Novel Operation of Granular Activated Carbon Contactors for
Removal of Disinfection Byproducts Precursors

by

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A Dissertation Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy

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ABSTRACT

Granular activated carbon (GAC) is effectively used to remove natural organic matter (NOM) and to assist in the removal of disinfection byproducts (DBPs) and their precursors. However, operation of GAC is cost- and labor-intensive due to frequent media replacement. Optimizing the use of GAC is necessary to ensure treatment efficiency while reducing costs. This dissertation presents four strategies to reduce improve GAC usage while reducing formation of DBPs. The first part of this work adopts Rapid Small Scale Tests (RSSCTs) to evaluate removal of molecular weight fractions of NOM, characterized using size exclusion chromatography (SECDOC). Total trihalomethanes (TTHM), haloacetic acids (HAA5) and haloacetonitriles (HAN) formation were quantified after treatment with GAC. Low MW NOM was removed preferentially in the early bed volumes, up until exhaustion of available adsorption sites. DBP formation potential lowered with DOC removal. Chlorination prior to GAC is investigated in the second part of this work as a strategy to increase removal of NOM and DBP precursors. Results showed lower TTHM formation in the effluent of the GAC treatment when pre-chlorination was adopted, meaning this strategy could help optimize and extend the bed life if GAC filters. The third part of this work investigates in-situ GAC regeneration as an alternative to recover adsorption capacity of field-spent GAC that could potentially offer new modes of operation for water treatment facilities while saving costs with reactivation of spent GAC in an external facility. Field-spent GACs were treated with different oxidant solutions and recovery in adsorption capacity was evaluated for NOM and for two micro pollutants. Recovery of GAC adsorption capacity was not satisfactory for most of conditions evaluated. This indicates that in-situ GAC
regeneration could be more effective when the adsorbates are present at high concentrations. Lastly, this work investigates the impact of low molecular weight polyDADMAC on N-nitrosodimethylamine (NDMA) formation. Water treatment facilities rely on polyDADMAC as a coagulant aid to comply with NOM removal and turbidity requirements. Since polymer-derived NDMA precursors are not removed by GAC, it is essential to optimize the use and synthesis of polyDADMAC to reduce NDMA precursors during water treatment.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td></td>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.1 References</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>IMPACT OF GRANULAR ACTIVATED CARBON ON NATURAL ORGANIC MATTER AND EFFLUENT ORGANIC MATTER MOLECULAR WEIGHT DISTRIBUTION</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2.1 Introduction</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2.2 Material and Methods</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>2.3 Results and Discussion</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>2.4 Conclusions</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>2.5 Figures and Tables</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2.6 References</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>CHLORINATION BEFORE GAC IMPROVES TOTAL TRIHALOMETHANES</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>3.1 Introduction</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>3.2 Material and Methods</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>3.3 Results and Discussion</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>3.4 Conclusions</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>3.5 Figures and Tables</td>
<td>61</td>
</tr>
</tbody>
</table>
### 4 IN-SITU REGENERATION USING IRON NANOPARTICLES AND LIQUID OXIDANTS OF FIELD-SPENT GRANULAR ACTIVATED CARBON

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>80</td>
</tr>
<tr>
<td>4.2 Material and Methods</td>
<td>83</td>
</tr>
<tr>
<td>4.3 Results and Discussion</td>
<td>85</td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>88</td>
</tr>
<tr>
<td>4.5 Figures and Tables</td>
<td>90</td>
</tr>
<tr>
<td>4.6 References</td>
<td>97</td>
</tr>
</tbody>
</table>

### 5 INFLUENCE OF LOW MOLECULAR WEIGHT POLYDADMAC ON NDMA FORMATION

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>100</td>
</tr>
<tr>
<td>5.2 Experimental Approach</td>
<td>107</td>
</tr>
<tr>
<td>5.3 Material and Methods</td>
<td>108</td>
</tr>
<tr>
<td>5.4 Results and Discussion</td>
<td>115</td>
</tr>
<tr>
<td>5.5 Implications for Water Treatment</td>
<td>121</td>
</tr>
<tr>
<td>5.6 Conclusions</td>
<td>122</td>
</tr>
<tr>
<td>5.7 Figures and Tables</td>
<td>123</td>
</tr>
<tr>
<td>5.8 References</td>
<td>133</td>
</tr>
</tbody>
</table>

### 6 SYNTHESIS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Figures</td>
<td>141</td>
</tr>
<tr>
<td>CHAPTER</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>6.2 References</td>
<td>142</td>
</tr>
<tr>
<td>7 CONCLUSIONS AND FUTURE RESEARCH</td>
<td>144</td>
</tr>
<tr>
<td>7.1 Impact of Granular Activated Carbon on Natural Organic Matter and Effluent Organic Matter Molecular Weight Distribution (Chapter 2)</td>
<td>144</td>
</tr>
<tr>
<td>7.2 Chlorination Before GAC Improves Total Trihalomethanes Control (Chapter 3)</td>
<td>145</td>
</tr>
<tr>
<td>7.3 In-situ Regeneration Using Iron Nanoparticles and Liquid Oxidants of Field-spent Granular Activated Carbon (Chapter 4)</td>
<td>146</td>
</tr>
<tr>
<td>7.4 Influence of Low Molecular Weight PolyDADMAC on NDMA Formation (Chapter 5)</td>
<td>147</td>
</tr>
<tr>
<td>7.5 References</td>
<td>149</td>
</tr>
</tbody>
</table>

APPENDIX

A SIMULATED DISTRIBUTION SYSTEM (SDS) TEST PROCEDURE (WRF 4607) 150

B NITROSAMINE FORMATION POTENTIAL: CHLORAMINATION AND SOLID PHASE EXTRACTION PROCEDURE 154
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Design Parameters for the RSSCTs</td>
<td>24</td>
</tr>
<tr>
<td>2.2</td>
<td>Characteristics of the GAC Used in the RSSCTs in this Study</td>
<td>24</td>
</tr>
<tr>
<td>2.3</td>
<td>GAC Influent Water Quality and Summary of the RSSCTs Run</td>
<td>25</td>
</tr>
<tr>
<td>3.1</td>
<td>Prechlorination and Influent Water Conditions of the RSSCTs and Pilot Scale</td>
<td>61</td>
</tr>
<tr>
<td>3.2</td>
<td>Bromine Incorporation Factor for Conditions of the RSSCTs and Pilot Scale</td>
<td>62</td>
</tr>
<tr>
<td>4.1</td>
<td>Loading Conditions Encountered in the Literature to Evaluate In-situ ChemicalRegeneration of GAC</td>
<td>90</td>
</tr>
<tr>
<td>4.2</td>
<td>Regeneration Conditions. (i) Applied Regen 2 and 3 For Different GACs and (ii)Applied All Treatments to the Same GAC</td>
<td>91</td>
</tr>
<tr>
<td>4.3</td>
<td>Characteristics of Micro Pollutants EDB and DBCP</td>
<td>91</td>
</tr>
<tr>
<td>4.4</td>
<td>pH of Regeneration Solutions Used in (ii)</td>
<td>92</td>
</tr>
<tr>
<td>5.1</td>
<td>Summary of FP and UFC Methods Used in this Work</td>
<td>72</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Research Questions Proposed to Guide the Work on GAC</td>
<td>4</td>
</tr>
<tr>
<td>2.1</td>
<td>DOC Breakthrough Curves for Carbon A and B</td>
<td>26</td>
</tr>
<tr>
<td>2.2</td>
<td>UV254 Breakthrough Curves for Carbon A and Carbon B</td>
<td>27</td>
</tr>
<tr>
<td>2.3</td>
<td>DON Breakthrough Curves for Carbon A and Carbon B</td>
<td>28</td>
</tr>
<tr>
<td>2.4</td>
<td>Molecular Weight Distribution for Treated Samples of SW (carbon A)</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Molecular Weight Distribution for the SW Influent and Treated Samples Based</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>on the SECDOC Integration of Peak Areas</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>Apparent Molecular Weight Distribution for samples of 90 SW Treated with</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Carbon A</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>Molecular Weight Distribution for the 90SW Influent and Treated Samples</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>(Carbon A) Based on the SECDOC Integration of Peak Areas</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>Molecular Weight Distribution of Influent and Samples of 90SW Treated with</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Carbon B</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>Molecular Weight Distribution for the 90SW Influent and Treated Samples</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>(Carbon B) Based on the SECDOC Integration of Peak Areas</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>Molecular Weight Distribution of Influent and Samples of WW Treated with</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>carbon B</td>
<td></td>
</tr>
<tr>
<td>2.11</td>
<td>Molecular Weight Distribution for the WW Influent and Treated Samples</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>(Carbon B) Based on the SECDOC Integration Of Peak Areas</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>2.12 - HAN Removal as a Function of DOC Breakthrough for SW, 90SW and SW Treated with Carbon A and 90SW Treated with Carbon B</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>2.13 - TTHM4 Removal as a Function of DOC Breakthrough for SW, 90SW and SW Treated with Carbon A and 90SW Treated with Carbon B</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>2.14 - HAA5 Removal as a Function of DOC Breakthrough for SW, 90SW and SW Treated with Carbon A and 90SW Treated with Carbon B</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>3.1 - DOC Breakthrough Curves for Pre-chlorinated and Non-chlorinated Water Treated With Virgin GAC. DOC₀ = 3 mgC/L</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>3.2 - DOC Breakthrough Curves for Prechlorinated and Non-chlorinated Water Treated with Virgin and Reactivated GAC. DOC₀ = 2.9 mgC/L</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>3.3 - UV254 Breakthrough Curves for Prechlorinated and non-chlorinated Water treated with Virgin GAC. UV254₀ = 0.044</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>3.4 - UV254 Breakthrough Curves for Prechlorinated and non-chlorinated Water Treated with Virgin and Reactivated GAC. UV254₀ = 0.045</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>3.5 Molecular Weight Distribution Based on Integrated Peak Areas For Samples Treated With Virgin GAC, With and Without Prechlorination (Columns B5 and B6)</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>3.6 - TTHM Breakthrough Curves For Prechlorinated SW Treated With Virgin And Reactivated GAC.</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>3.7 - HAA5 Breakthrough Curves For Prechlorinated SW Treated With Virgin And Reactivated GAC.</td>
<td>69</td>
<td></td>
</tr>
</tbody>
</table>
3.8 - TTHM Formation and Speciation After 24h in the Effluent of the RSSCTs Treated With Virgin GAC Under Different Pre-Chlorination Conditions. ............70

3.9 - TTHM Formation and Speciation After 72h In The Effluent of the RSSCTs Treated With Virgin GAC Under Different Pre-Chlorination Conditions. ............71

3.10 - TTHM Formation And Speciation After 24h In The Effluent of the RSSCTs Treated With Virgin and Regenerated GAC Under Different Pre-Chlorination Conditions. ........................................................................................................72

3.11 - TTHM Formation and Speciation After 48h in the Effluent of the RSSCTs Treated With Virgin And Regenerated GAC Under Different Prechlorination Conditions. ..................................................................................................................73

3.12 - TTHM formation (Expressed as TTHM Formed Per DOC Concentration) in the Effluent of the Pilot Scale Columns (Composed Effluent from 3300 to 4700BV).
.......................................................................................................................................................74

4.1 - Experimental Setup Used in the Regeneration Experiments. .................93

4.2 - DOC Remaining Fraction (C/C0) For Adsorptions Tests Using GAC Treated With Regen 2 (Sodium Persulfate). Results Were Plotted Against Concentration of GAC (g/L). ..........................................................................................................................................94

4.3 - DOC Remaining Fraction (C/C0) For Adsorptions Tests Using GAC Treated With Regen 3 (Sodium Percarbonate). Results Were Plotted Against Concentration Of GAC (g/L).........................................................................................................................................95
4.4 - Concentrations of EDB After The Adsorption Test. Results Were Plotted Against Concentration of GAC (g/L). Initial Theoretical Concentration of EDB is 100 μg/L. ................................................................. 96

4.5 - Concentrations of DBCP After the adsorption Test. Results Were Plotted Against Concentration of GAC (g/L). Initial Theoretical Concentration of DBCP is 100 μg/L. ................................................................. 96

5.1 - Chemical Structure of PolyDADMAC Source: [28].......................... 126

5.2 - NDMA Yield of UFC and FP Methods. ............................................. 126

5.3 - NDMAFP of Secondary Effluent Upon SPE Using Cartridges Supplied By UCT and Restek................................................................. 127

5.4 - DOC and TDN Mass Balance For The UF Using 1g/L of Active PolyDADMAC Though 1kDa and 3kDa Membranes. ............................. 127

5.5 - NDMAFP (ngNDMA/L) for the UF Using 1g/L of Active PolyDADMAC Through 1kDa and 3kDa Membranes........................................... 128

5.6 - Reactivity (ngNDMAFP/mgC) of the Different Fractions Of PolyDADMAC After UF Using Membranes With MWCO = 1kDa and 3kDa. ................. 129

5.7 - DOC and TDN Mass Balance For the UF Using 1g/L of Active PolyDADMAC Through 1kDa and 10kDa Membranes................................. 130

5.8 - Reactivity (ngNDMAFP/mgC) of the Different Fractions of polyDADMAC after UF Using Membranes with MWCO = 1kDa and 10kDa................. 131
6.1 - Overarching structure of this dissertation
.................................................................................................................................................. 141
CHAPTER 1
INTRODUCTION

Promulgation of the Stage 2 of the Disinfection By-products Rule by the U.S. Environmental Protection Agency tightened monitoring compliance for total trihalomethanes (TTHM) and haloacetic acids (HAA5) maximum contaminant levels (MCL). TTHM levels were lowered from 100 to 80 μg/L, compelling water agencies to improve removal of TTHM and their precursors [1]. Since then, water utilities have been adopted granular activated carbon (GAC) as an effective technology to control disinfection byproducts (DBPs). GAC has the advantage of allowing water utilities to keep using chlorine for post disinfection instead of switching to technologies such as ultraviolet light or ozonation. However, current operation of GAC is expensive and labor intensive because it requires frequent media replacement [2]. This dissertation research investigates new modalities of GAC operation to lengthen periods between GAC replacements while providing TTHM control and it includes four components, summarized in Figure 1.1. The following research questions are addressed in this work:

1. How is molecular weight distribution altered by GAC treatment?
2. Why are TTHM and HAA5 formation reduced with pre-chlorination and GAC?
3. Can in situ chemical oxidation recover NOM adsorption capacity of field-spent GAC?
4. Is NDMA formation dependent on polyDADMAC molecular weight?
First, this work investigates the effectiveness of GAC to remove different molecular weight organics that contribute to TTHM formation. Rapid small scale column tests (RSSCTs) were used to investigate the impact of GAC on the removal of natural organic matter (NOM) and on the formation of disinfection byproducts downstream of the treatment. Specifically, this work addresses how the GAC impacts molecular weight distribution of NOM.

Second, pre-chlorination is investigated as a strategy to reduce TTHM precursors prior to treatment with GAC. This part of the work was motivated by the research question: is TTHM and HAA5 formation reduced with pre-chlorination and GAC? Rapid small scale column tests were used to evaluate pre-chlorination used with virgin and reactivated GAC to remove TTHM and HAA5 precursors. Simulated distribution system (SDS) tests were performed in the treated water to evaluate the impact of pre-chlorination on TTHM formation potential downstream of the treatment. This work was funded by the Water Research Foundation Project 4607 - Influence of pre-oxidation prior to GAC treatment in controlling DBPs and was conducted with Corona Engineering and the City of Scottsdale.

Third, in-situ regeneration of GAC was investigated with the purpose of minimizing GAC media replacement. Traditionally, GAC has been thermally reactivated, which implies that the spent material is removed from the filters and transported to a reactivation facility. In-situ regeneration of GAC can potentially provide new ways of operating the GAC filters, eliminating the necessity to remove and transport the exhausted media to an external reactivation facility. The research question motivating this
work was: can in situ chemical oxidation recover NOM adsorption capacity of field-spent GAC? In situ reactivation of GAC was part of a collaboration project with Arcadis Inc.

Last, this work looks at N-nitrosodimethylamine (NDMA), an unregulated DBP that is not as effectively controlled by GAC. NDMA is listed in the contaminant candidate list 4 of the EPA [3] and is expected to undergo regulations. GAC can be used to remove wastewater-derived NDMA precursors [4] but not polymer-derived precursors. PolyDADMAC use as a coagulant aid represents one of the major contributors to NDMA precursors in the water treatment. Chloramination of polyDADMAC and of impurities found in the polymer can yield NDMA [5-8]. The goal is to investigate the mechanisms involved in polymer production and how they can affect NDMA formation, as applied under real-world conditions. With that, the following research question is investigated: Is NDMA formation dependent of polyDADMAC molecular weight? This work was funded by the Water Research Foundation Project 4622 - Understanding the Source and Fate of Polymer-Derived Nitrosamine Precursors.

Figure 1.1 – Research questions proposed to guide the work on GAC.
This dissertation is organized in the following chapters:

- Chapter 1 - Introduction

- Chapter 2 – describes work completed on how GAC affects removal of NOM molecular weight

- Chapter 3 – describes work completed on the use of pre-chlorination to reduce TTHM precursors prior to treatment with GAC

- Chapter 4 – presents completed work on in-situ regeneration of GAC

- Chapter 5 – presents work on how the molecular weight of polyDADMAC influences NDMA formation

- Chapter 6 – synthesis of the research findings

- Chapter 7 – conclusions and recommendations for future research
1.1. References


CHAPTER 2
IMPACT OF GRANULAR ACTIVATED CARBON ON NATURAL ORGANIC MATTER AND EFFLUENT ORGANIC MATTER MOLECULAR WEIGHT DISTRIBUTION

Research question: How is molecular weight distribution altered by GAC treatment?

2.1 Introduction

This work is part of a collaboration between ASU, Metropolitan Water District of Southern California, Clemson University and University of Toronto. An outcome of this work was a paper entitled “Granular activated carbon treatment may result in higher predicted genotoxicity in the presence of bromide” authored by Stuart W. Krasner, Tiffany Chih Fen Lee, Paul Westerhoff, Natalia Fischer, David Hanigan, Tanju Karanfil, Wilson Beita-Sandi, Liz Taylor-Edmonds and Robert C. Andrews [1], published in 2016. I was responsible for conducting the experiments together with David Hanigan, as well as conducting the bulk organics analysis.

2.1.1 Characterization of Natural Organic Matter

Natural organic matter (NOM) is a complex mixture of colloidal, particulate and dissolved organic compounds present in water sources. Characterization of NOM represents a difficult task given the variety of chemical functionalities and wide range of molecular weight sizes that comprise the aquatic NOM. [2]. Effluent organic matter (EfOM) is a term used to describe the organic compounds in wastewater, which contains
NOM from water, trace and degradation compounds from wastewater treatment and soluble microbial products. Dissolved organic carbon (DOC) is commonly used as a surrogate to characterize EfOM, although it does not reflect its complex constitution [3]. Most often, one single analytical method, such as DOC, provides limited information on the NOM reactivity and the use of multiple methods is necessary to provide a better indication on the behavior of aquatic NOM, such as measuring DOC combined with ultraviolet absorbance at 254 nm (UV254) [2, 4].

Formation of disinfection byproducts (DBP) depends upon the type and amount of disinfectant used, as well on the NOM characteristics and composition [5, 6]. Physical and chemical NOM properties influence DBP formation and determining hydrophobicity, molecular size distribution and aromaticity of the NOM present in water sources may benefit water treatment facilities in optimizing DBP control [7].

Humic and fulvic acids characteristics in aquatic NOM are water source-dependent and vary greatly based on the material originating NOM at a specific watershed. [8]. Allochthonous NOM is soil-derived and consisted mostly of humic material. [2, 8]. Soil type, geology, hydrology and terrestrial occupation are among the factors influencing allochthonous NOM characteristics [2]. Algae and microbial activity are responsible for originating autochthonous NOM, comprised of less aromatic components than soil-derived NOM. It is known that fulvic acids present moderate molecular weight, heterogeneous constitution and yellow color [8]. Humic acids comprise most of the aromatic portion of aquatic NOM [9, 10] and might be specifically targeted for removal since they are associated with formation of disinfection byproducts (DBP) [11]. Humic substances were found to be mostly in the 1 to 10kDa and have
greater DBP formation than the fraction lower than 1kDa [12]. Smaller MW size NOM has been shown to react more with bromine and favor formation of brominated DBPs [12, 13].

While DOC and UV254 have been used as surrogates to predict and control DBP formation during water treatment [14], they do not allow elucidation of mechanisms ruling NOM removal and oxidation [8, 15]. Other techniques, such as size exclusion chromatography (SEC) allow for a more complete characterization of the DOM fractions and their molecular weight [11, 15-17]. Size exclusion chromatography (SEC) permits characterization of the molecular weight distribution of NOM using a system that requires minimal sample preparation and low sample volume [11].

SEC is used in conjunction with detection systems such as UV absorbance (UVA) and DOC-specific detection methods to identify UV-absorbing material as well as organic carbon. An advantage of the latter is that the intensity of the detector response is proportional to the DOC concentration of the sample [7, 11, 15]. However, some limitations of SEC must be noted. Non-ideal interactions between the sorbates and the column might impact MW separation and result in separation governed by interactions other than size exclusion, such as adsorption and electrostatic interactions with the separation column [18]. The use of DOC coupled with UV detector allows for the identification of any type of organic carbon, with signal response being proportional to the DOC concentration [11].

2.1.2 Granular activated carbon and control of disinfection byproducts
Since the establishment of promulgation of the Stage 2 Disinfectant/Disinfection Byproduct (D/DBP) Rule by the United States Environmental Protection Agency, water utilities have been required to comply with more stringent total trihalomethanes (TTHM) and haloacetic acids (HAA5) Maximum Contaminant Level (MCL) regulations in the distribution system [19]. While the primary approach taken by utilities to control TTHM and HAA5 has been switching from free to combined chlorine, many utilities have installed GAC to remove DBP precursors and achieve other treatment goals (e.g., TOC removal, improved bio stability of treated water).

RSSCTs have been extensively used to represent DBP precursor removal and generate data that is representative of the full scale GAC treatment performance for control of DBPs [20]. Proper scaling down of empty bed contact time, particle size and hydraulic load are necessary to ensure the similarity between RSSCTs and full scale columns. The most important parameters for the design of RSSCTs are the hydraulic loading rate or superficial velocity (v) and the empty bed contact time (EBCT). The scaling relationship governing RSSCTs design can be expressed as [20, 21]:

\[
\frac{EBCT_{\text{SC}}}{EBCT_{\text{LC}}} = \left[ \frac{d_{p, \text{SC}}}{d_{p, \text{LC}}} \right]^{2 - X} = \frac{t_{\text{SC}}}{t_{\text{LC}}} \quad (1)
\]

Where:

- \(EBCT_{\text{SC}}\): empty bed contact time for the small column (SC);
- \(EBCT_{\text{LC}}\): empty bed contact time for the large column (LC);
- \(d_{p, \text{SC}}\): GAC particle size for the small column (SC);
- \(d_{p, \text{LC}}\): GAC particle size for the large column (LC);
X = diffusivity factor;

t_{SC} = time elapsed in the small column;

t_{LC} = time elapsed in the large column.

RSSCTs design can follow two approaches:

(i) Constant diffusivity: assumes that intraparticle diffusion does not depend on the
GAC size and therefore X = 0. Direct similitude between the large and small
columns is adopted.

(ii) Proportional diffusivity (PD): treats intraparticle diffusion as linearly proportional
to the GAC particle size; i.e., X = 1. However, this approach results in long
columns with excessive pressure drop and hard to operate in bench scale [20]. To
overcome this limitation, internal mass transfer is assumed to dominate over
external mass transfer and the superficial velocity of the RSSCT is established to
the minimum value which the column can still operate, i.e., the velocity
equivalent to the minimum Reynolds number [20, 21]. With that, the following
equation is used to design the RSCCTs according to this approach:

\[
\frac{v_{SC}}{v_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} X \frac{Re_{SC, min}}{Re_{LC}}
\]  

Where:

\( v_{SC} \): velocity for the small column (SC);

\( v_{LC} \): velocity for the large column (LC);

\( Re_{SC} \) = minimum Reynolds number for the small column;
\[ \text{Re}_{\text{LC}} = \text{Reynolds number for the large column.} \]

The minimum recommended Reynolds number is usually around 1 but smaller values can be adopted [20, 21]. Moreover, maintaining the ratio between particle size and column diameter at a minimum value 50 is necessary to reduce channeling effects in the columns [21-24]. RSSCTs have been successfully used to evaluate NOM removal by GAC and can predict GAC performance in a shorter time than pilot or full-scale testing [25].

Low MW organics sorb well to GAC, while larger MW organics can block GAC pores. NOM with MW size higher than 10kDa is usually not well removed by GAC but rather by coagulation [3, 26, 27]. Size exclusion of larger NOM may cause adsorption of low MW substances to be limited to mesopores and macropores [11, 28-30]. Influences of NOM on competitive removal of trace organics is well documented but less is known on actual changes in MW of NOM by GAC and most studies focus on waters with high humic content [3]. However, many utilities with low SUVA after coagulation still require GAC to achieve TTHM and HAA5 MCL in their distribution system. While relative removal of different NOM fractions by coagulation and membranes are well documented, less information is available on selective changes in NOM MW by GAC treatment.

Haloacetonitriles are toxic unregulated nitrogenous DBPs, which are up to two orders of magnitude more cytotoxic than haloacetic acids [31]. HAN formation is related to the humic acids content of surface waters [32] and such as TTHM and HAA5, removal of HAN precursors can potentially benefit from the use of GAC. Although not regulated,
these DBPs have been identified in occurrence studies throughout the United States [33] and are therefore included in this study due to their higher toxicity and to their potential health risk [31, 34].

This chapter investigates how GAC alters molecular weight of NOM with the combined use of DOC, UV254 and SEC-DOC measurements. RSSCTs are used to simulate treatment with GAC and were run using a surface water, secondary wastewater effluent and a blend of both to represent surface water impacted by wastewater. The hypothesis investigated is that GAC alters the MW distribution of the NOM present in the water sources, therefore impacting DBP formation in the treated effluent.

2.2 Material and Methods

2.2.1 Simulated GAC treatment.

Rapid small scale columns (RSSCTs) were adopted in this work since they enable simulation of full-scale GAC treatment in a shorter time than pilot scale columns while using only a fraction of the feed water. RSSCTs were designed according the proportional diffusivity (PD) design constraints simulating an empty bed contact time (EBCT) of 10 minutes [21, 24]. The Reynolds number was kept at 1.12 and the ratio Reynolds x Schmidt number was kept at 1000 to minimize channeling effects. Additional details on the RSSCT design parameters, as well a summary of the respective full-scale parameters are presented in Table 2.1. RSSCTs were packed with bituminous coal-based GAC (Calgon F400, referred to as Carbon A), obtained from Calgon Carbon Corp. (Pittsburg, PA), and lignite-coal based GAC (Norit HD3000, referred to as Carbon B),
obtained from Norit Americas (Marshall, TX). Characteristics of both GACs used are summarized in Table 2.2. GACs were manually crushed using a ceramic mortar and pestle. Wet crushed GAC was sieved to select particles within 140 x 170 mesh size (mean diameter of 0.0098 cm) to prevent channeling effects in the columns. Columns were run up to 12000 bed volumes (BV) and samples for DBPs, DOC and toxicity were taken at designated times. Samples were stored in pre-cleaned amber bottles in a refrigerated chamber at 4°C and shipped in coolers packed with ice to for DBP analysis at the Metropolitan Water District of Southern California and Clemson University.

2.2.2 Feed waters.

A surface water (SW), secondary effluent from a wastewater treatment plant (WW) and blend of 90% SW and 10% WW (90SW) were used for this study. Colorado River surface water (SW) from the Central Arizona Project (CAP) canal was collected from a water treatment plant in the Phoenix metropolitan area (AZ). WW was collected after secondary treatment from a wastewater treatment plant in the same region. SW and WW were filtered through 1 μm filters (CLR 1-10 Pall Corporation, Port Washington, NY) at the sampling site. Samples were collected less than 24 hours prior to the start of experiments and kept at room temperature (25°C) during this time. RSSCTs were run on each water source for Carbon A (including one condition in duplicate) and on one water source for Carbon B, totaling five columns. Table 2.3 summarizes the conditions of the RSSCTS and the water quality of the SW, 90SW and WW used.
2.2.3 Dissolved organic carbon, dissolved organic nitrogen and UV absorbance analysis.

Dissolved organic carbon was analyzed by high temperature combustion using a Shimadzu TOC Analyzer (Shimadzu Corp, Tokyo, Japan). All samples were filtered through 0.45 µm glass fiber filters (GF/F, Whatman GE) and acidified to pH < 3 with 0.1N HOCl. Dissolved organic nitrogen (DON) was quantified by the difference between total dissolved nitrogen and total inorganic nitrogen. [35] Nitrite, nitrate and ammonia were measured by ion chromatography (Dionex ICS 500, Thermo Scientific). All samples were subjected to 24 to 98 hours dialysis pre-treatment using a cellulose ester dialysis membrane with nominal molecular weight cutoff of 100 Da (Spectra/ Por, Spectrum Laboratories Inc., CA) before inorganic nitrogen quantification [36]. UV254 was measured using a DR5000 spectrophotometer (HACH Comp., Loveland, CO).

2.2.4 Size exclusion chromatography (SEC-DOC) analysis.

Molecular weight distribution of DOM was characterized using a SEC-DOC system. The system, described in previous work ([37]), is composed by a High-Performance Liquid Chromatography system (Waters 2695 Separation Module, Millford, MA) followed by TOC detector (Sievers Total Organic Carbon Analyzer 800) and an inorganic carbon remover (900 ICR, GE). A TSK 50S (Tosho Toyopearl resin, Japan) column was used for isocratic separation with a mobile phase with ionic strength of 0.1M (conductivity = 4.6 µScm$^{-1}$) prepared with nanopore water and a phosphate buffer stock solution. The buffer stock solution was prepared with nanopure water (> 18.2 MΩ-cm)
and 0.064M Na$_2$HPO$_4$.7H$_2$O, 0.020M Na$_2$H$_2$PO$_4$.H$_2$O and 1M Na$_2$SO$_4$ (Sigma-Aldrich) and stored at room temperature until use. The SEC-DOC system was calibrated using polyethylene glycol (PEG) standards within the molecular size range of 600 to 10,000 Da [37]. Nanopure water was used as a blank control and a stock solution of 12 mgC/L of Suwannee River natural organic matter (SRNOM) was adopted as a standard reference. Samples were pre-filtered using ashed 0.45 μm glass fiber filters (GF/F, Whatman GE) and had their conductivity adjusted to equal that of the eluent (4.4 to 4.8 μScm$^{-1}$) by slowly adding the phosphate buffer stock solution to the filtered sample. Analysis of data was done through integration of the peak areas in the MW range of 600 – 1000Da, 1000 – 2000Da, 2000-10kDa and 10kDa – 30kDa. Each integrated area range was divided by the total area of the curve to quantify its fraction of the total, expressing therefore the contribution of each MW range to the total as a proportion.

2.2.5 Formation potential tests and analysis of disinfection byproducts.

DBP formation was evaluated under uniform formation conditions (UFC), where samples were chlorinated at room temperature at pH 8 and held for 24 h [38]. The initial chlorine dose was selected to achieve 1.0 mgCl$_2$/L residual after 24h. Four trihalomethanes (chloroform, bromoform, dibromochloromethane and bromochloromethane) and haloacetonitriles (bromoacetonitrile, chloroaetonitrile, tribromoacetonitrile, bromodichloroaetonitrile, dibromochloroaetonitrile) were analyzed with solid-phase extraction (SPE) and gas chromatography and mass spectrometry (GC/MS) [39]. Haloacetic acids (HAA5) analysis followed the EPA Method 552.3, which uses diazomethane derivatization and liquid/liquid extraction to later run the
samples using GC followed by electron capture detection. Samples were run by the Metropolitan Water District of Southern California (MWDSC).

2.2.6 Statistical analysis of the data

Two sample Student’s t-tests were used to compare data sets. Student’s t-test shows whether the difference between two samples is significant or casual. Student’s t-tests are based on hypothesis tests, i.e., a null and an alternative hypothesis are defined and the test provides evidence whether to accept or reject the null hypothesis. The null hypothesis (H₀) assumes that there is no difference between the samples, i.e., \( \mu_1 - \mu_2 = 0 \), where \( \mu \) represents the sample mean. The alternative hypothesis is \( H_1: \mu_1 - \mu_2 \neq 0 \). From the calculated t-value:

\[
t = \frac{\bar{x} - \mu_0}{S/\sqrt{n}}
\]

Where \( \bar{x} \) is the sample mean, \( \mu_0 \) is the mean value defined by the null hypothesis (\( \mu_0 = 0 \)), S is the sample standard deviation and n is the number of samples in the data set. From the calculated t value, the correspondent p value is obtained from a table of tabulated t values [40]. The null hypothesis is rejected if \( p < 0.05 \). If \( p > 0.05 \), there is not enough evidence to reject the null hypothesis [40].

Effluent of the 90SW treated with Carbon A and B were treated as paired samples, since these are the same influent water under different treatment conditions. All the other cases and samples were treated as non-paired. Paired t-tests follow the equation:
\[ t = \frac{\bar{x}_1 - \bar{x}_2}{S_1/\sqrt{n} - S_2/\sqrt{n}} \]

Where \( \bar{x}_1 \) and \( \bar{x}_2 \) are the mean of the first and second data set, respectively; \( S_1 \) and \( S_2 \) are the standard deviation for each data set and \( n \) is the number of data points in each data set (\( n \) should be the same for both data sets). Confidence interval of 95% (i.e., \( \alpha = 0.05 \)) and two-tailed normal distribution were adopted. All tests were run using Microsoft Excel 2013 [40].

2.3 Results and Discussion

2.3.1 Behavior of bulk organics during GAC treatment

Multiple treatment scenarios (5 RSSCTs with 3 different water sources and 2 types of GAC; one condition run in duplicate) were designed to evaluate the changes in MW distribution of NOM upon GAC adsorption. DOC and UV254 breakthrough curves for these scenarios are presented in Figures 2.1 and 2.2. The initial DOC concentration for the source waters varied from 3 mgC/L (SW) and 3.2 mgC/L (90SW) to 5.7 mgC/L (WW), while UV254 values varied from 0.045 cm\(^{-1}\) (SW) and 0.054 cm\(^{-1}\) (90SW) to 0.121 cm\(^{-1}\) (WW), as summarized in Table 2.3.

A blend of 10%WW and 90%SW was run through two GAC different types. At 10000BV, when operation of RSSCTs ended, Carbon A had achieved 65% DOC breakthrough, while Carbon B achieved ~83% DOC breakthrough. Results show that Carbon A removed more DOC than Carbon B, as confirmed by paired t-tests (\( p<0.01 \))
comparing the difference between the DOC breakthrough curves of the 90SW influent treated with GAC A and GAC B.

For the same scenario; i.e., 90SW influent treated with Carbon A and B, UV254 breakthrough (Figure 2.2) also occurred slower for Carbon A than for Carbon B. At the end of the RSSCTs operation (10147BV), Carbon A had about 44% UV254 breakthrough while Carbon B was at 61% breakthrough. SUVA values therefore decreased during GAC treatment, indicating that the most aromatic part of the DOC was removed by GAC. Adsorption of UV254 absorbing material by GAC is better compared to non-UV254 absorbing material, due to the higher aromaticity of this portion of NOM. Removal of aromatic NOM is specially desired when GAC is used to remove DBP precursor, since this fraction of NOM has higher DBP formation potential [20, 28-30, 41].

Carbon A performed better than Carbon B both for removal of DOC and UV254, which is explained by the different characteristics of both GACs (Table 2.2). Carbon A has larger surface area and larger fraction of micropores than Carbon B. Carbon A has been previously used for removal of NOM from other surface waters and also performed better than its counterparts due to its surface area and pore size distribution [24, 30, 42].

The remaining treatment scenarios focused on using the same GAC (Carbon A) to treat different water sources (WW, SW and 90SW). When using Carbon A, DOC breakthrough was similar for all water sources (SW, WW and 90SW0 during the early treatment bed volumes. At 4500BV, all influent waters treated with GAC A had DOC breakthrough values varying between 43 and 49%, i.e., 6% variation only. GAC adsorption therefore did not appear to be dependent on the initial DOC concentration of the influent water up until 4500BV. Latter bed volumes show a greater difference in the
DOC removal. At 10000BV, WW had a DOC breakthrough value of 77%, while SW and 90SW achieved 62% and 65% DOC removal, respectively. This behavior is a consequence of the exhaustion of the GAC available adsorption sites.

Figure 2.3 shows DON breakthrough curves for all the RSSCTs run. DON was not as effectively removed by GAC as DOC or UV254 absorbing compounds, regardless of GAC type or source water. SW treated with Carbon A, for instance, had DON breakthrough values between 46% and 78%. WW has similar values, with DON breakthrough varying from 46% to 88%. DON can act as an important precursor for the formation of nitrogenous DBPs, such as HANs. Bromide is also not removed by treatment with GAC, which affects the Br/DOC and Br/DON ratios in the treated effluent and it consequently affects the formation of C-DBPs and N-DBPs [43]. This effect was explored in the companion study part of this work [1] and it is one of the key observations of this work. As shown by Krasner et al (2016), Br/DOC ratios increase along the DOC breakthrough curve, which impacts the bromine incorporation upon disinfection and increases formation of brominated DBP species. This is mostly accentuated in the earlier BVs of the DOC breakthrough curve, which means that the effluent with lower DOC will likely have a predominance of brominated DBP species [44-46].

2.3.2 Molecular weight distribution

A possible explanation to justify these observations is related to the MW distribution of the samples and to the selective adsorption of NOM by GAC. The 90SW
and SW water sources had similar MW distribution and the DOC adsorption by GAC A was not affected by selective removal of MW sizes for these water sources [30].

Changes in MW distribution of NOM were initially explored for the 90SW influent water sample treated with Carbon A and Carbon B. Changes in MW distribution of NOM following DOC removal by Carbon A are presented in Figures 2.6 and 2.7. While changes in MW after treatment with Carbon B are presented in Figures 2.8 and 2.9.

For Carbon B (Figure 2.9) removal of low MW NOM (600 – 1000Da) occurs preferentially for the low DOC breakthrough values. Contribution of NOM from 600 to 1000Da lowers from 21% in the 90SW influent to 9%, 15% and then 20% in the effluent of DOC breakthrough equal to 27%, 53% and 66%, respectively. Little to no variation in the contribution of the 2000 - 10000 Da range is observed; the contribution of this fraction to the total remained around 24 ± 0.01% in all treated effluent samples. The same trend is observed in Figures 2.6 and 2.7, when Carbon A is used to treat the same water source.

The other water sources, WW and SW, treated with Carbon A showed similar behavior. NOM from 600 – 1000Da reduced from 26% to 12% with 14% DOC breakthrough and down to 16% with 26% DOC breakthrough. The most dramatic change for WW happened for the NOM in the 1000 – 2000Da, which was reduced from 40% of the total in the influent down to 9% and 31% of the total for 14% and 26% DOC breakthrough, respectively.

Carbon A and Carbon B altered the MW distribution of the 90SW, WW and SW during early DOC breakthrough values through preferential removal of low MW NOM. No changes were observed in the later bed volumes of the treatment, due to exhaustion of
available adsorption sites on the GAC surface. Preferential removal of low MW compounds occurs in the beginning of the treatment. After exhaustion of the available adsorption sites, only adsorption of high MW NOM occurs. This confirms previous studies showing that the high MW NOM fraction is not preferentially adsorbed by GAC and is impacted by selective adsorption of low MW NOM. Due to the GAC size distribution, compounds with sizes between 500 to 4000Da are usually well removed by GAC [3, 29]. This study observed highest removal of NOM in the 500 to 1000 Da MW range.

These observations are in agreement with Kilduff et al (1996), who postulated that the composition (MW distribution) of a mixture determines the adsorption and not the concentration at equilibrium. For a given concentration of adsorbent, only the most adsorbable components are removed. The following adsorbable components are only removed when there is enough adsorbent available [29, 30].

2.3.3 Formation of DBPs in the GAC effluent

UFC HAN, UFC TTHM and UFC HAA5 removal as a function of DOC breakthrough are presented in Figures 2.12 to 2.14. Removal of UFC HAN and UFC TTHM correlated well with the DOC removal, both for Carbon A and Carbon B, as seen in Figures 2.12 and 2.13. DOC has been shown to be a good surrogate for removal of TTHM and HAA5 precursors by many studies [20, 41, 43, 47].

HAN precursors were also efficiently removed by GAC, despite poor DON removal by GAC (Figure 2.12). HAN breakthrough reached up to 62% for the WW
treated with Carbon A, for 67% DOC breakthrough. DON also acts as a major precursor for HAN, yet, this work shows that GAC could also potentially be used to reduce HAN in waters with low DON. This is likely due to the size exclusion effect of GAC and removal of humic acids that can also form HAN upon chlorination [49].

2.4 Conclusions

GAC has been used to assist water treatment facilities in complying with TTHM and HAA5 regulations by removing their precursors. While DOC and UV254 are good surrogates for removal of NOM and DBP precursors, DON is poorly removed by GAC. Despite poor removal of DON, GAC effectively removed HAN precursors and could potentially be used for this purpose. This study investigated the hypothesis that GAC alters the MW distribution of NOM during treatment due to selective adsorption of low MW compounds, which contributes to lower DBP formation in the effluent. For the water samples tested, 90SW, WW and SW, and both GACs, changes in MW distribution were observed as a consequence of treatment with GAC. Low MW NOM (600 – 1000Da) was adsorbed preferentially than the larger MW fraction (>10kDa) for the earlier DOC breakthrough values.

The observations on this work answer to the research question: How is molecular weight distribution of NOM altered by GAC treatment? Low MW NOM (600 – 1000Da) is selectively removed during the early treatment volumes and therefore MW distribution of NOM is altered. As DOC breakthrough increases, selective adsorption of NOM can no
longer take place due to exhaustion of the available adsorption sites on the GAC surface and MW distribution of NOM is similar to the influent.

This work also demonstrated that the, as shown by the companion study by Krasner et al (2016), the formation of DBPs followed the DOC breakthrough; UV254 removal by GAC was better than DOC removal and DON was not as well removed as DOC and UV254. The conclusions presented in this work also suggest that DBP formation and speciation are related to the Br/DOC and DON/DOC ratios in the effluent than to the MW distribution of the treated samples.
2.5 Figures and Tables

Table 2.1 – Design parameters for the RSSCTs.

<table>
<thead>
<tr>
<th>Design parameters</th>
<th>Full scale column</th>
<th>RSSCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter (m)</td>
<td>8.32</td>
<td>0.011</td>
</tr>
<tr>
<td>Empty bed contact time (min)</td>
<td>10</td>
<td>0.61</td>
</tr>
<tr>
<td>Particle mean diameter (cm)</td>
<td>0.1605</td>
<td>0.0098</td>
</tr>
<tr>
<td>Bed length (m)</td>
<td>1.219</td>
<td>0.093</td>
</tr>
<tr>
<td>Flow rate (m³/h)</td>
<td>797.4</td>
<td>8.70E-04</td>
</tr>
<tr>
<td>Hydraulic loading rate (m³/m².h)</td>
<td>14.7</td>
<td>9.2</td>
</tr>
<tr>
<td>Reynolds</td>
<td>29.28</td>
<td>1.12</td>
</tr>
<tr>
<td>Schmidt</td>
<td>893.7</td>
<td>893.7</td>
</tr>
</tbody>
</table>

Table 2.2 – Characteristics of the GAC used in the RSSCTs in this study.

<table>
<thead>
<tr>
<th>GAC</th>
<th>Surface area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Average pore radius (nm)</th>
<th>V micro (&lt;2nm) %</th>
<th>V meso (2-50 nm) %</th>
<th>V macro (&gt;50nm) %</th>
<th>V meso and macro &gt;2nm %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon A: Calgon F400[28]</td>
<td>948</td>
<td>0.566</td>
<td>1.2</td>
<td>83.7</td>
<td>NA</td>
<td>NA</td>
<td>16.3</td>
</tr>
<tr>
<td>Carbon B: Norit HD3000</td>
<td>642</td>
<td>0.775</td>
<td>4.45</td>
<td>13.9</td>
<td>57.9</td>
<td>28.1</td>
<td>86</td>
</tr>
</tbody>
</table>

Source: Carbon A data was obtained from [28] and Carbon B data was obtained from [48]. *NA = Not available in the cited source.
Table 2.3 – GAC influent water quality and summary of the RSSCTs run.

<table>
<thead>
<tr>
<th>RSSCT</th>
<th>GAC</th>
<th>Source water</th>
<th>UV254nm (cm⁻¹)</th>
<th>DOC (mgC/L)</th>
<th>DON (mgN/L)</th>
<th>Br (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon A (F400)</td>
<td>SW</td>
<td>0.045</td>
<td>3.0</td>
<td>0.21</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Carbon A (F400)</td>
<td>90SW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Carbon A (F400)</td>
<td>90SW</td>
<td>0.054</td>
<td>3.2</td>
<td>0.26</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Carbon B (HD3000)</td>
<td>90SW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Carbon A (F400)</td>
<td>WW</td>
<td>0.121</td>
<td>5.7</td>
<td>0.53</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 2.1 – DOC breakthrough curves for Carbon A and B.
Figure 2.2 – UV254 breakthrough curves for Carbon A and Carbon B.
Figure 2.3 – DON breakthrough curves for Carbon A and Carbon B.
Figure 2.4 – Molecular weight distribution for treated samples of SW (carbon A).
Figure 2.5 - Molecular weight distribution for the SW influent and treated samples based on the SECDOC integration of peak areas. Values showed represent the contribution of each MW range to the total area for each DOC breakthrough value.
Figure 2.6 – Apparent molecular weight distribution for samples of 90 SW treated with carbon A.
Figure 2.7 – Molecular weight distribution for the 90SW influent and treated samples (Carbon A) based on the SECDOC integration of peak areas.
Figure 2.8 – Molecular weight distribution of influent and samples of 90SW treated with carbon B.
Figure 2.9 - Molecular weight distribution for the 90SW influent and treated samples (Carbon B) based on the SECDOC integration of peak areas.
Figure 2.10 - Molecular weight distribution of influent and samples of WW treated with carbon B
Figure 2.11 - Molecular weight distribution for the WW influent and treated samples (Carbon B) based on the SECDOC integration of peak areas.
Figure 2.12 – HAN removal as a function of DOC breakthrough for SW, 90SW and SW treated with Carbon A and 90SW treated with Carbon B.
Figure 2.13 – TTHM4 removal as a function of DOC breakthrough for SW, 90SW and SW treated with Carbon A and 90SW treated with Carbon B.
Figure 2.14 – HAA5 removal as a function of DOC breakthrough for SW, 90SW and SW treated with Carbon A and 90SW treated with Carbon B.
2.6 References


[29] T. Karanfil, M. Kitis, J. E. Kilduff, and A. Wigton, "Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural


CHAPTER 3

CHLORINATION BEFORE GAC IMPROVES TOTAL TRIHALOMETHANES CONTROL.

Research Question: Why are total trihalomethanes and haloacetic acids formation reduced with prechlorination and GAC?

3.1 Introduction

Promulgation of the Stage 2 Disinfectant/Disinfection Byproduct (D/DBP) Rule by the United States Environmental Protection Agency is leading water utilities to develop strategies that lower total trihalomethanes (TTHM) and haloacetic acids (HAA5) in the distribution system [1]. Effective and economic strategies to control DBP formation include adopting alternative disinfectants (e.g. chloramines or ozone) and removing DBP precursors through adsorption by granular activated carbon (GAC).

Operation of GAC contactors is cost- and time- intensive due to periodic replacement of the exhausted media with virgin or reactivated GAC [2-4]. Novel in-situ GAC regeneration strategies have been explored to reduce downtimes and media replacement costs [5-7]. Additionally, improving pre-treatment practices can delay breakthrough of dissolved organic carbon (DOC) that serve as DBP precursors. Optimizing coagulation reduces the DOC loading to GAC filters. Pre-ozonation transforms DOC to lower molecular weight compounds, including those that are biodegradable (e.g., aldehydes). Less well studied is the use of pre-chlorination, which
also oxidizes DOC and can result in greater DOC adsorption, although pre-chlorination
does form DBPs [8-11]. An unresolved question is the trade-off upon pre-chlorination
between forming DBPs versus making TOC more adsorbable.

Surrogate measurements such as ultraviolet absorbance (UV) and dissolved
organic carbon (DOC) are used to characterize NOM and predict DBP formation
potential in natural waters. UV absorbance, measured at 254 nm (UV\textsubscript{254}), indicates the
aromatic fraction of NOM. SUVA is the ratio of UV\textsubscript{254} (m\textsuperscript{-1}) divided by DOC (mgC/L)
values and expresses a quantitative measure of aromatic and humic compounds in the
water [12-14]. Despite being widely used, DOC and UV\textsubscript{254} are not the only means
tracking NOM responsible for DBP formation [15-18]. NOM reactivity with chlorine can
also be predicted by characterization of the molecular weight size distribution of the
NOM. The hydrophilic fraction of NOM has been linked to THM and HAA5 formation
and therefore increasing removal of these compounds is desired to control DBP formation
[10, 13, 14, 19]. Low MW NOM, preferentially removed by GAC [20, 21], is usually
associated with the hydrophilic NOM fraction, constituted of aliphatic ketones and
alcohol, showing lower UV\textsubscript{254} absorbance and higher reactivity with HOBr [22, 23]
Hydrophobic NOM has higher MW and more phenolic groups than the hydrophilic NOM
fraction [23].

The goal of this study was to investigate if prechlorination increases the
operational life of GAC to remove DOC and decrease TTHM or HAA5 levels. Because
HAA5 levels were well below regulatory limits on this water, this paper focuses on
TTHM control by pre-chlorination prior to GAC treatment. Bench and pilot scale
research was performed on Colorado River water, which is a water supply for over 20
million people in the southwestern USA and can be difficult for water utilities to use and comply with DBP regulations. RSSCTs conducted with and without prechlorination were conducted to understand the impacts on GAC contactor run time and DBPs. Because prechlorination results in carry-over of a chlorine residual onto the top of GAC contactors, both virgin and regenerated (exposed to chlorine) GAC were investigated. DOC, UVA, DOC molecular weight, and THM species were monitored in both influent and effluent from the GAC contactors. Simulated distribution system (SDS) chlorination tests were conducted on GAC effluent, with subsequent quantification of THMs.

3.2. Material and Methods

3.2.1 Source water

Colorado River surface water from the Central Arizona Project (CAP) was collected from a water treatment plant in Central Arizona (AZ) that uses coagulation and ultrafiltration prior to GAC. Non-chlorinated membrane permeate water was used for all testing. A summary of the RSSCTs conditions and influent water characteristics is presented in Table 3.1. Collapsible containers, sealed and with low headspace, were used to store the RSSCTs influent water, preventing TTHM losses by volatilization. Sodium hypochlorite (Reagent grade, Fisher Scientific) was used to pre-chlorinate the influent water. Chlorine concentrations were measured using the colorimetric DPD total chlorine method by HACH (HACH, Germany). Operation of the RSSCTs started 30 minutes after chlorine was dosed and residual chlorine was not quenched to prevent changes in the
TTHM speciation during the SDS tests. The influent water was kept at room temperature during the experiments.

3.2.2 Bench scale simulated GAC treatment

RSSCTs were designed according to the proportional diffusivity (PD) design constraints, given the unknown composition of the source water NOM [3, 24]. RSSCTs simulated full-scale GAC contactors at the participating utility with hydraulic loading rate equal to 14.8 m$^3$/h.m$^2$ (4.91 gpm/ft$^2$) and empty bed contact time equal to 17.1 min. The Reynolds number was kept at 1.12 and the ratio Reynolds x Schmidt number was kept at 1000 to minimize channeling effects. Virgin and reactivated bituminous coal-based GAC (Calgon F400) were obtained from Calgon Carbon Corp. (Pittsburg, PA) and manually crushed using a ceramic mortar and pestle. Wet crushed GAC was sieved to select particles within 140 x 170 mesh size (mean diameter of 0.0098 cm) to prevent channeling effects in the columns. A unique approach of this study is adopting columns with only 0.5 cm of diameter, enabling columns to run for up to 17000BV. Flowrate of the columns were checked and readjusted every 48 to 72 hours to minimize interferences. Eight columns were run using virgin and reactivated GAC. Duplicate RSSCTs were run to assess variations. Samples for TTHM, HAA5, DOC and UV 254 nm were taken at designated times and stored in pre-cleaned amber bottles at 4°C until analysis.

3.2.3 Pilot Scale columns

Parallel to the RSSCTs, pilot-scale columns (2 or 6 in diameter) were operated at the participating utility for two years. Details can be found in the final report for WRF Project #4607 [25]. The pilot-scale design constraints were similar to the RSSCTs, i.e.,
columns were designed to emulate full-scale columns from the participating utility. Four columns were run in pilot scale and their conditions are summarized in Table 3.1. Sampling and monitoring of the columns was done once on a week during the columns operational time. The chlorinated influent water had 30 min reaction time prior to entering the columns. All the pilot columns were equipped with sampling ports along the length of the columns that were occasionally used for tracking DOC or DBP breakthrough vertically during operation of the columns. Columns were not backwashed during the entire course of their operation, except when GAC was first loaded into the columns. The primary difference between RSSCTs and pilot columns were 1) potential role of biological processes in the pilot column, and 2) fixed influent water quality for RSSCTs (i.e., water collected on individual days) whereas pilot tests were exposed to daily changes in water quality (i.e., operated on-line at the WTP).

3.2.4 Analysis of GAC Breakthrough curves

Two parameters were used to assess impacts of prechlorination on GAC operational life. First, the number of bed volumes treated to react 50% DOC breakthrough was used. The water treatment plant collaborating with this project normally stops the GAC operation at this point, so this value was selected to evaluate how much operation of the columns could be extended with the pre-chlorination. Second, comparisons between breakthrough curves with differing levels of prechlorination was performed using paired Student’s t-tests. Normalized breakthrough curves (e.g., DOC/DOC₀) were compared by calculating the difference between two
breakthrough curves, using two-tailed t-distribution and interval of confidence = 95% (α = 0.05) [4, 26]. The null hypothesis is defined as: H0: μd0 = μd1 - μd2 = 0, while the alternative hypothesis is: H1: μd0 = μd1 - μd2 ≠ 0; where μd is the mean difference between breakthrough curves run in duplicate (residual).

The test statistic \( t_{obs} \) is then calculated following Equation 1:

\[
t_{obs} = \frac{\bar{x}_d - \mu_{d0}}{S_d / \sqrt{n}} \quad \text{(Equation 1)}
\]

Where:

\( \bar{x}_d \): sample mean difference

\( \mu_{d0} \): mean difference between duplicate breakthrough curves

\( S_d \): standard deviation of the difference

\( n \): number of observations (i.e., data points collected at different BV treated)

A \( t \)-critical (\( t_{crit} \)) value for a \( t \)-distribution with \((n-1)\) degrees of freedom is defined using tabulated values of probabilities of \( t \) distribution. The probability of rejecting the null hypothesis, \( p \), is calculated based on the \( t_{obs} \) value, for \( n-1 \) degrees of freedom. The null hypothesis is rejected (i.e., breakthrough curves are considered statistically different, if \( p < \alpha \)). Breakthrough curves are considered statistically similar when \( p > \alpha \) (fail to reject the null hypothesis).

3.2.5 Organic matter measurements

DOC was analyzed by high temperature combustion using a Shimadzu TOC Analyzer (Shimadzu Corp, Tokyo, Japan). All samples were filtered through pre-cleaned
0.45 μm glass fiber filters (GF/F, Whatman GE). UV 254 nm was measured with a DR5000 spectrophotometer (HACH Comp., Loveland, CO).

Molecular weight distribution of DOM was characterized using size exclusion chromatography with in-line DOC detection[27]. The SEC-DOC system consists of a High-Performance Liquid Chromatography system (Waters 2695 Separation Module, Millford, MA) followed by Photodiode Array (PDA) detector (Waters 2998, Millford, MA), TOC detector (Sievers Total Organic Carbon Analyzer 800) and inorganic carbon remover (900 ICR, GE). A TSK 50S (Tosho Toyopearl resin, Japan) column was used for separation with a phosphate buffer eluent solution. The buffer solution was prepared with nanopure water (> 18.2 MΩ-cm) by adding a stock solution containing 0.064M Na₂HPO₄.7H₂O, 0.020M Na₂H₂PO₄.H₂O and 1M Na₂SO₄ (Sigma-Aldrich). The SEC-DOC system was calibrated using polyethylene glycol (PEG) standard solutions varying from 600 to 10,000 Da. For each run, nanopure water was used as a blank control and a stock solution of 12 mgC/L of Suwannee River fulvic acid (SRFA – International Humic Substances Society) was adopted as a standard quality control. Samples were pre-filtered through ashed 0.45 μm glass fiber filters (GF/F, Whatman GE). Conductivity of all samples were adjusted to equal that of the eluent (4.4 to 4.8 µS/m) by slowly adding the stock solution to the filtered sample. Analysis of data was done through integration of the peak areas in the MW range of 600 – 1000Da, 1000 – 2000Da, 2000-10kDa and 10kDa – 30kDa. Each integrated area range was divided by the total area of the curve to quantify its fraction of the total, expressing therefore the contribution of each MW range to the total as a proportion.
3.2.6 DBP Related Measurements

SDS tests were performed on the effluent of the columns, collected in three intervals of time. Chlorine demand tests defined the necessary chlorine dose to achieve 1 mgCL\textsubscript{2}/L chlorine residual after 24 hours hold time. After chlorine doses were defined, samples were held for 24, 48 and 72 hours. Residual chlorine, TTHM and HAA5 concentrations were measured in each sample. SDS tests were chosen instead of formation potential (FP) tests due to its similarity to full scale water treatment conditions. FP tests are designed to maximize the reactions between chlorine and DBP precursors using high concentrations of chlorine. High concentrations of chlorine has been linked to changes in TTHM speciation by inhibiting the formation of iodinated TTHM [28]. Appendix A presents further details on the SDS tests procedure.

All samples for TTHM and HAA5 were quenched and preserved with ascorbic acid and stored at 4°C until analysis. TTHMs were analyzed with solid-phase extraction (SPE) and gas chromatography and mass spectrometry (GC/MS) by a certified lab [29]. TTHM species were measured by GC-MS with EPA Method 524.2 [30] HAA5 was measured using EPA Method 552 [31] modified to LC-MSMS HAA5.

Bromide is a DBP precursor and was measured using ion chromatography (EPA Method 300.0) [32]. Bromine incorporation factors (BIFs) for THMs were calculated as follows:

\[
BIF = \frac{0 \times \text{CHCl}_3 + 1 \times \text{CHCl}_2\text{Br} + 2 \times \text{CHClBr}_2 + 3 \times \text{CHBr}_3}{\text{CHCl}_3 + \text{CHCl}_2\text{Br} + \text{CHClBr}_2 + \text{CHBr}_3}
\]

Where \(\text{CHCl}_3\), \(\text{CHCl}_2\text{Br}\), \(\text{CHClBr}_2\) and \(\text{CHBr}_3\) are the correspondent THM concentration (µmol/L) [33]. BIF values indicate the average THM species in a given
water source. A BIF of 1 indicates that bromodichloromethane (CHCl\textsubscript{2}Br) is the average species detected, while a BIF of 3 indicates that bromoform (CHBr\textsubscript{3}) is the average species found. [34]

3.3. Results and Discussion

3.3.1 Impact of pre-chlorination on DOC and UV254 removal

Figure 3.1 shows columns B1 (no pre-chlorination), B2 (1 mgCl\textsubscript{2}/L) and the average of B3 and B4 (2 mgCl\textsubscript{2}/L, duplicate), designed to evaluate the impact of pre-chlorination the DOC breakthrough with virgin GAC. There is a high level of reproducibility between the duplicate columns (\(\mu_{d0} = 0.04\)). While 50% of DOC breakthrough occurred around 5000 BV for the RSSCT operated with no pre-chlorination (B1), 15% more BVs could be operated with 1 mgCl\textsubscript{2}/L pre-chlorination. With 2 mgCl\textsubscript{2}/L pre-chlorination was adopted, the 50% DOC breakthrough level occurred 30% later (at 6500BV) than when no pre-chlorination was practiced. Paired t-tests showed that 1 mgCl\textsubscript{2}/L resulted in statistically longer DOC breakthrough curves (p = 0.02), when compared to no prechlorination (B1). When a higher concentration of chlorine was used (2 mgCl\textsubscript{2}/L), longer DOC breakthrough compared to no prechlorination was also observed (p<0.01). Since both 1 and 2 mgCl\textsubscript{2}/L had positive impacts on the DOC removal by GAC, the lowest concentration (1mgCl\textsubscript{2}/L) was adopted for the further RSSCTs and SDS testing. Despite nearly 50% improvement in using 2 mgCl\textsubscript{2}/L, one of the goals of the participating water utility was using the lowest chlorine concentration that would extend the GAC treatment.
Figure 3.2 shows RSSCT breakthrough curves comparing virgin to regenerated GAC. Column B7 (no pre-chlorination) reached 65% breakthrough around 11500BV, whereas column B8 (1 mgCl₂/L pre-chlorination) reached the same DOC breakthrough around 14500BV. Paired Student’s t-tests showed that RSSCT breakthrough curves for DOC were statistically similar for both curves (p > 0.05). Thus, there appears to be minimal impacts of chlorine residual carry-over onto GAC which could affect adsorption characteristics after thermal regeneration.

Improvement in DOC removal was expected due to formation of low MW compounds upon chlorination. Since lower MW compounds are adsorbed more easily by GAC, pre-chlorination could facilitate NOM removal by GAC [35]. Low chlorine doses lead to formation of substituted polyhalogenated compounds and oxygenated functional groups through reactions with the phenolic rings from humic and fulvic acids. Higher concentrations of chlorine may cleavage the ring from these compounds, resulting in molecules of lower molecular weight [35, 36]. Increased adsorption of NOM to graphite sheets has been observed after pretreatment with chlorine due to changes in the NOM characteristics that led to increased sorption to hydrophobic surfaces [35].

Figure 3.3 shows the fractional removal (C/C₀) of UV254 absorbing material was delayed compared with DOC breakthrough in the GAC. Removal of UV254 absorbing compounds reached less than 50% of the total at the end of the virgin GAC operation. This represents more than 1000BV (~10%) increase in bed volumes treated before reaching 50% UV254 breakthrough. Pre-chlorination with 1 or 2 mgCl₂/L resulted virgin GAC breakthrough curves for UVA254 that were different when compared to the non-chlorinated RSSCT (p < 0.01 and p = 0.02, respectively).
Figure 3.4 shows UV254 breakthrough for regenerated GAC operated with and without pre-chlorination. 50% UV254 breakthrough occurred at 10000BV when no pre-chlorination was used. The same breakthrough value was seen at 15000BV when 1 mgCl2/L prechlorination was used, a 50% increase. Removal of aromatic compounds results in lower TTHM formation, therefore impacting downstream TTHM formation downstream of the GAC treatment [10, 13, 37].

Bromide is not effectively removed by GAC and therefore waters with high bromide levels, such as drinking water sources impacted by industrial effluents and salt water, are more susceptible to changes in DBP speciation [38, 39]. TTHM speciation impacts the potential toxicity of the effluent, since brominated THM and HAA are more cyto- and genotoxic than their chlorinated counterparts [40-42]. Free bromine reacts faster than free chlorine, resulting in higher oxidation of NOM by bromine [38]. Smaller MW NOM reacts at a higher rate with bromine and favors formation of brominated DBPs [43, 44].

3.3.2 Impact of pre-chlorination on molecular weight distribution

We hypothesized that pre-chlorination enhanced removal of lower MW compounds by GAC. SEC-DOC was run for selected samples of columns B5 to B6, run with virgin GAC. Figure 3.5 shows SEC-DOC chromatograms for GAC effluent at three points along the breakthrough (between 15% and ~55% DOC breakthrough). At 14% DOC breakthrough, prechlorination (red-lines) indicate preferential lower concentration of DOC with MW below 2000 Da. When DOC reaches 50-60% breakthrough there is
marginal differences, as calculated by integrated areas under the SECDOC chromatograms. The difference between the prechlorinated and non-chlorinated samples reduces as DOC breakthrough increases and as the number of available adsorption sites in the GAC reduces.

3.3.3 Breakthrough curves for preformed TTHM and HAA5 and speciation

Figure 3.6 shows breakthrough curves for TTHM for the RSSCTs operated with pre-chlorination. Without prechlorination, influent TTHM levels were below 1 µg/L. With 1 or 2 mgCl₂/L the influent level of TTHMs were 17 and 45 µg/L, respectively. All four THM species were detected in the influent water.

TTHM levels in the GAC effluent remained below 15 µg/L after 10,000 bed volumes. The GAC effluent did not exceed the MCL for TTHM (80 µg/L). TTHMs are neutral molecules and adsorb readily to GAC, but chloroform has a lower octanol water partition coefficient (K_{OW}) than bromoform (i.e., chloroform more readily adsorbed than bromoform). Chloroform was the prevalent species detected in the RSSCTs effluent and it was the only species detected when 1 mgCl₂/L was used. Low concentrations of bromodichloromethane (1 µg/L or less) were detected in the RSSCTs effluent of the RSSCTs prechlorinated with 2 mgCl₂/L.

Figure 3.6 shows HAA5 breakthrough curves for the pre-chlorinated RSSCTs. Less than 10% of the influent HAA5 were adsorbed by the GAC. Acids are not as well removed by GAC, compared with neutral organic compounds.
3.3.4 Impact of pre-chlorination on downstream formation potential (SDS tests)

The GAC effluent was chlorinated or re-chlorinated, in the case when prechlorination was practiced, during SDS tests. No chlorine residual was present after GAC treatment. Figure 3.8 shows TTHM formation and speciation for treated samples from columns B1, B2 and B3 upon chlorination (SDS tests) after 24 hours chlorine contact time. Dibromochloromethane (DBCM) is the dominant TTHM specie in the samples with lower DOC (0.8 to 1 mgC/L) treated with virgin GAC and no pre-chlorination (B1).

More chloroform and less bromoform were also formed when pre-chlorination was used. After 24 hours contact time in the SDS tests, maximum chloroform formation was 8 µg/L in the B1 effluent and 5 µg/L in the B2 effluent and B3 effluent. Bromoform decreased from the maximum concentration 8 µg/L in column B1 to 4 µg/L and to 2 µg/L in column B3, under the same conditions, a 50% and 75% reduction in the bromoform concentrations. Reducing bromoform concentrations is beneficial from a regulatory perspective since although the TTHM MCL is based on the sum of all four trihalomethanes species, the Stage 2 of the DBP Rule defined absence of bromoform as a goal MCL [45]. Figure 3.9 shows similar trends after 72 h chlorine contact time, indicating that longer chlorine reaction times (during distribution, for example), would not significantly alter the THM speciation in finished water.

Figure 3.10 shows SDS results for the SDS testing for the water treated using reactivated GAC. Again, DBCM is the prevalent THM species in the samples with lower
DOC (1mgCl₂/L). THM speciation was similar for the RSSCTs operated with regenerated GAC, and TTHM concentrations after 24h were lower than the regulatory limit of 80 μg/L.

However, longer chlorine reaction times (72h) in the water treated with reactivated GAC exceeded the regulatory limit for TTHM, as seen in Figure 3.11. In this case, TTMH was 86 μg/L in the effluent with highest DOC concentration (2.2 mgC/L). When pre-chlorination was used, TTHM was reduced to 62 μg/L, under the same conditions (DOC = 2.0 mgC/L). These results suggest that full scale GAC columns could potentially be used for longer periods without compromising the TTHM MCL in the distribution system when pre-chlorination is adopted.

Table 3.2 shows the bromine incorporation factor (BIF) for the GAC effluent after SDS testing. BIF values changed by less than 10% across the three different holding times from 24 to 72 hours of the SDS tests. BIF values decreased slightly with longer GAC column run times (i.e., higher effluent DOC concentrations). Since bromide is not removed by GAC, but DOC is removed, higher Br/DOC ratios exist earlier in the GAC breakthrough. This results in higher bromine incorporation. BIF values were always higher without prechlorination, compared against data collected when prechlorination was applied prior to GAC treatment.

3.3.5 Pilot-scale columns results and similarity to RSSCTs

Pilot-scale results confirmed nearly all the trends observed in the RSSCTs. Prechlorination with 1 mgCl₂/L was found to delay the breakthrough of DOC. At the end
of the operation of pilot-scale operation (11000BV), the fraction of DOC remaining varied between 66% (P4, virgin GAC, 1 mgCl₂/L prechlorination, and 80% (P1, virgin GAC operated with 1 mgCl₂/L.

Figure 3.13 summarizes results from the SDS testing on GAC effluents from the pilot columns collected as a composite sample between 3300 to 4700 BV. Because each column had different DOC concentrations, we normalize THM formation relative to the DOC concentration in the sample. The highest TTHM reactivity was observed without pre-chlorination (column P4). GAC columns operated with pre-chlorination (P1, P2 and P3) had roughly 30% lower TTHM yield. TTHM yield of the pilot scale column operated with virgin GAC and 1 mgCl₂/l pre-chlorination had the lowest TTHM yield. There was not a significant detrimental impact by using reactivated GAC. Higher prechlorination levels (2 versus 1 mgCl₂/L) lead to only slightly higher THM yields.

Similar SDS THM yields were observed between pilot and RSSCTs. For virgin GAC with 1 mgCl₂/L prechlorination (B6), the RSSCT had TTHM yields of 10 to 32 µg TTHM/mgC for the 24 to 72 hours which is comparable with the 20 to 30 µg TTHM/mgC observed in the pilot test (P1).

3.4. Conclusions

Pre-chlorination with 1 and 2 mgCl₂/L improved removal of DOC and UV254 by virgin GAC, while TTHM formation was reduced in the effluent of pre-chlorinated columns when SDS tests were conducted. Prechlorination results in lower concentrations of organic matter with size below 2000 Da in GAC effluent, compared against non chlorinated GAC influents. Bromide is not removed by GAC, resulting in varying
Br/DOC ratios across the operation time of the GAC (i.e., during DOC breakthrough with longer bed volumes treated). GAC effectively removed preformed TTHM but not HAA5, indicating that GAC was effective at TTHM control and could be used for this purpose without exceeding the TTHM MCL.

Results from pilot scale column confirmed findings obtained in the RSSCTs. The RSSCTs were operated in a fraction the time of pilot columns. Thus future optimization of prechlorination can employ RSSCTs to save time and evaluate a broader range of operational conditions or GAC types. Results from this study show that GAC could potentially be operated for longer bed volumes without compromising the effluent quality or the MCL for TTHM, resulting in potential economical and operational benefits for the water facilities adopting GAC to comply with the existing TTHM regulatory limits.
### 3.5 Figures and Tables

Table 3.1: Pre-chlorination and influent water conditions of the RSSCTs and pilot scale columns.

<table>
<thead>
<tr>
<th>Column</th>
<th>Pre-chlorination conditions</th>
<th>GAC</th>
<th>Influent water</th>
<th>DOC (mgC/L)</th>
<th>UV254 (cm(^{-1}))</th>
<th>TTHM (µg/L)</th>
<th>HAA5 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSSCT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>None</td>
<td>Virgin GAC</td>
<td></td>
<td>3</td>
<td>0.044</td>
<td>17.4</td>
<td>12.5</td>
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<tr>
<td>B2</td>
<td>1 mgCl(_2)/L</td>
<td>Virgin GAC</td>
<td></td>
<td></td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>2 mgCl(_2)/L</td>
<td>Virgin GAC</td>
<td></td>
<td>46.5</td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>2 mgCl(_2)/L (B3 duplicate)</td>
<td>Virgin GAC</td>
<td></td>
<td>44.1</td>
<td>15.8</td>
<td></td>
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<tr>
<td>B5</td>
<td>None</td>
<td>Virgin GAC</td>
<td></td>
<td></td>
<td>2.5</td>
<td>4</td>
<td></td>
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<tr>
<td>B6</td>
<td>1 mgCl(_2)/L</td>
<td>Virgin GAC (reactivated)</td>
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<td></td>
<td></td>
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<tr>
<td>B7</td>
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<td>0.045</td>
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<td>Virgin GAC (reactivated)</td>
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<td>Pilot-scale column</td>
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<td>P1</td>
<td>1 mgCl(_2)/L</td>
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<td>2.6 - 3.8</td>
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<td>1 mgCl(_2)/L</td>
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<td>8.0 - 21.0</td>
<td>4.2 - 11.0</td>
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</tr>
<tr>
<td>P4</td>
<td>None</td>
<td>Virgin GAC</td>
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Table 3.2 – Bromine incorporation factor for conditions of the RSSCTs and pilot scale columns.

<table>
<thead>
<tr>
<th>RSSCT</th>
<th>Pre-chlorination conditions</th>
<th>GAC</th>
<th>Effluent DOC (mgC/L)</th>
<th>Bromine Incorporation Factor (BIF)</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>24h</td>
<td>48h</td>
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<tr>
<td>B1</td>
<td>None</td>
<td>Virgin</td>
<td>0.8</td>
<td>1.9</td>
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<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>1.4</td>
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<td></td>
<td>2.6</td>
<td>1.3</td>
</tr>
<tr>
<td>B2</td>
<td>1 mgCl₂/L</td>
<td>Virgin</td>
<td>0.5</td>
<td>1.3</td>
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<td></td>
<td></td>
<td></td>
<td>1.7</td>
<td>1.3</td>
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<td></td>
<td></td>
<td>2.0</td>
<td>1.3</td>
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<td>Virgin</td>
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<td>1.2</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>B5</td>
<td>None</td>
<td>Virgin</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
<td>1.5</td>
</tr>
<tr>
<td>B6</td>
<td>1 mgCl₂/L</td>
<td>Virgin</td>
<td>1.0</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>B7</td>
<td>None</td>
<td>Reactivated</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.2</td>
<td>1.3</td>
</tr>
<tr>
<td>B8</td>
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<td>Reactivated</td>
<td>1.0</td>
<td>1.8</td>
</tr>
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<td></td>
<td></td>
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<td>1.3</td>
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<tr>
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<td></td>
<td>2.0</td>
<td>1.3</td>
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Figure 3.1 – DOC breakthrough curves for pre-chlorinated and non-chlorinated water treated with virgin GAC. DOC₀ = 3 mgC/L.
Figure 3.2 – DOC breakthrough curves for pre-chlorinated and non-chlorinated water treated with virgin and reactivated GAC. DOC$_0$ = 2.9 mgC/L.
Figure 3.3 – UV254 breakthrough curves for pre-chlorinated and non-chlorinated water treated with virgin GAC. UV254₀ = 0.044.
Figure 3.4 – UV254 breakthrough curves for pre-chlorinated and non-chlorinated water treated with virgin and reactivated GAC. UV254₀ = 0.045.
Figure 3.5 - Molecular weight distribution based on integrated peak areas for samples treated with virgin GAC, with and without pre-chlorination (columns B5 and B6).
Figure 3.6 – TTHM breakthrough curves for pre-chlorinated SW treated with virgin and reactivated GAC.
Figure 3.7 – HAA5 breakthrough curves for pre-chlorinated SW treated with virgin and reactivated GAC.
Figure 3.8 – TTHM formation and speciation after 24h in the effluent of the RSSCTs treated with virgin GAC under different pre-chlorination conditions.
Figure 3.9 - TTHM formation and speciation after 72h in the effluent of the RSSCTs treated with virgin GAC under different pre-chlorination conditions.
Figure 3.10 - TTHM formation and speciation after 24h in the effluent of the RSSCTs treated with virgin and regenerated GAC under different pre-chlorination conditions.
Figure 3.11 - TTHM formation and speciation after 72h in the effluent of the RSSCTs treated with virgin and regenerated GAC under different pre-chlorination conditions.
Figure 3.12 – TTHM formation (expressed as TTHM formed per DOC concentration) in the effluent of the pilot scale columns (composed effluent from 3300 to 4700 BV).
3.6 References


CHAPTER 4

IN-SITU REGENERATION USING IRON NANOPARTICLES AND LIQUID OXIDANTS OF FIELD-SPENT GRANULAR ACTIVATED CARBON

Research Question: Can in-situ chemical oxidation recover NOM and micro-pollutants adsorption capacity of field-spent GAC?

4.1 Introduction

The goal of granular activated carbon (GAC) regeneration is to remove the adsorbates from the GAC pores and recover the original adsorption capacity of the material. Ideally, regeneration should not adversely alter the porous structure of the GAC or cause loss of material [1, 2]. While thermal, chemical and biological regeneration methods are available for this purpose, thermal regeneration is the most widely used method.

One of the reasons for adopting thermal regeneration is economical, since thermally regenerated GAC costs 60-70% of the virgin material, including transportation and energy costs [2]. Regeneration of GAC can represent up to one third of the costs of replacing the material and it is therefore favored by many water utilities [3]. However, thermal regeneration has disadvantages, such as generation of furnace exhaust gas (off-gas) containing oxidation by-products resulting from the combustion of spent GAC and system fuel. Furthermore, each thermal reactivation cycle causes a loss of 10 – 15% of the GAC adsorption capacity due to surface oxidation. [1, 2, 4]. GAC losses also occur
when contactors are taken out of operation for transportation of the exhausted material to an external reactivation site [2].

Chemical in-situ regeneration is assessed as an alternative regeneration technique since it can potentially shorten the downtime of the GAC contactors during regeneration and minimize GAC losses. In-situ regeneration could also offer novel operation modes for treatment facilities. While GAC is traditionally run to complete exhaustion, in-situ regeneration could allow more frequent reactivation cycles. This could maintain high adsorptive driving forces during treatment and optimize removal of organics from water.

In-situ regeneration could be adopted by water treatment plants to optimize GAC usage for control of natural organic matter (NOM), disinfection by-products precursors and pollutants of emerging concern. Chemical in-situ regeneration displaces the contaminants from the surface of GAC into solution while the GAC contactor is still online. Chemical regeneration must facilitate desorption by modifying the adsorbate molecule, solution property or GAC surface. Ideally, chemical regeneration does not alter GAC surface, since that could reduce the adsorption capacity of the regenerated GAC. However, oxidation of the sorbates is desired; since the wash solution would not require additional treatment if the contaminant is decomposed during regeneration. Successful regeneration of methyl-tert-butyl ether (MTBE)-spent GAC has been achieved using persulfate [5, 6] and Fenton-driven oxidation processes [7, 8]. Hydrogen peroxide activated with iron nanoparticles recovered phenol adsorption capacity of spent GAC up to 4 treatment cycles without significant loss on the GAC sorption capacity [9].

Testing the recovery of sorption capacity requires loading the virgin GAC with a probe organic compound [5-7, 9], unless a spent GAC is obtained from a water treatment
in operation [10, 11]. GAC is typically loaded at high concentrations to demonstrate better depletion of capacity, since higher adsorption capacities are obtained with increasing loading concentrations. However, unrealistically high loading concentrations (Table 4.1) don’t reflect field-operation of GAC and two major concerns arise regarding the use of high loading rates in regeneration studies: i) the adsorption-desorption hysteresis may be concentration dependent and ii) sorbed compounds may interact with compounds (through van der Waals interactions, H-bonding, π-π interactions or electrostatic forces) in the bulk aqueous phase altering the desorption efficiency. The first concern is described as meta-stable adsorption theory [9]. Higher loading rates favor intermolecular competition and change the packing of molecules on the surface, occupying both low- and high-energy sorption sites. Therefore, denser packing of molecules on the surface may favor desorption. This deviation in desorbability can cause a false positive response in the regeneration tests. Secondly, the high loading may enable free molecules to interact with sorbed ones. This interaction can cause multiple layers of adsorption and, depending on the intermolecular interactions between the compounds, it can either favor or hinder desorption (i.e. regeneration efficiency). Although identifying and differentiating the individual mechanisms that are caused by high loading concentrations is a challenging task, they should be taken into account to design loading conditions reflecting environmentally relevant concentrations.

The goal of this project was to evaluate the potential regeneration of granular activated carbon (GAC) using novel, non-thermal, in-situ methods to reduce long-term operational costs of GAC facilities. Specifically, this project focuses on two types of GAC: (i) saturated with natural organic matter and (ii) saturated with micro-pollutants.
The research was designed to screen a few regeneration scenarios and to identify which holds the greatest potential to desorb and destroy the pollutants. Percarbonate has been proposed in this study as an alternative to hydrogen peroxide, since it is more stable than hydrogen peroxide and it does not require activation. Few studies have been conducted using sodium percarbonate but positive results were observed for remediation of soil contaminated with polycyclic aromatic hydrocarbon [12].

4.2 Material and methods

4.2.1 Field-spent GAC samples

Two field spent GACs were used in this work: (i) Lignite, coconut and bituminous coal GACs spent with natural organic matter (NOM) and (ii) coconut derived GAC spent with micro-pollutants ethylene-dibromide (EDB) and 1,2-Dibromo-3-chloropropane (DBCP). Virgin coconut based GAC was used as a control samples in (i). GACs were received from full and pilot scale water treatment plants and soaked in distilled water for a minimum of 24 hours before regeneration experiments.

4.2.2 Regeneration Experiments

Regeneration experiments were performed using a custom-made column (Figure 4.1, diameter equal to 2.5 cm and length equal to 25 cm) designed to regenerate the GAC without crushing it prior to regeneration. A custom conical Teflon insert designed to control the flow of the regeneration solutions and ensure that the GAC bed remained fluidized during the experiments. GAC was packed in the column (bed height of 4 cm)
and after that a regeneration solution prepared using reagent-grade chemicals (Sigma Aldrich, St Louis, MO) was recirculated in up flow mode for one hour. Table 4.2 shows the experimental conditions investigated (Regen 1 to 7). Experiments were divided in two phases: (i) Regen 2 and 3 were investigated for multiple GACs spent with NOM and (ii) all treatments were applied to the same GAC spent with EDB and DBCP. A percarbonate-based stain remover (Oxy-clean™) was used as a commercially available alternative to percarbonate. When iron nanoparticles were used, a solution containing 500 ppm as iron (FeCl$_3$.6H$_2$O, Sigma-Aldrich) was recirculated prior to adding the regeneration solution [9]. After one hour, the GAC was thoroughly washed with distilled water and used for bench-scale adsorption experiments. The GAC remained intact (visual inspection) after the regeneration process and subsequent pH values during adsorption experiments remained constant. Glassware used was previously cleaned for 24 hours in 10% hydrochloric acid, rinsed with distilled water and heated to 500°C in a muffle furnace.

4.2.3 Adsorption experiments

Adsorption experiments for (i) were performed using Colorado River (CAP) water. Different quantities of GA, varying from 50 to 1000 mg, were added to clean amber vials with 30 mL of Colorado River water. A 3-day sorption experiment was then performed on a shaker table at room temperature, after which samples were analyzed for DOC. All adsorption experiments for (ii) were performed using groundwater from the water treatment site. Groundwater was shipped from the treatment site to ASU and spiked with
EDB and DBCP at concentrations higher than those encountered at the field site (100 µg/L for both EDB and DBCP). Characteristics of EDB and DBCP are presented in Table 4.3. A 3-day sorption experiment was performed for those samples on a shaker table at room temperature.

4.2.4 Analyses

DOC analyses were performed using a Shimadzu TOC-VCSH analyzer (high temperature combustion at 720°C, CV < 2%; non-dispersive infrared detection) (Shimadzu Corp., Tokyo, Japan). All samples were filtered through pre-cleaned 0.45 µm glass fiber filters (GF/F, Whatman GE). Analyses of EDB and DBCP were performed by an outside laboratory. Samples were stored at 4°C and shipped overnight in refrigerated containers for analysis.

4.3 Results and Discussion

4.3.1 Regeneration experiments (i)

Results for (i) describe the experiments conducted to evaluate the recovery capacity of two GACs spent with NOM. Results for DOC adsorption of the GACs treated with Regen 2 (sodium persulfate) are presented in Figure 4.2. Recovery of DOC sorption capacity after regeneration varied for each type of GAC and bituminous coal based GAC had the greatest recovery in adsorption capacity at certain GAC doses. Lignite- and coconut-based GAC were adversely affected by the treatment with persulfate, as seem by
the increase in DOC values of the surface water upon adsorption experiments. At a GAC
dose equal to 7.5 g/L, the remaining DOC fraction in solution was 2.5, i.e., the surface
water DOC after adsorption was 2.5 times higher than its initial value. No recovery in
adsorption capacity was observed for the coconut and coal-based GAC, suggesting that
persulfate was not successful at accessing the GAC pores and oxidizing the adsorbate.

Different results were observed when the same GAC types were treated with
sodium percarbonate. Percarbonate had an adverse impact on lignite, coal and coconut-
based GAC. DOC values in the surface water after adsorption were up to two times
higher than the initial DOC, for a GAC dose of 7.5 g/L. This indicates that the surface of
these GACs was oxidized by the percarbonate, causing the increase in DOC observed
upon adsorption.

Since regeneration of GAC involves diffusion into the GAC of the regeneration
solution or desorption of the pollutant from the surface into the pore and bulk solution,
GAC properties such as particle size, pore size distribution and surface area may affect
the regeneration efficiency [13, 14]. In addition, commercially available GACs have
different porosity, reactivity and metals content, which could all influence regeneration
efficiency. Similar conclusions have been observed previously for thermal regeneration
processes, when different GAC types resulted in different levels of recovery of
adsorption capacity [15]. Results indicate that the regeneration process requires
optimization to improve the amount of recoverable sorption capacity. Improving the
regeneration process could also help selecting the most adequate GAC for in-situ
regeneration.
4.3.2 Regeneration experiments (ii)

Figure 4.4 shows concentrations of EDB after adsorption tests. Reduction of EDB concentrations was observed as dose of virgin GAC increased and the lowest concentration was around 5µg/L of EDB when 0.4 g/L of virgin GAC was used. No recovery in adsorption capacity of EDB was observed. Adsorption capacity of the regenerated GACs was similar to the adsorption capacity of the spent GAC, which means that the treatments were not effective for this type of GAC.

Figure 4.5 shows concentrations of DBCP after adsorption tests with the regenerated GAC. Again, no recovery of adsorption capacity of the GACs was observed, except for the GAC treated with hydrogen peroxide activated with iron nanoparticles. In this case, DBCP concentrations were reduced to up to 25 µg/L for 0.4 g/L of GAC dose. The virgin GAC final concentration of DBCP was 5 µg/L under the same dose conditions (0.4g/L). The slight recovery of adsorption capacity with the hydrogen peroxide treatment indicates that, potentially, this treatment could be improved (e.g., use of higher concentrations of hydrogen peroxide or longer reaction times) to increase recovery of adsorption capacity of GAC spent with DBCP.

All regeneration solutions were monitored for their pH values before and after the regeneration experiments, as this could influence scale-up of the regeneration technology. Results are presented in Table 4.4. The initial and final pH levels were similar throughout the regeneration step, except for the acid wash regeneration (Regen 5). During the acid wash regeneration the pH increased from 3.44 to 6.43, presumably as the GAC adsorbed protons.
Regeneration solutions were also analyzed for EDB and DBCP, in order to verify if they were desorbed from the GAC during the regeneration experiments. Results presented in Table 4.4 show that DBCP was not detected in any of the regeneration solution samples. EDB was detected at low concentrations in the solutions from Regeneration Experiments 2, 5 and 7. These are positive results and show that the oxidation process could be responsible for not only desorbing but also by oxidizing EDB and DBCP. Further studies would need to be conducted to evaluate the mechanisms involved in oxidation of EDB and DBCP by the reagents used during regeneration.

4.4 Conclusions

Literature existing on in-situ regeneration of GAC does not provide a standardized test to evaluate the efficiency of regeneration or to evaluate the adsorption capacity of the regenerated GAC. This study indicates that bench scale testing of in-situ regeneration need to be improved, particularly on the way the adsorption tests are conducted. Bench-scale tests were proposed, as most studies adopt these [5, 16]. However, the experiments conducted in (i) resulted in higher TOC on the SW samples after the 3-day adsorption period. This indicates that the GAC was either oxidized by the oxidants used or that NOM was still being desorbed when the tests were carried out, despite the GAC being thoroughly washed with DI water before adsorption. Based on that, column adsorption tests seem more appropriate to evaluate adsorption after regeneration, such as those presented in [9]. In-situ regeneration of GAC is case-specific and more improvement on the regeneration technique would be necessary to apply it to full-scale water treatment.
It may be possible to improve the regeneration capacity of spent GAC through a different GAC selection process. It is likely the field-spent GACs received were selected for its high adsorption capacity of NOM and of the micro-pollutants EDB and DBCP but not selected for optimal regeneration conditions. Regeneration of GAC involves diffusion into the GAC of the regeneration solution and / or desorption of the pollutant from the surface into the pore and into the bulk solution. For this purpose, a more macroporous GAC may be more effective to improve the kinetics and mass transfer of the chemicals. Smaller GAC particle sizes could mean that the regeneration solutions would take less time to diffuse to the GAC pores and oxidize and/or desorb the adsorbates. These GAC properties may not be ideal for single use GAC applications, but may be better in development of a GAC that is regenerated in situ. Similar conclusions were observed also for thermal regeneration of spent GAC [15]. In this study, a bituminous-coal based GAC was the commercially available GAC with best regeneration performance for NOM, since both experiments focusing on recovery of NOM sorption capacity had a positive impact on this type of GAC.
4.5 Figures and Tables

Table 4.1 – Loading conditions encountered in the literature to evaluate in-situ chemical regeneration of GAC.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Probe Compound</th>
<th>Batch/Column</th>
<th>Loading conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Okawa et al. 2007 [17]</td>
<td>TCE</td>
<td>Batch</td>
<td>2 mg TCE/g GAC</td>
</tr>
<tr>
<td>Liang et al. 2009 [18]</td>
<td>TCE</td>
<td>Batch</td>
<td>10 mg TCE/g GAC</td>
</tr>
<tr>
<td>Alvarez et al. 2004 [19]</td>
<td>Phenol</td>
<td>Batch</td>
<td>0.06 to 0.6 g phenol/g GAC</td>
</tr>
<tr>
<td>Huling et al. 2009 [8]</td>
<td>Phenol</td>
<td>Batch</td>
<td>1000 mg/L of phenol</td>
</tr>
<tr>
<td>Tang et al. 2013 [20]</td>
<td>Phenol</td>
<td>Batch</td>
<td>5000 mg/L, varying GAC mass</td>
</tr>
<tr>
<td>Bercic et al. 1996 [21]</td>
<td>Phenol</td>
<td>Column</td>
<td>5-30000 mg/L</td>
</tr>
<tr>
<td>Bach et al. 2008 [22]</td>
<td>Phenol</td>
<td>Column</td>
<td>1000 mg/L of phenol</td>
</tr>
<tr>
<td>An-Chiu et al. 2013 [9]</td>
<td>Phenol</td>
<td>Column</td>
<td>10 - 1000 mg/L phenol</td>
</tr>
<tr>
<td>Liu et al. 2004 [23]</td>
<td>PCP</td>
<td>Batch</td>
<td>20 mg PCP/g GAC</td>
</tr>
<tr>
<td>Newcombe and Drikas 1997 [10]</td>
<td>NOM</td>
<td>Column</td>
<td>Field-spent</td>
</tr>
<tr>
<td>Huling et al. 2012 [25]</td>
<td>MTBE</td>
<td>Column</td>
<td>190 - 820 mg/L MTBE</td>
</tr>
<tr>
<td>Huling et al. 2011 [5]</td>
<td>MTBE</td>
<td>Batch</td>
<td>44.9 mg MTBE/kg GAC</td>
</tr>
<tr>
<td>Hutson et al. 2012 [6]</td>
<td>MTBE</td>
<td>Batch</td>
<td>2 mg/L of MTBE, varying GAC mass</td>
</tr>
<tr>
<td>Huling et al. 2007 [7]</td>
<td>MTBE</td>
<td>Batch</td>
<td>0.04 mg MTBE/g GAC</td>
</tr>
<tr>
<td>Yang et al. 2015 [26]</td>
<td>Methyl Bromide</td>
<td>Batch</td>
<td>0.1 mg MB/g GAC</td>
</tr>
<tr>
<td>Weng 2008 [27]</td>
<td>Methyl Bromide</td>
<td>Column</td>
<td>Field-spent</td>
</tr>
<tr>
<td>Bach et al. 2008 [22]</td>
<td>Ethylene Glycol</td>
<td>Column</td>
<td>6400 mg/L EG</td>
</tr>
<tr>
<td>Wang et al. 2009 [28]</td>
<td>DSD Wastewater Acid</td>
<td>Batch</td>
<td>Field-spent</td>
</tr>
<tr>
<td>Qu et al. 2009 [29]</td>
<td>Orange 7 Dye</td>
<td>Column</td>
<td>50 mg/L AO7</td>
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Table 4.2 - Regeneration conditions. (i) applied Regen 2 and 3 for different GACs and (ii) applied all treatments to the same GAC.

<table>
<thead>
<tr>
<th>Treatment ID</th>
<th>Fe-NP Concentration (mg/L)</th>
<th>Initial Hydrogen Peroxide Concentration (M as H₂O₂) (g/L)</th>
<th>Initial Persulfate Concentration (M as H₂O₂) (g/L)</th>
<th>Initial Percarbonate Concentration (M as H₂O₂) (g/L)</th>
<th>Initial Stain remover (Oxy Clean™ Concentration)</th>
<th>pH</th>
<th>React. Time (min)</th>
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<tbody>
<tr>
<td>Regen 1</td>
<td>500</td>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Regen 2</td>
<td>--</td>
<td>--</td>
<td>40</td>
<td>--</td>
<td>--</td>
<td>&gt;11</td>
<td>60</td>
</tr>
<tr>
<td>Regen 3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.25</td>
<td>--</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Regen 4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.25</td>
<td>--</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Regen 5</td>
<td>Acid wash: DI water with H₂SO₄, pH&lt;3</td>
<td>&lt; 3 (H₂SO₄)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Regen 6</td>
<td>Base wash: DI water with NaOH, pH&gt; 11</td>
<td>&gt; 11 (NaOH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Regen 7</td>
<td>Neutral wash: DI water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
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Table 4.3 – Characteristics of the micro pollutants EDB and DBCP

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>C₀ (μg/L)</th>
<th>Solubility in water (20°C) (g/L)</th>
<th>Log Kow</th>
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<tbody>
<tr>
<td>EDB</td>
<td>100</td>
<td>40</td>
<td>135</td>
</tr>
<tr>
<td>DBCP</td>
<td>100</td>
<td>1.23</td>
<td>2.43</td>
</tr>
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</table>
Table 4.4– pH of regeneration solutions used in (ii)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH initial</th>
<th>pH final</th>
<th>EDB (μg/L)</th>
<th>DBCP (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regen 1</td>
<td>2.66</td>
<td>2.69</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 2</td>
<td>2.61</td>
<td>2.11</td>
<td>2.3</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 3</td>
<td>10.77</td>
<td>10.87</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 4</td>
<td>11.22</td>
<td>11.23</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 5</td>
<td>3.44</td>
<td>6.43</td>
<td>0.03 (estimated)</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 6</td>
<td>11.60</td>
<td>11.16</td>
<td>not detected</td>
<td>not detected</td>
</tr>
<tr>
<td>Regen 7</td>
<td>7.60</td>
<td>7.41</td>
<td>0.03 (estimated)</td>
<td>not detected</td>
</tr>
</tbody>
</table>
Figure 4.1 – Experimental setup used in the regeneration experiments.
Figure 4.2 – DOC remaining fraction ($C/\left(C_0\right)$) for adsorptions tests using GAC treated with Regen 2 (sodium persulfate). Results were plotted against concentration of GAC (g/L).
Figure 4.3 - DOC remaining fraction (C/C₀) for adsorptions tests using GAC treated with Regen 3 (sodium percarbonate). Results were plotted against concentration of GAC (g/L).
Figure 4.4 – Concentrations of EDB after the adsorption test, plotted against concentration of GAC (g/L). Initial theoretical concentration of EDB is 100 μg/L.

Figure 4.5 – Concentrations of DBCP after the adsorption test, plotted against concentration of GAC (g/L). Initial theoretical concentration of DBCP is 100 μg/L.
4.6 References


CHAPTER 5

INFLUENCE OF LOW MOLECULAR WEIGHT POLYDADMAC ON NDMA FORMATION

Research Question 4: Is NDMA formation dependent on polyDADMAC molecular weight?

5.1 Introduction

N-nitrosodimethylamine (NDMA) has been identified as a disinfection by-product (DBP) of greater concern than the current regulated trihalomethanes and haloacetic acids. NDMA has a $10^{-6}$ risk of cancer based on 0.6 ng/L exposure levels [1]. NDMA exposure has demonstrated to cause liver, kidney and lung cancer in adult mice [2]. NDMA is currently a probable human carcinogen included in the Contaminant Candidate List 4 (CCL4) and it should undergo regulation for establishment of a drinking water standard by the U.S. EPA [1]. So far, the State of California established a notification limit of 10 ng/L of NDMA [3] and Canada adopted a maximum acceptable concentration of NDMA of 40 ng/L [4].

NDMA is a low viscosity liquid, highly soluble in water, fat and organic solvents. It is photosensitive and it undergoes photolytic reduction [2]. NDMA formation occurs mostly from the reaction of organic precursors with chloramine, dichloramine being the major specie contributing to its formation [5]. Dichloramine is believed to be the dominant chloramine specie involved in NDMA formation as a result of the reaction with amine precursors, while monochloramine does not play a significant role in NDMA
formation in surface waters [6-8]. Formation of NDMA upon chlorination has been described as occurring through an intermediate compound, unsymmetrical dimethylhydrazine (UDMH), formed as the result of a nucleophilic substitution reaction between dichloramine and dimethylamine (DMA). UDMH is then oxidized with oxygen to form NDMA [5, 6, 9, 10]. However, DMA is not a significant precursor in drinking water or in wastewater impacted water sources and cannot account for all the NDMA formed [11]. Compounds with secondary and tertiary amines account for the majority of NDMA precursors in these water sources, although quaternary amines also yield NDMA upon chloramination [5, 12-14]. Secondary and tertiary amines have similar NDMA yields upon chloramination, around 2% [13, 14]. A special group of tertiary amine compounds containing an aromatic functional group in the β position (in the N) exhibits higher NDMA formation during chloramination. Pharmaceutical compounds such as ranitidine contain this functional group and are significant NDMA precursors, showing NDMA yields up to 90% [11, 13]. The mechanism through which this reaction occurs is not yet clear, it is likely that the reaction occurs without a secondary amine intermediate [13]. Quaternary amines show much lower NDMA yield (0.2%) but are found in personal care products, polymers and resins (e.g., ion exchange resins) used during water treatment [13, 15].

Water quality parameters also impact NDMA formation. Maximum formation of NDMA occurs at pH 7 to 8 [2] and previous research has shown that the chlorine to ammonia ratios (Cl₂:NH₃) impact formation of dichloramine and therefore NDMA formation [6, 10, 16]. Chloramination increases formation of NDMA, but chlorination (using hypochlorite) can also form NDMA at a lower rate from the reaction with
secondary amines, in absence of ammonia [6]. Monochloramine (NH₂Cl) and dichloramine (NHCl₂) are found in solution when chloramines are formed at Cl:N molar ratios less than 1.5 (Equation 5.1).

\[
2NH₂Cl + H^+ \leftrightarrow NHCl₂ + NH₄^+ \quad \text{Equation 5.1}
\]

Research has shown that dichloramine forms significantly more NDMA than monochloramine. A nucleophilic attack takes place in the unprotonated dichloramine secondary amines, forming a chlorinated intermediate product, Cl-UDMH [5, 9]. NDMA formation occurs at slow reaction rates and can happen for days, therefore accumulation of NDMA is expected in the distribution system [10, 13, 17]. Direct addition of chlorine to waters containing ammonia results in high NDMA formation and therefore should be avoided [16]. Maximum NDMA formation was observed at Cl₂:NH₃ values around 1.7, i.e., near breakpoint. Ratios above breakpoint decreased NDMA formation, since free chlorine was the dominant specie [9].

Advanced treatments such as GAC or oxidation can be effectively used to remove wastewater-derived NDMA precursors [18]. NDMA precursors are not well known and characterized in the available literature yet. It seems that most precursors are wastewater-derived; pharmaceuticals such as ranitidine and methadone, among others, have also been identified as contributors to NDMA formation [13, 19].

5.1.1 PolyDADMAC and NDMA formation

The use of polyDADMAC as a coagulant aid has been linked to NDMA formation and indicated as the main source of NDMA precursors [20]. While disinfectants can oxidize polymer precursors, they can also lead to the formation of regulated and
unregulated DBPs. Park et al (2015) demonstrated that chloramination of polymer (polyamine) increased NDMA formation and also the concentration of DMA in the water, caused by oxidation of the polymer chain due to exposure to free chlorine before addition of ammonia in the chloramination. Even though polyDADMAC increases NDMA formation in the water treatment, water utilities still need to use cationic polymers to achieve the required NOM removal and comply with other water quality regulations, such as turbidity. PolyDADMAC has also been used as a filter aid due to its lower MW and chance of decreasing filter run time, when compared to commonly used polyamines [21]. Current guidelines for use of polyDADMAC include compliance with the NSF Standard for drinking water chemicals, which determines a maximum use level of 15 mg/L of polyDADMAC and maximum monomer (DADMAC) residual of 50 ppb. The proposed method for quantification of DADMAC residual uses high performance liquid chromatography (HPLC) with a ultraviolet light (UV) detector [22]. Total allowable concentration of polyDADMAC is 5 mg/L [22]. Maximum dimethylamine (DMA) and DADMAC residual contents are also established by the NSF standard as well as the AWWA standard for polyDADMAC polymers. AWWA standard also requires the supplier to provide an estimate of the impurities based on the DADMAC monomer content in the polymer for each batch of the polymer [23]. Future regulations will likely increase the necessity of strategies to reduce and remove NDMA precursors prior to chloramination. Therefore, understanding NDMA formation resulting from the use of polyDADMAC is crucial to optimize and improve its use. Moreover, reducing the contribution of DBP precursors to the water treatment is essential to guarantee safe levels of exposure to DBPs.
Chloramination of the backwash water from filters operated with water coagulated with polyDADMAC showed high NDMA formation [20]. Different NDMA FP concentrations have been quantified upon chloramination of the same polymer obtained from different sources [24]. To this date, no compound has been identified as the single contributor to polyDADMAC-derived NDMA formation. One of the potential mechanisms described to explain NDMA formation is based on the polymer-bound tertiary amines groups. Pre-treatment of the polymer with alkylating agents could convert tertiary amine groups to quaternary amines, leading to up to 70% reduction of NDMA formation [25].

PolyDADMAC was the first cationic polymer approved for use in water treatment by the Food and Drug Administration (FDA) [26]. PolyDADMAC is a cationic polymer with a quaternary ammonium function, which is highly hydrophilic and results in a polymer that is water soluble and extensively hydrated [27]. Figure 5.1 shows the polyDADMAC structure with the quaternary ammonium ring in the center [28].

Dimethylamine (DMA) is a NDMA precursor [6] and one of the compounds used in polyDADMAC synthesis [27]. Manufacturing of polyDADMAC starts by the reaction of allyl chloride and DMA, forming DADMAC. DADMAC undergoes cyclopolymerization, which is responsible for forming the ring structures of polyDADMAC. Park et al [18] dialyzed samples of polymer to reduce DMA residuals in the polymer and observed that even though DMA concentrations and subsequent NDMA formation were reduced in the treated polymer, NDMA formation was not eliminated by the polymer purification. This is an indication that compounds of low molecular weight, i.e. which were not removed by dialysis, can be responsible for polymer-related NDMA
formation. NDMA formation can therefore be a product of the chloramination of polymer impurities as well as of chloramination of the polymer itself [18]. Park et al (201) hypothesized that NDMA formation from chloramination of polyDADMAC mechanism involves Hoffman elimination, a mechanism where an amine reacts to create a tertiary amine and an alkene. Through this mechanism, the quaternary ammonium group in the polymer is degraded to a tertiary amine. DMA is released during this process, causing NDMA formation [18].

Diallyldimethylammonium chloride (DADMAC), the polyDADMAC monomer, is a product of the reaction between dimethylamine (DMA) and allyl chloride. Depending on the desired polymer purity, different qualities of DADMAC can be produced, namely: (i) solid DADMAC; (ii) purified aqueous monomer solution without sodium chloride and (iii) aqueous monomer solution with sodium chloride [29]. PolyDADMAC polymerization occurs mainly through copolymerization in a process denominated cyclopolymerization [26, 29, 30]. The polymerization mechanism, an alternating intramolecular chain propagation, has been extensively investigated and it leads to five-membered ring structures. The polymer may still contain monomer units if only one double bond reacts; the latter acting as the beginning point of branching in the polymer chains [29, 30]. The extent of chain branching depends on the purity of the reagents used for the monomer and polymer synthesis. Laboratory synthesized polymer will have less chain branching than technical polymers due to the impurities present in the technical monomer and during the process [26, 29]. The presence of methyl triallyl ammonium chloride (MTAAC), for instance, has been found to produce crosslinked polymers that are insoluble in water [29, 30]. For this reason, knowledge of the portion of branched
structures is important to the characterization of the polymer structure [30]. Characterization of the molecular weight distribution of the polymer is a challenging task, since the polymer should not contain impurities and the polymer concentration needs to be accurately measured, which is challenging when using commercial solutions [30]. Techniques to control molecular weight of polyDADMAC include adding a crosslinking agent at the end of the polymerization [28].

Coagulation using polyDADMAC relies on the cationic charges located among the quaternary ammonium groups on the polymer backbone structure and on ion pairing with negatively charged NOM. Zeng et al (2016) [25] showed that altering the backbone or converting tertiary ammonium groups to quaternary ammonium groups in the polymer by addition of an alkylating step could reduce NDMA formation up 70%. However, the solvent wash proposed by the authors is not feasible for full scale application, given the use of costly and polluting solvents such as methanol in the process.

This work did not focus on the mechanistic investigation behind the higher reactivity of the low MW fraction of polyDADMAC. However, some hypothesis can be indicated from the literature:

(i) Higher concentration of residual materials in the filtrate: commercial polymer solutions contain residuals of monomer, DMA and oligomer, which may contribute to higher NDMA formation [18]

(ii) Lower MW of the polymer available in the filtrate fraction could mean higher availability of chain ends to react with monochloramine [18]. Park et al (2009) have shown that NDMAFP depends more on the DMA released due to
polymer degradation by monochloramine than to the DMA existing in the polymer solution. More availability of chain ends would increase the release of DMA upon chloramination.

(iii) Higher polymer branching in the low MW fraction. Wandrey and Gortiz (1992) emphasize the importance of the extent of polymer branching to the characterization of the polymer, rather than focusing on molecular weight alone. To prove this hypothesis, it would be necessary to investigate the reactivity of the linear and branched fractions of the polymer through a separation study, such as the ultracentrifugal method proposed by the authors [30].

5.2 Experimental Approach

Ultrafiltration is proposed in this work to remove low MW impurities from polyDADMAC. As proposed, ultrafiltration could be an alternative to the solvent wash [25] shown to separate the low MW fraction from polyDADMAC. As hypothesized, this purification process would reduce NDMA formation during treatment. Ultrafiltration has not been previously used to assess the contribution of low MW compounds in polyDADMAC solutions to formation of NDMA but it has been used before to characterize NDMA precursors in natural effluent organic matter by Mantas and Sedlak (2008), Krauss et al (2010), Wang et al (2013) and Chen et al (2014). Chen et al (2014) demonstrated that low MW NOM (<1kDa) were the major contributors to NDMA
formation in tertiary effluent, while high MW NOM (>10kDa) was the fraction that accounted for most of the NDMAFP in secondary effluent. This observation showed how the efficient removal of high MW NOM compounds during tertiary treatment increased the significance of low MW compounds to the NDMA formation in the tertiary effluent. Wang et al (2013) attributed the high NDMAFP of NOM smaller than 1kDa to the presence of more functional nitrogen groups in this fraction, which represented more than 60% of the total DON in the surface water used [31].

The goal of this work is to evaluate the contribution of low MW compounds to NDMA formation potential resulting from chloramination of polyDADMAC. With that, the objective of this work is to quantify and understand the contribution of high and low molecular weight fractions of polyDADMAC to the total NDMA formation post-sedimentation. The research question “Is NDMA formation dependent on polyDADMAC molecular weight?” is investigated in this chapter. The research hypothesis investigated is that the lower MW fraction of polyDADMAC is more reactive than the higher MW fraction, i.e., it has a higher NDMAFP and therefore has a bigger contribution to NDMA formation post-sedimentation.

5.3 Material and Methods

5.3.1 Polymer samples: Samples from polyDADMAC (C358, 20% active polymer, SNF Group, USA) were obtained from a water treatment plant in the Phoenix metropolitan area and stored at 4°C until use. MW distribution for this polymer is not available by the manufacturer. Dilutions of the polymer for the ultrafiltration were
prepared in nanopure water and using glassware cleaned and ashed in a muffle furnace to remove organic contaminants.

5.3.2 Ultrafiltration experiments. Ultrafiltration experiments (UF) were performed following the procedure presented by Esparza-Soto et al (2006) [32]. PolyDADMAC was diluted to a 1g/L solution of active polymer and buffered with 10mM borate buffer (pH = 8). UF was performed in 400 mL stirred cell units (Amicon, Massachusetts) pressurized with nitrogen gas at 40 psi during experiments. Regenerated cellulose UF membranes (Ultracel, 760mm, Millipore) with molecular weight cutoff (MWCO) equal to 1kDa, 3kDa and 10kDa molecular weight cutoff (MWCO) were pre-conditioned according to the manufacturer recommendations. Membranes were soaked overnight in nanopure water, thoroughly rinsed with nanopure water, soaked in 0.1M sodium hydroxide, thoroughly rinsed with water and again rinsed with nanopure water for 15 minutes at 55 psi. After that, 150mL of the 1g/L polyDADMAC solution was filtered and 5 aliquots of 25 mL and the remaining retentate were collected. Samples were kept at 4°C until analysis.

5.3.3 DOC and TDN analysis. Dissolved organic carbon (DOC) and Total Dissolved Nitrogen were analyzed by high temperature combustion using a Shimadzu TOC/TDN Analyzer (Shimadzu Corp, Tokyo, Japan). For the UF experiments conducted following the procedure presented by Esparza-Souto et al (2006), DOC values were corrected by membrane rejection following Equation 5.2 [32, 33]

\[
\ln C_p = \ln (p \cdot C_{r0}) + (p - 1) \cdot \ln F
\]

Equation 5.2
$C_p = \text{permeate concentration at } F \text{ (mgC/L or mgN/L)}$;
$p = \text{permeate coefficient};$
$F = \text{Fraction of the initial sample remaining in the UF cell};$
$C_{ro} = \text{initial concentration passing through the filter}$

Coefficients were determined with plot of Ln$C_p$ versus Ln$F$, where the permeate coefficient is determined by the slope and the initial concentration $C_{ro}$ is determined by the y-intercept. A mass balance was performed with the different fractions, as presented in Equation 5.3.

$$V_{\text{retentate}} * C_{\text{retentate}} + \sum_{i}^{n} (V_{\text{filtrate}} * C_{\text{filtrate}}) = V_0 * C_{r0} \quad \text{Equation 5.3}$$

Where:

$V_{\text{retentate}} = \text{Volume of the retentate}$
$C_{\text{retentate}} = \text{Concentration of the retentate}$
$n = \text{number of filtrate fractions}$
$V_{\text{filtrate}} = \text{Volume of filtrate}$
$C_{\text{filtrate}} = \text{Concentration of filtrate}$
$V_0 = \text{total initial volume of sample}$

5.3.4 Validation of ultra-filtration for polyDADMAC separation.

The next phase of this work consisted in validating the UF method for molecular weight separation of polyDADMAC. Initially, a control test was conducted filtering nanopure
water (DOC = 0.14 mgC/L) through the 3 kDa membrane to confirm that the membrane used did not leach DOC after pre-treatment. Nevertheless, it was still necessary to validate the UF experiments for the polyDADMAC solution to confirm that no polymer would be retained in the membrane. For this phase, 1 kDa and 3 kDa membranes were adopted to perform UF of a 1g/L solution of active polymer, collecting 5 fractions of the filtrate [32]. DOC and TDN were measured and values were corrected by the membrane rejection factor [33]. A mass balance was performed between the different fractions. Experiments for membranes with MWCO equal to 1kDa and 10kDa were conducted in triplicate.

5.3.5 NDMA formation potential

NDMA formation was evaluated under formation potential conditions (FP) following the procedure presented by Hanigan et al (2012) [34]. A summary of the NDMAFP method is presented in Table 5.1 and a detailed description of the NDMAFP procedure is presented in Appendix B. For each test, a fresh monochloramine solution was prepared on the same day by adding a sodium hypochlorite solution to a ammonium chloride solution buffered with 1M borate (pH = 8). Concentration of the ammonium chloride solution was determined based on the measured concentration of the chlorine solution (HACH colorimetric free chlorine method, DR 5000) to result in a N:Cl molar ratio of 1:2. The monochloramine solution was allowed to react in the dark for 1h before used for the NDMAFP. Samples for the NDMAFP were prepared by adding the desired concentration of polymer (from a stock solution) to 500mL of nanopure water buffered at pH 8 with 10mM borate. Monochloramine was dosed at 18 mgCl₂/L based on the
measured concentration of the monochloramine solution (Monochlor F Reagent, HACH) [34]. Samples were allowed to react at room temperature for 72 hours before they were quenched with 5mM of ascorbic acid. After the reaction was stopped, 200 ng/L of NDMA-d6 isotope (Cambridge Isotopes, MA) was added to the samples. Samples were processed by solid phase extraction (SPE) following a protocol similar to EPA Method 521, described elsewhere [34]. SPE cartridges purchased from Restek (Restek Corporation, Inc) were used for the experiments described. NDMA adsorbed in the SPE cartridges was eluted with 5mL of DCM (HPLC grade, Fisher Chemicals) and dried using sodium sulfate cartridges (BondElut, Agilent). Samples were concentrated to 1 mL final volume using high purity nitrogen gas. Samples were analyzed by gas chromatography/mass spectrometry (GC-MS) and the system was operated in positive chemical ionization mode using ammonia as the reagent gas and helium as a carrier gas. NDMA-d6 internal standard was used as the calibration internal standard. NDMA yields from FP tests don’t reflect NDMA formation under typical treatment conditions but rather reflect precursor loading [13, 35]. The higher yield from FP tests is desired for this work since the major focus is on the identification of precursors and on the formation potential from polyDADMAC.

5.3.6 NDMA Uniform Formation Conditions (UFC):

Two Uniform Formation Conditions (UFC) tests were performed in this work. UFC1 is based upon [35], where chlorine is added to samples to achieve a free-chlorine residual of ~2.5 mg/L as Cl₂ after 3 min, followed by post-chloramination at a Cl₂/NH₃-N weight ratio of 4.75/1 mg/ mg. The samples are held for 3 days at pH 8 at room
temperature or at 25°C. The second UFC method (UFC2) is a modified procedure from [35], where chlorine is added at a 2.5 mg/L as Cl₂ dose and ammonia is added within 30 sec to be at a Cl₂/N weight ratio of 4.75:1. Free chlorine contact time is kept low (i.e., 30 sec) to avoid destruction of nitrosamine precursors by the chlorine. Samples are held for 72 hours at pH 8 at room temperature or at 25°C, after which they were quenched with 5 mM of ascorbic acid. After the reaction was stopped, 200 ng/L of NDMA-d6 isotope (Cambridge Isotopes, MA) was added to the samples. Samples were processed by solid phase extraction (SPE), following the same procedure described above.

5.3.7 Validation of NDMA FP and SPE methods.

The second phase of this work consisted in validating the NDMAFP and SPE methods to determine their intra and cross-university adequacy and reproducibility to determine NDMAFP from polyDADMAC. Samples of the polymer used in this work were shipped to Curtin University in Australia and both laboratories conducted NDMAFP tests using similar conditions, adding 10 mg/L of active polymer in nanopure water and proceeding with the NDMAFP tests and SPE. Furthermore, two SPE cartridges used for EPA Method 521 and supplied by different companies (Restek and UTC) were compared to quantify their adjustability to a real water matrix. For that, a secondary wastewater effluent, collected after the clarifiers at a wastewater treatment plant in the Phoenix Metropolitan area, was used. Triplicate samples of the secondary effluent were extracted, as well as triplicate samples of the same secondary wastewater effluent spiked with 10 mg/L of active polymer. The objective was to verify if the presence of polyDADMAC in solution could impact the SPE and NDMA quantification. Samples
were spiked with 200 ng/L labeled NDMA-d6 isotope for NDMA quantification and all samples were extracted in triplicate for both cartridges (resulting in a total number of 12 samples), following the SPE method described in this chapter.

5.3.8 Contribution of low molecular weight polyDADMAC to post-sedimentation NDMA formation potential

Contribution of low MW polyDADMAC was quantified based on Equation 5.4, developed from a similar model presented elsewhere [24]. The scenario described is for surface water from the Central Arizona Project (CAP) coagulated with polyDADMAC and aluminum sulfate. Equation 5.4 was developed to estimate the increase of NDMAFP in the settled coagulated water as a function of the low (<10kDa) MW fraction in polyDADMAC. Empirical NDMAFP values for the surface water and removal of NDMA precursors post sedimentation were adopted from Hanigan et al (2015) [24].

\[
\begin{align*}
\text{NDMAFP}_{\text{post-sed}} &= \text{NDMAFP}_{\text{SW}} + (1 - \eta_{\text{sed}})C_{cpDMC}[R_{LM}X_{LM} + R_{HM}(1 - X_L)] \\
\end{align*}
\]

Equation 5.4

Where:

\(\text{NDMAFP}_{\text{post-sed}}\) = NDMA formation potential in the settled water

\(\text{NDMAFP}_{\text{SW}}\) = NDMAFP of CAP surface water

\(\eta_{\text{sed}}\) = removal during sedimentation
\[ C_{DPDMC} = \text{dose dependent concentration of } C \text{ in polyDADMAC (mgC/mg active polyDADMAC)} \]

\[ R_{LM} = \text{reactivity of low molecular weight polyDADMAC precursors} \]

\[ (\text{ngNDMAFP/mgC}) \]

\[ X_{LM} = \text{percentage of low MW fraction} \]

\[ R_{HM} = \text{reactivity of high molecular weight polyDADMAC precursors} \]

\[ (\text{ngNDMAFP/mgC}) \]

\[ R_{LM} \text{ and } R_{HM} \text{ were based on the results of ultrafiltration of polyDADMAC using the 10kDa membrane. Carbon concentration of the polymer was measured as DOC, 0.57 ± 0.2 mgC/mg active polymer. } \eta_{sed} \text{ is an empirical value based on [24], which demonstrated that one third of the NDMA precursors in polyDADMAC were not removed after sedimentation. NDMAFP}_{SW} \text{ was determined previously, 15 ngNDMAFP/L [24]. } X_{LM} \text{ depends on the polymer MW distribution, not available by the manufacturer (SNF Group, USA).} \]

5.4 Results and Discussion

5.4.1 Comparison of NDMA Formation Potential and Uniform Formation Conditions methods

NDMA yield of two different UFC methods against one FP method were compared using polyDADMAC (C358, SNF). Polymer was dosed at the same concentration (10mg/L of active polymer) for all the triplicate samples. Maximum yield
of NDMA is desired for the UFC or FP, since these are intended to maximize the reactions between precursors and oxidants [35, 36]. Both UFC methods allow free chlorine contact time before addition of ammonia for further formation of monochloramine, whereas the FP method adds pre-formed monochloramine to a buffered sample. Results for the comparison between the methods are summarized in Figure 5.2.

Both UFC methods yielded comparable concentrations of NDMAFP. UFC1 yielded 2.3 ± 0.5, whereas UFC 2 yielded 2.3 ± 0.3 ng NDMAFP/mg active polymer. The FP yielded a concentration of 99 ± 19 ng NDMAFP/mg active polymer. Lower yield of UFC method was expected, since the FP method uses much higher concentrations of monochloramine to maximize the reaction of precursors with the oxidant. Therefore, the FP method was chosen for this work, despite being more labor and time consuming than the UFC methods.

5.4.2 Validation of the reproducibility of the NDMAFP and SPE method for polyDADMAC

FP tests yielded a concentration of NDMAFP of 99 ± 19 ng NDMAFP/mg active polymer at Arizona State University and 64 ± 1 ng NDMAFP/mg active polymer at Curtin University. Despite the 35% difference in the results, they were considered acceptable due to inherent analytical errors from both laboratories. Even though both laboratories adopted the same FP procedure and used the same polymer sample for the tests, differences in the way the SPE was conducted and on the speciation of the chloramine solution might have influenced the results. Dichloramine is less reactive than
monochloramine and preparation of the chloramine solution can affect the speciation and therefore the exposure of the precursors to the strongest oxidant [37]. Despite the differences, the results were considered acceptable within the scope of this work.

Results are presented in Figure 5.3 and show that recoveries were similar to both cartridges for both samples tested and the triplicates had low variability. NDMA quantification of the secondary effluent with the first cartridge (UCT) resulted in $370 \pm 2 \text{ ng/L}$, with 0.6% variation among the triplicate extractions. For the samples of secondary effluent with polyDADMAC, NDMAFP was $545 \pm 9 \text{ ng/L}$ of NDMA, with 2% variation among the triplicate samples. Similar NDMA values were observed with the second cartridge (Restek). Quantification of the secondary effluent NDMAFP with the Restek cartridge resulted in NDMA concentration equal to $373 \pm 2 \text{ ng/L}$, with 0.5% variation among the triplicate extractions. For the samples of secondary effluent with polyDADMAC, FP was $540 \pm 11 \text{ ng/L}$ of NDMA, with 2% variation among the triplicate samples. Concentrations between the two cartridges varied by 2% and t-tests ($\alpha = 0.05$) comparing the means of the UCT and Restek NDMA values of secondary effluent ($p = 0.07$) and secondary effluent with 10mg/L of polyDADMAC ($p = 0.40$) show that both cartridges are comparable and can be used interchangeably for NDMA analysis. Also, this comparison showed that addition of polyDADMAC did not interfere on NDMA extraction.

5.4.3 Validation of the UF experiments

DOC values for the filtrate fractions averaged $0.34 \pm 0.05 \text{ mgC/L}$ and $0.23 \text{ mgC/L}$ for the retentate fraction. No TDN was detected in these samples. Therefore, the pre-
conditioning method used to remove UV254 absorbing material from the membrane was adequate for the UF experiments conducted and it was is in accordance with a previous study that did not observe NDMA precursors leaching from regenerated cellulose UF membranes [38]. The DOC and TDN mass balance for these are presented in Figure. For the 1kDa mass balance, the sum of the retentate and permeate fractions DOC (84.3 mgC) and TDN (15.2mgN) were 0.6% lower and 14.2% higher, respectively, different than the initial polymer solution values (84.8 mgC and 13.3mgN). The difference for the 3kDa membrane was somewhat similar and the sum of the retentate and permeate fractions DOC (90.7 mgC) and TDN (12.6 mgN) were 7% higher and 5.3% lower than the initial polymer solution values, respectively. The differences observed were not considered significant, i.e., the DOC and TDN mass balances were considered acceptable and therefore show that this approach can be used for the experiments with polyDADMAC. As observed in these results, there was no indication of polymer losses in the membrane as UF was performed. Also, since the 1kDa and 3kDa are in the same order of magnitude in size (MWCO), the difference between the DOC values was 7.5% and TDN values was 20.6%.

5.4.4 Quantification of reactivity of the low MW polyDADMAC fraction

To investigate the research hypothesis, the first step was to determine reactivity of each fraction of the 1kDa and 3kDa UF experiments described above through NDMAFP tests. Results are presented in Figure 5.4 and are based on duplicate FP tests for each fraction of the UF. As presented in Error! Reference source not found., NDMAFP of the permeate fractions is about one order of magnitude higher than for the polymer and
retentate fraction. However, these results can be misleading since not all samples had equal carbon content. For this reason, the results were normalized by the carbon content of each sample. This normalization also allows estimation of the sample reactivity. Higher NDMAFP/mgC signifies that the sample was more reactive, i.e., that more NDMA was formed upon chloramination. Results are presented in Figure 5.6 and show that the normalized NDMAFP/mgC is higher for the permeate samples than for the retentate and the polymer solution. An average of 181 ±52 ng NDMAFP/mgC was quantified for the filtrate fractions using a MWCO of 1kDa and 223 ±47 ngNDMAFP/mgC for the filtrate fractions from the experiment using MWCO = 3kDa. These values are 97% and 142% higher, respectively, than the NDMAFP/mgC of the polymer solution (92 ± 3 ngNDMAFP/mgC). The retentate reactivity is about 25 times lower than the filtrate, 9 ngNDMAFP/mgC for MWCO = 1kDa and 4 ngNDMAFP/mgC for MWCO = 3kDa. However, the carbon concentration in these particular samples was low (≤ 0.5 mgC/L) given the low available volume of each filtrate fraction (~20mL for each fraction, each with ~20mgC/L), which might have increased experimental uncertainty. Also, the MWCO of the membranes was too close (same order of magnitude), so the observed results were consequently very similar. Therefore, to address these experimental issues, the next step of this work evaluated UF using membranes with MWCO = 1kDa and 10kDa and collecting the filtrate in a single fraction instead of five fractions. This enabled the NDMAFP experiments to be performed with higher DOC (~5 mgC/L) given the bigger available volume of the filtrate fraction after DOC and TDN analysis (~120mL available rather than ~20mL).
DOC and TDN mass balances for the experiments with 1kDa and 10kDa membranes are shown in Figure 5.7. The MWCO equal to 1kDa and 10kDa both yielded similar masses of carbon and nitrogen for each respective filtrate and retentate. The filtrate from the 1kDa MWCO had $3.8 \pm 1.4$ mgC and $0.8 \pm 0.2$ mgN, while the filtrate from the 10kDa MWCO had $2.5 \pm 0.1$ mgC and $0.6 \pm 0.0$ mgN. These values represent less than 5% of the initial carbon and nitrogen mass in the polymer solution, 82.5 mgC and 11.8mgN. The retentate from the 1kDa MWCO had $74.8 \pm 5.6$ mgC and $10.4 \pm 0.8$ mgN, while the retentate from the 10kDa MWCO had $86.3 \pm 8.3$ mgC and $12.1 \pm 1.2$ mgN. Again, the DOC and TDN mass balance show that no polymer was adsorbed on the membrane.

The DOC reactivity of the each fraction is presented in Figure 5. and it shows that the DOC reactivity of the 1kDa and 10kDa MWCO filtrates are about 11 times higher than the reactivity of the initial unfiltered polymer solution. The 1kDa filtrate reactivity was $2112 \pm 618$ ngNDMA/mgC and the 10kDa filtrate showed similar reactivity, $2092 \pm 267$ ngNDMA/mgC. These values are also significantly higher (~20 times more) than the reactivity of the retentate, which was $106 \pm 43$ ngNDMA/mgC for 1kDa MWCO and $135 \pm 31$ ngNDMA/mgC. The higher MW fraction (i.e. > MWCO) reactivity of the 1kDa and 10kDa MWCO were 55% and 70%, respectively, smaller than that of the initial unfiltered polymer solution. These findings prove the initial research hypothesis that the low MW (<MWCO) fraction of polyDADMAC is more reactive (i.e., there is higher NDMA formation per mass of carbon) than the high molecular weight fraction (>MWCO), for the MWCO conditions in this work. The similarity observed between the reactivity of the filtrate from the membranes with 1kDa and 10kDa MWCO also suggests that the 10kDa
MWCO could be used as a pre-treatment process for the polymer. However, pilot and full scale are still needed to assess the feasibility of the UF as a pre-treatment to reduce NDMA formation in drinking water treatment.

5.5 Implications for water treatment

Simulated NDMAFP in settled CAP water treated with polyDADMAC and aluminum sulfate as a function of polyDADMAC MW distribution (percentage of fraction < 10kDa) in the polymer is presented in Figure 5.9. NDMAFP increases as the concentration of low MW (<10kDa) compounds increases in the polymer. As the concentration of low MW compounds increases to up to 15%, NDMAFP reaches up to 24 ngNDMAFP/L. This is an increase of 60% in the NDMAFP compared to the NDMA formation of the CAP water. If the polymer is treated with ultrafiltration, i.e., no compounds lower than 10kDa are present in the polymer, NDMAFP decreases to 17 ngNDMAFP/L, only 13% higher than NDMAFPSW.

NDMAFP increase in the settled water becomes even more apparent when 0.5 mg of active polymer/L is used for coagulation. In this case, NDMAFP increases from 28 ng NDMAFP/L to 53 ng NDMAFP/L when the percentage of low MW fraction in polyDADMAC increases from 0 to 15%. NDMAFP in the settled water can therefore be 3.5 times higher than that of the CAP water. This observations support evidence that ultrafiltration can enable NDMA formation to be reduced in the settled water coagulated with polyDADMAC by reducing the concentration of highly reactive NDMA precursors present in the polymer. These results are theoretical and need yet to be confirmed in experimental conditions.
5.6 Conclusions

This work showed that the low MW fraction of polyDADMAC has higher reactivity (i.e., higher NDMAFP normalized per mass of carbon) than the higher MW fraction. The low MW polymer fraction is poorly removed during coagulation and therefore the higher reactivity of this fraction can imply in higher NDMA formation during disinfection. This work also provides evidence that the UF experimental approach is valid and adequate to measure the reactivity of different MW fractions of polyDADMAC. Even though this work did not focus on the mechanistic explanation of the higher reactivity of the low MW fraction, some hypothesis to explain this observation are suggested. The extent of branching and the higher availability of chain ends to be oxidized by chloramine are some of the likely hypothesis to explain the observations. The biggest contribution of this work was demonstrating that low MW fraction, as fractionated using UF, has higher reactivity than the higher MW fraction during chloramination. Through a model developed for CAP water coagulated with polyDADMAC, this work shows that an increase in the low MW fraction results in increased NDMA formation potential in the settled water.
5.7 Figures and Tables
Table 5.1 – Summary of Formation Potential (FP) and Uniform Formation Conditions (UFC) methods adopted in this work.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
<th>pH</th>
<th>Buffer</th>
<th>Time</th>
<th>Monochloramine or chlorine dose</th>
<th>Cl2/N ratio</th>
<th>Quenching</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP</td>
<td>Hanigan et al (2015)</td>
<td>8</td>
<td>10mM Borate</td>
<td>3 days, room temperature or 25°C</td>
<td>Monochloramine dose = 18 mgCl₂/L</td>
<td>1.2 mol N/mol Cl₂</td>
<td>5mM ascorbic acid</td>
<td>Prepare solution of monochloramine at least one hour before the test. Buffer samples (pH =8), add monochloramine (18mgCl₂/L), let sample stand in the dark for 72h, quench with 5mM ascorbic acid and add 200ng/L NDMA isotope. Samples were adjusted to a pH ~8 using a pH 8 buffered chlorine solution. The chlorine solution was added to samples to achieve a free-chlorine residual of ~2.5 mg/L as Cl₂ after 3 min, and was followed by post-chloramination at a Cl₂/NH₃-N weight ratio of 4.75/1 mg/ mg. A typical chloramine residual in plant effluents is ~2 to 3 mg/L as Cl₂. The samples were then incubated at 25°C for 3 days. The majority of water treatment facilities in the U.S. distribute water at around a pH of 8.</td>
</tr>
<tr>
<td>UFC 1</td>
<td>Krasner et al (2012)</td>
<td>8</td>
<td>10mM Borate</td>
<td>3 days, room temperature or 25°C</td>
<td>Chlorine dose to achieve 2.5 mgCl₂/L after 3 min</td>
<td>Cl₂/N weight ratio = 4.75:1 (1.1 mol N/mol Cl₂)</td>
<td>5mM ascorbic acid</td>
<td></td>
</tr>
</tbody>
</table>
Continued - Table 5.1 – Summary of Formation Potential (FP) and Uniform Formation Conditions (UFC) methods adopted in this work.

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
<th>pH</th>
<th>Buffer</th>
<th>Time</th>
<th>Monochloramine or chlorine dose</th>
<th>Cl2/N ratio</th>
<th>Quenching Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFC 2</td>
<td>Krasner, S.; C. Lee, W. Mitch, and U. von Gunten. 2012a. Development of a Bench-Scale Test to Predict the Formation of Nitrosamines. Denver, Colo.: Water Research Foundation. (WRF4452) 8</td>
<td>7</td>
<td>Borate</td>
<td>3 days, room temperature or 25°C</td>
<td>10mM</td>
<td>2.5 mgCl₂/L</td>
<td>Chlorine was added at a 2.5 mg/L as Cl₂ dose and ammonia was added within 30 sec to be at a Cl₂/N weight ratio of 4.75:1 (just less than the 5.0:1 weight ratio for maximum chloramine formation). Free chlorine contact time was kept low (i.e., 30 sec) to avoid destruction of nitrosamine precursors by the chlorine. The samples were held for 3 days at pH 8 at room temperature or at 25°C.</td>
</tr>
</tbody>
</table>
Figure 5.1 - Chemical structure of PolyDADMAC Source: [28]

Figure 5.2 - NDMA yield of UFC and FP methods.
Figure 5.3 - NDMAFP of secondary effluent upon SPE using cartridges supplied by UCT and Restek.

Figure 5.4 – DOC and TDN mass balance for the UF using 1g/L of active polyDADMAC though 1kDa and 3kDa membranes.
Figure 5.5 – NDMAFP (ngNDMA/L) for the UF using 1g/L of active polyDADMAC though 1kDa and 3kDa membranes
Figure 5.6 – Reactivity (ngNDMAFP/mgC) of the different fractions of polyDADMAC after UF using membranes with MWCO = 1kDa and 3kDa.
Figure 5.7 – DOC and TDN mass balance for the UF using 1g/L of active polyDADMAC through 1kDa and 10kDa membranes.
Figure 5.8 – Reactivity (ngNDMAFP/mgC) of the different fractions of polyDADMAC after UF using membranes with MWCO = 1kDa and 10kDa
Figure 5.9 – Simulated NDMA formation potential in settled CAP water
References


Providing affordable safe drinking water has become a challenge for water utilities worldwide, as more disinfection byproducts (DBPs) have been identified since the discovery of TTHM in the 1970s [1-3]. Besides that, an increasing number of chemicals enters the drinking water supply each year as a consequence of human activity, such as endocrine disruptors, pharmaceuticals, pesticides and non-regulated drugs [4, 5].

Existing treatment technologies, such as granular activated carbon (GAC), can remove DBPs and their precursors, although at high operational costs [6]. In Europe, DBP formation is minimized through use of non-persistent disinfectants (such as ultraviolet light and ozone). Ultimately, eliminating the use of chlorine as a disinfectant is the goal of most European countries. Unfortunately, this strategy is not economically viable in many countries, since it is rather costly and it demands proper risk management to prevent water contamination during distribution [6].

Cost of treatment is a major concern in the United States, where utilities are switching to chloramine disinfection to comply with newly established TTHM and HAA5 limits [7]. Regulations such as the Stage 2 of the Disinfection Byproducts Rule, promulgated by the U.S. EPA in 2006, have taken place to ensure compliance to TTHM and HAA5 limits (80 µg/L and 60 µg/L, respectively). Recent assessments show a 20 µg/L reduction of TTHM levels since implementation of the Stage 2 DBP Rule by the
EPA [8]. However, while the use chloramines reduces the formation of TTHM and HAA5, it also enhances formation of NDMA, an emerging DBP of health concern.

GAC is considered a best available technology (BAT) to aid in DBP control by the U.S. EPA and many utilities are adopting GAC to enhance removal of NOM and DBP precursors. Although GAC is an effective and consolidate technology to remove NOM and DBP precursors, few works focus on how water utilities can optimize operation and reactivation of spent material. Most works focus on media improvement, such as the development of iron impregnated carbons, or on the removal of micro-contaminants [9]. This work focuses on the operation, rather than on the media improvement, and adopts pre-chlorination and as an operational strategy to improve the performance of GAC for removal of TTHM and HAA5 precursors. The goal of this dissertation was to optimize operation of GAC, while controlling regulated and emerging disinfection byproducts (Figure 6.1).

Chapters 2 and 3 adopted rapid small scale columns (RSSCTs) to simulate GAC treatment and restated the adequacy of this approach to simulate NOM removal by GAC. A unique aspect of Chapter 3 is the use of 0.5 cm columns, which due to their small size allowed the RSSCTs to be run for more than 15000BV while reducing the required volume of influent water. This work was done with the support of a full-scale water treatment plant planning to implement pre-chlorination in their GAC system. The experiments shown here, along with pilot scale GAC columns run, will support implementation of pre-chlorination by the water treatment plant. Results indicate positive benefits of adopting chlorination prior to GAC contactors, such as an increased number
of bed volumes treated. Another contribution of this work was showing that pre-chlorination can help control the effluent potential toxicity by switching TTHM speciation to more chlorinated TTHM than brominated TTHMs.

Despite the benefits of adopting GAC, operation of the contactors has yet to be optimized to reduce reactivation cycles. Previous works have demonstrated that in-situ GAC regeneration could be an alternative to thermal regeneration cycles. Reactivation cycles with hydrogen peroxide activated with iron nanoparticles, for example, recovered GAC adsorption capacity on multiple reactivation cycles [10]. However, the literature available on GAC regeneration lacks standardized conditions to evaluate reactivation (batch versus column experiments).

Batch scales tests and conditions averaged from the literature were adopted to evaluate the recovery of NOM adsorption capacity using real surface waters. An innovative and unique aspect of this work was the use of bench scale column tests to evaluate the recovery of adsorption capacity of real spent GAC and using real water matrices for the adsorption assays. The main contribution of this chapter was showing that chemical regeneration of GAC is not feasible for waters with low NOM concentration, i.e., with low adsorbate concentrations. Another main contribution was showing that column reactivation is more adequate to assess reactivation efficiency on bench scale, given the easiness of operation and of washing the reactivated GAC to remove the reactivation solution.

Previous research showed that activated carbon can only remove watershed-originated NDMA precursors and cannot be used to control polymer-originated NDMA
precursors [11]. PolyDADMAC is the most used cationic polymer for water coagulation in the U.S. and also a major source of NDMA precursors during drinking water treatment [12-14]. The available literature has provided evidence that impurities and low MW compounds present in polyDADMAC are NDMA precursors [15].

Chapter 5 showed that the low MW fraction of polyDADMAC, as separated by ultrafiltration, is more reactive and it forms more NDMA per unit of carbon than the higher MW fraction. A unique aspect of this work was providing enough evidence to support the use of ultrafiltration as a valid experimental approach to evaluate the NDMA formation potential of different MW fractions of polyDADMAC.
6.1 Figures

Figure 6.1 – Overarching structure of this dissertation
6.2 References


CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH

7.1 Impact of granular activated carbon on natural organic matter and effluent organic matter molecular weight distribution (Chapter 2)

Chapter 2 focused on removal of NOM from a surface water treated with GAC to answer the research question: How is molecular weight distribution of NOM altered by GAC treatment?

For the water samples tested, 90SW, WW and SW, changes in MW distribution were observed as a consequence of treatment with GAC. Low MW NOM (600 – 1000Da) was adsorbed preferentially than the larger MW fraction (>10kDa) during the earlier DOC breakthrough values. As DOC breakthrough increases, selective adsorption of NOM can no longer take place due to exhaustion of the available adsorption sites on the GAC surface. MW distribution of NOM becomes then similar to the influent. Despite using two GACs with distinct characteristics, changes in the effluent MW were similar for both carbons.

Removal of UFC HAN and UFC TTHM correlated well with the DOC removal, both for Carbon A and Carbon B. DOC has been shown to be a good surrogate for removal of TTHM and HAA5 precursors by many studies HAN precursors were removed by GAC and followed DOC breakthrough, despite poor DON removal by GAC. DON
also acts as a major precursor for HAN, yet, this work shows that GAC could also potentially be used to reduce HAN in waters with low DON.

The companion study resulting from this work, published by Krasner et al (2016) [1], focused on the cito- and genotoxicity of brominated DBPs that had their formation enhanced by the altered DOC/Br ratios in the effluent of the GAC treatment. Future research needs are directly related to the realization of the impact GAC has on DBP speciation. Toxicity of brominated DBPs has been thoroughly explored in the literature [2-4]. These observations are important because they might indicate a need to regulate the brominated TTHM species individually.

7.2 Pre-chlorination to improve TTHM removal and promote longer GAC usage: a column and pilot test (Chapter 3).

Chapter 3 proposed the use pre-chlorination to minimize TTHM and HAA5 formation in water treated with GAC, through enhanced removal of their precursors. Pre-chlorination enhanced removal of DOC and UV254 when 1 and 2 mgCl₂/L were applied prior to GAC adsorption. Virgin GAC performed better than regenerated GAC in the experiments.

Pre-chlorination was effective for enhancing removal of TTHM precursors and TTHM formation was reduced in the effluent of pre-chlorinated columns, as determined by simulated distribution system tests. GAC effectively removed preformed TTHM but not HAA5, indicating that GAC was effective at TTHM control and could be used for this purpose without exceeding the TTHM MCL.
The initial hypothesis, enhanced removal of low MW NOM due to pre-chlorination, could not be supported by the SECDOC results. Lower TTHM formation when pre-chlorination was used may be due to oxidation of the most reactive NOM fraction and efficient removal of preformed TTHM and TTHM precursors by GAC. Results from this study show that GAC could potentially be operated for longer bed volumes without compromising the effluent quality or the MCL for TTHM, resulting in potential economical and operational benefits for the water facilities adopting GAC to comply with the existing TTHM regulatory limits.

This work focused on an influent water with low SUVA and with limited chlorine contact time. Higher chlorine dosages and longer contact times should be explored, as well as water sources with varying SUVA values. Furthermore, based on the findings from Chapter 2, the formation of brominated species under other conditions should be explored.

7.3 In-situ regeneration using iron nanoparticles and liquid oxidants of field-spent granular activated carbon (Chapter 4)

Literature existing on in-situ regeneration of GAC does not provide a standardized test to evaluate the efficiency of regeneration or to evaluate the adsorption capacity of the regenerated GAC. Chapter 4 adopted averaged conditions from the literature to evaluate in-situ regeneration of multiple GAC types spent either with NOM or with micro pollutants.
It may be possible to improve the regeneration capacity of spent GAC through a different GAC selection process. Adopting a more macroporous GAC with smaller particles could improve kinetics and mass transfer of the regeneration chemicals. Bench scale testing of in-situ regeneration needs to be improved and column adsorption tests seem more appropriate to evaluate adsorption after regeneration. In-situ regeneration of GAC is case-specific and more improvement on the regeneration technique is necessary to apply it to full-scale water treatment.

Based on the findings from Chapter 4, the most important research need is the development of a standardized approach to evaluate chemical GAC regeneration. The results of this work suggest that column experiments are more adequate to this purpose than batch tests. More macroporous GAC might have better recovery of adsorption capacity and smaller particles could improve kinetics and mass transfer of the regeneration chemicals. Future research should focus on the use of in-situ chemical reactivation for GAC used in the treatment of waters with high concentration of organics. Moreover, future research focusing on disposal and treatment of the regeneration solution is needed. This work analyzed the regeneration solutions and little to no of EDB or DBCP were detected. However, no potential byproducts formed in the regeneration solution were investigated.

7.4 Influence of low molecular weight polyDADMAC on NDMA formation (Chapter 5)
Chapter 5 showed that the low MW fraction of polyDADMAC has higher reactivity (i.e., higher NDMAFP normalized per mass of carbon) than the higher MW fraction. The low MW polymer fraction is poorly removed during coagulation and therefore the higher reactivity of this fraction can imply in higher NDMA formation during disinfection. A model developed for CAP water coagulated with polyDADMAC showed that an increase in the low MW fraction results in increased NDMA formation potential in the settled water.

A main contribution of this chapter was also providing evidence that the UF experimental approach is valid and adequate to measure the reactivity of different MW fractions of polyDADMAC.

This work is part of the initial steps for further investigation of the mechanisms involved in formation of NDMA from reaction of chloramines and polyDADMAC. Even though this work did not focus on the mechanistic explanation of the higher reactivity of the low MW fraction, some hypothesis to explain this observation are suggested. The extent of branching and the higher availability of chain ends to be oxidized by chloramine are some of the likely hypothesis to explain the observations. Park et al (2009) hypothesized that formation of NDMA happens through Hofmann elimination but that has yet to be proven [5]. Future research topics lie on investigating the mechanisms involved in NDMA from polyDADMAC.
7.5 References


APPENDIX A

SIMULATED DISTRIBUTION SYSTEM (SDS) TEST PROCEDURE (WRF 4607)
Objectives

The specific objectives of the SDS testing are as follows:

- Determine DBP formation upon chlorination in GAC treated water under pre-determined target chlorine residual and hold time conditions
- Determine acceptable levels of TOC in treated water in order to achieve distribution system water quality goals

Materials and Methods

The following equipment and materials will be needed for SDS testing:

- 1.5 gallon (or larger) containers
- 250 mL amber glass bottles with soft septa caps
- Sodium hypochlorite solution
- Pipets and tips, or syringes

The following water quality analyses will be performed as part of the SDS testing:

- Chlorine residual
- pH
- TOC
- Bromide
- TTHM
- HAA5

Procedure
Prior to performing the SDS tests, store the water at 4°C. Bring the water back to room temperature prior to performing SDS tests.

The SDS tests will be performed in two stages – chlorine demand test and SDS tests. Chlorine demand tests will be performed prior to the SDS tests. The procedure for the chlorine demand tests and SDS tests are described below.

**Chlorine demand tests**

- Perform chlorine demand tests on each of the 3 water samples listed above.
- For each of the water samples, apply the following procedure:
  - Pour collected water into 3 (three) X 250 mL bottles
  - Fill the bottles approximately 90% (water level somewhere near neck of the bottle, level doesn’t have to be exact)
  - Calculate chlorine doses for the 3 bottles as follows:
    - Bottle 1: chlorine dose = (1.5 X TOC) mg/L
    - Bottle 2: chlorine dose = (1.5 X TOC + 0.5) mg/L
    - Bottle 3: chlorine dose = (1.5 X TOC + 1) mg/L
  - Apply these chlorine doses to the 3 bottles for each water sample
  - Fill the bottles to the brim and screw on soft septa cap (ensure no air bubble in the bottle)
  - Turn the bottle over its head a few times to mix applied chlorine
  - Store bottles in dark space
  - Measure chlorine residual in all 3 bottles after 24 hours

**SDS tests**
• SDS tests will be performed upon completion of chlorine demand tests.

• Target chlorination conditions for SDS tests are: 1 mg/L chlorine residual after 24 hour hold time

• Two chlorine doses will be selected per water sample during SDS tests.

• For each of the water samples, follow the following procedure:
  o Pour collected water into 6 (six) X 250 mL bottles
  o Fill the bottles approximately 90% (water level somewhere near neck of the bottle, level doesn’t have to be exact)
  o Apply the following chlorine doses to the 6 bottles
    ▪ Bottles 1-3: chlorine dose 1
    ▪ Bottles 4-6: chlorine dose 2
  o Fill the bottles to the brim and screw on soft septa cap (ensure no air bubble in the bottle)
  o Turn the bottle over its head a few times to mix applied chlorine
  o Store bottles in dark space
  o After 24 hours, measure chlorine residual, TTHM, and HAA5 in bottles 1 and 4
  o After 48 hours, measure chlorine residual, TTHM, and HAA5 in bottles 2 and 5
  o After 72 hours, measure chlorine residual, TTHM, and HAA5 in bottles 3 and 6
APPENDIX B

NITROSAMINE FORMATION POTENTIAL - CHLORAMINATION AND SOLID PHASE EXTRACTION PROCEDURE
• Prepare 0.0223M Borax, 0.9107 Boric acid Solution (=1M Borate)
  o pH should =8 when diluted to mM range
  o This buffer needs some heat to completely dissolve, and will precipitate over time (days), be careful, measure pH.

• Dilute ~20mL of 5% chlorine stock solution with 230 mL nanopure water (=250mL)

• Measure free chlorine of chlorine solution with Hach kit (program 80 in the DR5000):
  o Dilute sample 2000X, add pillow pack, swirl, and wait 3 minutes before measurement (use program timer)
  o Stock should be near 4000mg/L (~2 mg/L from Hach at this dilution) – will be diluted half with ammonia solution to near 2000 mg/L

• Find required NH\textsubscript{4}Cl addition for 500mL of monochloramine stock solution, where X is readout from Hach instrument

\[ Y (g \text{NH}_4\text{Cl}) = 1.2 \frac{\text{molN}}{\text{molCl}_2} \times \frac{[X] \text{mgCl}_2/L}{2212} \times 1000 \frac{g}{mg} \]

• Dissolve NH\textsubscript{4}Cl into 245mL nanopure water with 5mL 1M buffer solution (=250mL)

• SLOWLY (use a burette) add chlorine solution into buffered ammonia solution while stirring rapidly (500mL amber bottle)
  o Final buffer concentration of NH\textsubscript{3}Cl solution = 10mM

• Allow monochloramine solution to equilibrate for >1hr in the dark
• Measure monochloramine concentration using Hach kit. All chlorine should be converted to monochloramine. Monochloramine concentration, as Cl₂, should be similar to that of the stock solution.
• Confirm buffer solution ~ pH 8
• Buffer 500mL samples with 5mL buffer 1M stock solution (samples buffer concentration = 10mM)
• Confirm sample = pH 8
• Dose samples with monochloramine solution at DOC X 3 = NH₂Cl as Cl₂ (we adopt 18 mgCl₂/L)
• Store samples at room temperature in the dark for 72 hrs
• Quench samples with 5 mL of 0.5M (88g/L) ascorbic acid solution
• Final concentration of ascorbic acid in the samples: 5mM
• Add 1 mL of 100µg/L NDMA-d6 to samples
• SPE samples into DCM, final concentration = 5mL using method “Nitrosamines in water”. More detail of the method is provided in EPA Method 521 but generally, the method rinses cartridges with DCM (solvent 3), MeOH (solvent 2), H₂O (solvent 5), loads samples onto cartridges, dries with N₂ gas for 10 min (~15psi), and elutes with 5 mL DCM.
• Push DCM eluate through anhydrous sodium sulfate cartridge to remove remaining water
• Turbovap (N₂) sample to 1mL and Pasteur pipette into GC vials (~10 psi for 10 min)