaching test and toxicity study is required for filtered water as an important indicator of a safe technology for drinking water.

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Appendix





Figure 6-1 Water Treatment System of Pouch Cove

Where: a) screen to remove large particles and tree branch; b) chlorination end of the system; c) overview of the underground pipe, pH monitoring