Can graphene-coated sand enhance water reuse by improving water quality in the presence of municipal treated wastewater?

Madelyn Barber

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CAN GRAPHENE-COATED SAND ENHANCE WATER REUSE BY IMPROVING WATER QUALITY IN THE PRESENCE OF MUNICIPAL TREATED WASTEWATER?

A Thesis Presented for the Degree of Master of Science in Engineering Science with an Emphasis in Environmental Engineering

The University of Mississippi

Madelyn Barber

May 2023
Abstract

The need for alternative water sources is dramatically increasing. Therefore, it is essential to develop alternative water sources to meet the current water scarcity challenges. Water reclamation, recycling, and reuse involving treated municipal and or animal wastewater address these challenges by resolving water resource issues and creating new sources of high-quality water supplies. However, the presence of bacteria, high levels of nutrients, and turbidity, as well as the occurrence of chemicals of emerging concern (CECs) in the treated wastewater, combined with the willingness of the public to use treated wastewater can undermine the wide application of water reuse. Implementing affordable but effective low-cost water treatments represents a key option to overcompensate the current limitations of water reuse. The objectives of this research were to 1) assess the ability of graphene-coated sand to improve water quality, expressed in terms of turbidity, nutrients, chemical oxygen demand (COD), and bacteria removal, and 2) investigate the ability of graphene-coated sand to remove CECs. Flow-through columns (length: 62 cm, ID: 5.2 cm) were used throughout the study. Three types of sand with different shapes and mineralogical compositions, Ottawa, Masonry, and Concrete, were used. Additionally, treated municipal wastewater (pre-UV) collected at the University of Mississippi Wastewater Treatment Plant was used as feed water for the different columns. Results from the study highlighted the ability of the proposed materials to successfully remove turbidity (> 85%), total coliforms (> 99%) and *E. coli* (> 99%), moderately remove COD (< 65%), and poorly remove nitrate (< 30%) and CECs (< 20%) with the exception of one type of sand, activated graphene-
coated sand, and one CEC, sulfamethoxazole). Even though nitrate removal was limited, it was consistently higher compared to previously published results. Results from the study suggested that the ability of the graphene-coated sand to remove nitrate was partially able to overcompensate the nitrification process occurring within the different columns. The presence of a post-treatment (e.g., activated graphene-coated sand) was able to enhance the ability of the columns packed with the raw materials and outperformed the columns packed with graphene-coated sand.
Dedication

This work is dedicated to my loving family who have motivated and supported me throughout this journey. My mother Stephanie continuously provided a voice of reason and guidance that allowed me to successfully complete my research and academic journey. My father Brad was always there for me when I needed emotional support and someone to lean on in a time of need. Lastly, my twin sister Mackenzie, and my older sister Laken have been my best friends and brought joy to my life when I needed it most.
Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGCCS</td>
<td>Activated Graphene Coated Concrete Sand</td>
</tr>
<tr>
<td>AGCMS</td>
<td>Activated Graphene Coated Masonry Sand</td>
</tr>
<tr>
<td>AGCOS</td>
<td>Activated Graphene Coated Ottawa Sand</td>
</tr>
<tr>
<td>AOPs</td>
<td>Advanced Oxidation Processes</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;5&lt;/sub&gt;</td>
<td>5-Day Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>CBOD&lt;sub&gt;5&lt;/sub&gt;</td>
<td>5-Day Carbonaceous Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>CECs</td>
<td>Contaminants of Emerging Concern</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>EC</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>GCCS</td>
<td>Graphene Coated Concrete Sand</td>
</tr>
<tr>
<td>GCMS</td>
<td>Graphene Coated Masonry Sand</td>
</tr>
<tr>
<td>GCOS</td>
<td>Graphene Coated Ottawa Sand</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>K&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Soil Adsorption Coefficient</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>RCS</td>
<td>Raw Concrete Sand</td>
</tr>
<tr>
<td>RMS</td>
<td>Raw Masonry Sand</td>
</tr>
<tr>
<td>ROS</td>
<td>Raw Ottawa Sand</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid Phase Extraction</td>
</tr>
<tr>
<td>SSF</td>
<td>Slow Sand Filter</td>
</tr>
<tr>
<td>TDS</td>
<td>Total Dissolved Solids</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>UM</td>
<td>University of Mississippi</td>
</tr>
<tr>
<td>UNESCO</td>
<td>United Nations Educational, Scientific and Cultural Organization</td>
</tr>
<tr>
<td>USGS</td>
<td>United States Geological Survey</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organization</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater Treatment Plant</td>
</tr>
</tbody>
</table>
### Units

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>cm³/min</td>
<td>Cubic Centimeter per Minute</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>in</td>
<td>Inch</td>
</tr>
<tr>
<td>L/kg</td>
<td>Liter per Kilogram</td>
</tr>
<tr>
<td>MGD</td>
<td>Millions of Gallons a Day</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>mg/L</td>
<td>Milligram per Liter</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>MPN</td>
<td>Most Probable Number</td>
</tr>
<tr>
<td>MPN/100 mL</td>
<td>Most Probable Number per 100 Milliliters</td>
</tr>
<tr>
<td>ng/L</td>
<td>Nanogram Per Liter</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric Turbidity Units</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts Per Billion</td>
</tr>
</tbody>
</table>
Acknowledgments

This research would not have been possible without the cooperation and assistance of numerous people. I would first like to express my sincere gratitude to my advisor, Dr. Matteo D’Alessio for his continuous support of my academic journey and guidance in the completion of this research. It is to him that I owe this achievement. Without his mentorship I could have never successfully completed this thesis or acquired a higher level of knowledge that can be carried with me to the next chapter of my life.

I would like to acknowledge some members of the Civil Engineering department at the University of Mississippi whose valuable expertise and insight helped me to improve my work. Particularly, I would like to extend my gratitude to Dr. Cristiane Surbeck and Dr. Hunain Alkhatheb for being members of my thesis committee.

I would also like to thank collaborators from the University of Mississippi Wastewater Treatment Plant for allowing me to collect wastewater throughout the study.
Keywords

Water reuse;
Low-cost water treatment;
Graphene-coated sand;
Treated municipal wastewater;
Chemicals of emerging concern;
Water quality;
Total coliform and *E. coli*. 
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CHAPTER 1. INTRODUCTION

1.1 Background

1.1.1 Water Reuse

As the result of a growing global population over the past two decades, there has been an increased pressure put on our available water resources. According to the latest edition of the United Nations World Water Development Report, 26% of the global population do not have access to safe drinking water. Additionally, two to three billion people experience water shortages for at least one month of the year\(^1\). These water shortages pose a severe risk to livelihoods, notably through food security and access to electricity. The global urban population that currently faces water scarcity is projected to double from 930 million in 2016 to 1.7-2.4 billion people in 2050\(^1\). In response to the rapid depletion of Earth’s water resources, alternative sources of water must be identified and used. Water security may be achieved by managing water resources in a way that they are accessible, in an appropriate quantity and quality for human uses while respecting water as an integral part of the ecosystem\(^2\). Advancements in wastewater treatment could prove to be a reliable and affordable solution. Water reclamation, recycling, and reuse address these challenges by resolving water resource issues and creating new sources of high-quality water supplies\(^3\). Municipal and animal wastewater reuse represents an economically as well as an environmentally advantageous method of water conservation and reuse. Wastewater reuse takes many forms, including non-potable reuse, where wastewater is
treated for purposes not requiring drinking quality water such as irrigation and landscaping, and potable reuse for drinking water needs.

While the use of reclaimed wastewater as an alternative source of water proves to be a suitable solution to this problem, a group of chemicals known as chemicals of emerging concern (CECs) pose a threat to this solution. CECs are synthetic or naturally occurring chemicals that are not commonly monitored in the environment but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects at ng/L levels of concentration. These contaminants include, but are not limited to, pharmaceuticals, surfactants, personal care products, endocrine disrupting compounds, analgesics, hormones, antibiotics, among others. These toxic substances are ubiquitous and may enter the aqueous environment via different wastewater streams, such as hospital wastewater, agricultural runoff, discharge from industrial effluents, and wastewater treatment plant effluents. Whereas there are well established technologies and treatments on how to remove “traditional” chemicals as well as microbial parameters, there is still no clear solution on how to remove the different CECs effectively and consistently. Therefore, it is essential to identify the most effective treatment(s) in removing CECs as well as developing and improving guidelines on the reuse of treated wastewater for various purposes.

1.1.2 Human Perception of Water Reuse

The success of a municipal wastewater reuse program is often dependent on public willingness to use recycled water. Psychological reactions that contribute to behavioral intention have varying levels of influence, with the reaction of disgust or “yuck factor” creating the primary behavioral barrier. However, research has shown that community education initiatives can increase willingness to support water reuse projects. In the southwest United States,
utilization of alternative water sources is becoming increasingly common, especially for landscape irrigation, environmental enhancement, cooling and power generation, potable reuse, and as a source water for agricultural irrigation. While much research has gone into identifying public perception towards water reuse schemes, little attention has been given to understanding grower attitudes, perceptions, and knowledge on the use of nontraditional water, including reclaimed water, in agriculture and how that may influence grower acceptance and production practices. A study was carried out in Arizona focusing on perceptions regarding water reuse and how these may affect future utilization of the resource. A telephone survey of 400 randomly selected Arizona residents was used to assess public opinion of water reuse in the state. Survey results indicated that residents feel it is important for their community to use recycled water with 76% of those surveyed showing support for the use of ‘consumer incentives for using recycled water.’ Over two-thirds of the respondents supported ‘increasing water or sewer rates to treat water to higher standards.’ Despite this support, the survey revealed that almost two-thirds of the respondents have concerns about recycled water. These concerns can be alleviated by providing more information about recycled water and its benefits. In this survey, education level proved to be the most significant demographic affecting perception of terminology and recycled water uses. College graduates were significantly more supportive or less negative in their responses with higher levels of education resulting in significantly greater support for all of the proposed uses of recycled water. In a survey conducted during the Spring 2023 semesters, students attending ENGR 598 (25) at the University of Mississippi assessed the general public’s perception (number of participants = 142) of wastewater reuse in Mississippi using a survey with questions ranging from defining wastewater reuse to asking participants what activities the participants would feel comfortable accomplishing with treated wastewater. Participants
favorably viewed the application of water reuse to fight fires (85% strongly or somewhat agreed) and to water private yards (77% strongly or somewhat agree), while they disagreed with the idea of using water reuse for drinking (56% strongly or somewhat disagreed) and cooking (49% strongly or somewhat disagreed)\(^9\).

Two approaches can be taken to change human perception of wastewater reuse. First, environmental laws and regulations can be established for different water reuse applications. Second, the community can be educated on the topic of wastewater treatment and its benefits for water reuse.

### 1.1.3 Standards and Regulations for Water Reuse

Many countries and some states in the United States have started to supplement potable and non-potable water resources with recycled wastewater. Some countries have partially relied on recycled wastewater for decades, and even in these places, most of the population is unaware water reclamation is happening\(^4\). Recycled wastewater can be used for various applications (e.g., agriculture, landscaping, and potable drinking water). Generally, the application of recycled water can be divided into seven categories including urban reuse, agricultural reuse, impoundments, environmental reuse, industrial reuse, groundwater recharge/non-potable reuse, and potable reuse\(^10\). Water reuse applications are different in various countries and depend on several factors such as levels of treatment, conditions of water resources, environmental status, and public willingness. Agricultural water reuse, by far, is the most dominant application of water reuse in the world\(^10\). According to the U.S. Environmental Protection Agency (EPA), in 2023, 28 states have regulations for wastewater reuse while the remaining 23 states have no
regulations or guidelines for wastewater reuse. Table 1 highlights the states adopting water reuse regulations based on the type of reuse application.

Table 1. List of states with water regulations and their applications

<table>
<thead>
<tr>
<th>Type of Reuse Application</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agriculture</td>
<td>AL, AZ, CA, CO, DE, FL, GA, HI, ID, IN, MA, MD, MN, MT, NC, NE, NJ, NM, NV, OK, OR, PA, RI, TX, UT, VA, WA, WY</td>
</tr>
<tr>
<td>Landscape</td>
<td>AL, AZ, CA, CO, DE, FL, GA, HI, ID, IN, MA, MD, MN, MT, NE, NJ, NM, NV, OK, OR, PA, RI, TX, UT, VA, WA, WY</td>
</tr>
<tr>
<td>Potable</td>
<td>CA, FL, MA, MT, NC, NM, NV, OK, OR, PA, TX, VA, WA</td>
</tr>
</tbody>
</table>

Although some states have implemented guidelines to be followed for the application of recycled water, these standards differ from state to state and there is no uniform standard across the United States. Different states also differ in the parameters that they monitor and vary in values for those parameters. For example, Alabama only focuses on the use of recycled water for agriculture and landscaping purposes (Table 2) while North Carolina has standards for agriculture, potable water reuse\(^\text{11}\), and environmental restoration (Table 3). At the moment, Mississippi doesn’t have any regulations for water reuse in place (Table 1).
### Table 2. State of Alabama water reuse standards for agriculture and landscaping purposes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Agriculture</th>
<th>Landscaping</th>
<th>Landscaping</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class B Reclaimed Water¹</td>
<td>Class A Reclaimed Water²</td>
<td>Class B Reclaimed Water³</td>
</tr>
<tr>
<td>Turbidity</td>
<td>N/A</td>
<td>≤3 NTU (at any time point)</td>
<td>N/A</td>
</tr>
<tr>
<td>Chlorine</td>
<td>≥1.0 mg/L entering distribution system</td>
<td>≥1.0 mg/L entering distribution system</td>
<td>≥0.5 mg/L entering distribution system</td>
</tr>
<tr>
<td></td>
<td>≥0.5 mg/L chlorine residual in the distribution system prior to transfer to storage ponds and/or distribution to customers</td>
<td>≥0.5 mg/L chlorine residual in the distribution system prior to transfer to storage ponds and/or distribution to customers</td>
<td>≥0.5 mg/L chlorine residual in the distribution system prior to transfer to storage ponds and/or distribution to customers</td>
</tr>
<tr>
<td>E. coli</td>
<td>≤18 organisms/100 mL (median from last 7 days of results)</td>
<td>≤18 organisms/100 mL (median from last 7 days of results)</td>
<td>≤18 organisms/100 mL (median from last 7 days of results)</td>
</tr>
<tr>
<td></td>
<td>≤34 organisms/100 mL (single sample maximum)</td>
<td>≤34 organisms/100 mL (single sample maximum)</td>
<td>≤34 organisms/100 mL (single sample maximum)</td>
</tr>
<tr>
<td>TSS</td>
<td>≤30 (30-day average)</td>
<td>N/A</td>
<td>≤30 (30-day average)</td>
</tr>
<tr>
<td>NO₃ + NO₂</td>
<td>≤10 mg/L (30-day average)</td>
<td>≤10 mg/L (30-day average)</td>
<td>≤10 mg/L (30-day average)</td>
</tr>
<tr>
<td>pH</td>
<td>≥6.0</td>
<td>≥6.0</td>
<td>≥6.0</td>
</tr>
<tr>
<td></td>
<td>≤8.5</td>
<td>≤8.5</td>
<td>≤8.5</td>
</tr>
<tr>
<td>CBOD₅</td>
<td>≤10 mg/L (30-day average)</td>
<td>≤10 mg/L (30-day average)</td>
<td>≤10 mg/L (30-day average)</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>Not Specified</td>
<td>Not Specified</td>
<td>Not Specified</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>Not Specified</td>
<td>Not Specified</td>
<td>Not Specified</td>
</tr>
</tbody>
</table>

¹Crops not intended for human ingestion, pasture for animals not producing milk for human consumption
²Land application on parks, ballfields, playgrounds, and school yards during periods of non-use; land application on residential landscapes and commercial campuses
³Land application on golf courses, highway medians, and cemeteries during periods of non-use

In Alabama, reclaimed water is defined by the Department of Environmental Management as wastewater that has received treatment which meets the criteria specified in Table X. The Class A and Class B requirements apply to the reuse of reclaimed water for landscape irrigation. The various classes of reclaimed water treatment are defined by their respective treatment requirements and applicable performance standards. For Class A reclaimed water, the treatment requirements are secondary treatment with an additional treatment
including, at a minimum, coagulation, clarification, filtration and disinfection, or an alternate process acceptable to the Department of Environmental Management. Chlorine is the preferred primary disinfectant, but other acceptable primary disinfectants include chlorine dioxide, UV light, ozone, or an equivalent process acceptable to the Department of Environmental Management. Facilities utilizing another disinfectant other than chlorine must add a disinfectant to maintain disinfectant residuals in the distribution system such that the minimum chlorine requirements are met. For Class B reclaimed water, the treatment requirements are secondary treatment with, at a minimum, disinfection. Chlorine is the preferred primary disinfectant, but other acceptable primary disinfectants include chlorine dioxide, UV light, ozone, or an equivalent process acceptable to the Department of Environmental Management. Facilities utilizing a disinfectant other than chlorine must add a disinfectant to maintain residuals in the distribution system such that the minimum chlorine requirements are met\textsuperscript{13}. The guidelines for agricultural water reuse only specify one type of reclaimed water (Class B) and one treatment category. The requirements for Class B reclaimed water for agriculture use is similar to that of the Class B requirements for landscape irrigation\textsuperscript{12}.

When reusing water for agriculture specifications in the state of North Carolina, there are two reclaimed water types (Type 1 and Type 2) that are differentiated by their specific treatment requirements, chemical contaminant, and microbiological removal requirements. Treatment requirements are not specified for Type 1 reclaimed water, but for treated effluent to be categorized as Type 1, the parameter limits provided in Table 3 must be met. Type 2 reclaimed water treatment facilities must provide dual disinfection systems containing UV disinfection and chlorination or equivalent dual disinfection processes to meet pathogen control requirements. Type 2 reclaimed water treatment facilities must demonstrate that the combined treatment and
disinfection processes are capable of the following reduction targets: $\geq \log 6$ reduction of \textit{E. coli}, $\geq \log 5$ reduction of coliphage, and $\geq \log 4$ reduction of \textit{Clostridium perfringens}\textsuperscript{14}. For the use of reclaimed water for environmental restoration purposes, there is only one type of reclaimed water (Type 1) and therefore only one water reuse treatment category to consider. Reclaimed water discharged to natural wetlands shall be treated to Type I reclaimed water standards. In addition to the water quality requirements associated with Type I reclaimed water, additional nitrogen and phosphorus requirements must be met prior to the discharge of reclaimed water to wetlands, unless net environmental benefits are provided. Metal concentrations in reclaimed water discharged to wetlands shall not exceed North Carolina surface water quality standards, unless acute whole effluent toxicity testing demonstrates absence of toxicity\textsuperscript{15}. 

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Agriculture</th>
<th>Environmental Restoration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>≤10 NTU</td>
<td>≤5 NTU</td>
</tr>
<tr>
<td>E. coli¹</td>
<td>≤14 organisms/100 mL (monthly geometric mean)</td>
<td>≤14 organisms/100 mL (monthly geometric mean)</td>
</tr>
<tr>
<td></td>
<td>≤25 organisms/100 mL (daily maximum)</td>
<td>≤25 organisms/100 mL (daily maximum)</td>
</tr>
<tr>
<td>Fecal Coliform*</td>
<td>≤14 organisms/100 mL (monthly geometric mean)</td>
<td>≤14 organisms/100 mL (monthly geometric mean)</td>
</tr>
<tr>
<td></td>
<td>≤25 organisms/100 mL (daily maximum)</td>
<td>≤25 organisms/100 mL (daily maximum)</td>
</tr>
<tr>
<td>Ammonia (NH₃-N)</td>
<td>≤4 mg/L (monthly average)</td>
<td>≤1 mg/L (monthly average)</td>
</tr>
<tr>
<td></td>
<td>≤6 mg/L (daily maximum)</td>
<td>≤2 mg/L (daily maximum)</td>
</tr>
<tr>
<td>TSS</td>
<td>≤5 mg/L (monthly average)</td>
<td>≤5 mg/L (monthly average)</td>
</tr>
<tr>
<td></td>
<td>≤10 mg/L (daily maximum)</td>
<td>≤10 mg/L (daily maximum)</td>
</tr>
<tr>
<td>BOD₅</td>
<td>≤10 mg/L (monthly average)</td>
<td>≤5 mg/L (monthly average)</td>
</tr>
<tr>
<td></td>
<td>≤15 mg/L (daily maximum)</td>
<td>≤10 mg/L (daily maximum)</td>
</tr>
<tr>
<td>Coliphages (type not specified)</td>
<td>N/A</td>
<td>≤5 organisms/100 mL (monthly geometric mean)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≤25 organisms/100 mL (daily maximum)</td>
</tr>
<tr>
<td>Clostridium Perfringens</td>
<td>N/A</td>
<td>≤5 organisms/100 mL (monthly geometric mean)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>≤25 organisms/100 mL (daily maximum)</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>4 mg/L</td>
<td>Not Specified</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>1 mg/L</td>
<td>Not Specified</td>
</tr>
</tbody>
</table>

¹Direct or indirect contact irrigation of food chain crops that will be peeled, skinned, cooked, or thermally processed before consumption; Crops irrigated by direct contact with reclaimed water shall not be harvested within 24 hours of irrigation.
²Indirect contact irrigation of food chain crops that will not be peeled, skinned, cooked, or thermally processed before consumption.
³Wetland augmentation.
⁴In reclaimed water effluent intended to be used for agricultural reuse applications, E. coli or fecal coliforms should be measured with the corresponding specifications met prior to storage, distribution, or utilization.

Table 3. State of North Carolina water reuse standards for agriculture and environmental restoration purposes.
1.1.4 Wastewater Treatment for Water Reuse

Wastewater treatment technologies have been implemented throughout history. According to ancient Sanskrit medical writings from the year 2000 BC, a primitive method of water purification was done by boiling water before passing it through sand and gravel. This water purification method is still being used in the modern world with a few enhancements. Slow sand filtration is a technology that has been used for potable water filtration for hundreds of years. It is a process well-suited for small, rural communities since it does not require a high degree of operator skill or attention. As the name implies, slow sand filtration is used to filter water at very slow rates and typically requires a large land area for the filtration basins. Remote areas, which are often beyond the reach of centralized water supply networks, rely heavily on decentralized supply systems such as slow sand filters. Slow sand filtration presents many advantages such as cost-effectiveness, simple setup and operation, and high removal efficiency for bacteria, metals (e.g. iron), and organics. In fact, slow sand filters are recommended by the World Health Organization (WHO) to address water needs in remote areas with hundreds of thousands of slow sand filtration units operating worldwide to supply clean water to multi-million people. Plain sand is mostly inert toward organic contaminants, therefore the main removal mechanism for organic contaminants in SSFs is the activity of the biolayer at the top of the filter called the schmutzdecke. Up to now, the reported removal efficiencies of micropollutants (MPs) by SSFs are generally low, which then has urged recent SSF studies to introduce the mechanism of adsorption for enhanced performance. Graphene oxide (GO) is a widely-known carbonaceous adsorbent that could be used to increase the surface area and thereby the adsorption of the filter media. However, GO-coated sand has not been investigated in
the setting of slow sand filtration particularly in real environment matrices that are relevant to practical applications\textsuperscript{18}.

In recent years, the increasing consumption of pharmaceutical and personal care products (PPCPs) and their adverse effects on ecological or human body has attained extensive attention. The emission of these emerging contaminants has emerged as an environmental problem and rather poor wastewater management could not effectively eliminate these compounds. Therefore, there is a widespread demand that this kind of contamination requires effective elimination\textsuperscript{19}. Several treatment technologies have been employed for the elimination of toxic pollutants from wastewater such as adsorption, advanced oxidation processes (AOPs), membrane separation, reverse osmosis, chemical precipitation, ion exchange, electrochemical treatment, and biological treatments. Of all the treatment approaches, adsorption has been considered as the most promising one because of its high efficiency, ease of operation, cost-effectiveness and feasibility to implement at large-scale. Moreover, it does not create any secondary pollution by generating toxic contaminants during the treatment process\textsuperscript{20}.

Graphene, a two-dimensional single layer sheet of carbon atoms organized in a sp\textsuperscript{2}-bonded honeycomb-like lattice structure has emerged as a “wonder material” with a number of potential applications. Since its discovery in 2004, graphene nanostructure has been successfully applied as the base materials in terms of basic research in many revolutionary fields due to its interesting mechanical and physiochemical properties. These properties include large surface area, good thermal stability, high electrical conductivity, big aspect ratio, excellent mechanical strength, flexibility, and negligible thickness\textsuperscript{20}. Recently, these exceptional properties have further expanded their application in environmental remediation as novel adsorbents for purifying wastewater due to very high theoretical surface area, abundant active sites and great
delocalized $\pi$-electron systems$^{20}$. Current studies have investigated and confirmed the ability of graphene-coated sand to remove heavy metals$^{21-23}$, microcystin-LR$^{24, 25}$, fluoride$^{26}$, and stormwater contaminants including phosphate, zinc, caffeine, and *E. coli*$^{27}$, atrazine (herbicide)$^{18}$ and atenolol (beta blocker)$^{18}$. In particular, Vu and Wu observed enhanced removal of atrazine, atenolol, and total organic carbon (TOC) in the presence of graphene-coated sand than in the presence of raw sand and suggested that the enhanced removal was mainly due to graphene-coated sand rather than the *schmutzedecke*.$^{18}$ If confirmed, the *schmutzedecke* growing phase might not be needed. Overall, the ability of graphene-coated sand to remove a broad range of CECs and nutrients is still largely unknown$^{28}$. In addition to the utilization of graphene-coated sand in removing a variety of water quality parameters, activated graphene-coated sand can also be used. Activation of carbon nanomaterials (e.g., graphene) is commonly used to improve the surface area and porosity of the material$^{29}$ while also producing a larger number of adsorption sites$^{16}$ and therefore increasing the adsorption capacity. Additionally, activation can vary or adjust the surface chemical nature of the starting material, graphene$^{29}$. The activation process significantly impacts the overall cost of the filtration unit due to the cost of activation chemicals (e.g., sulfuric acid). Therefore, the activated graphene-coated sands were tested against the non-activated graphene-coated sands to evaluate the economic feasibility of this additional step$^{16}$.

### 1.2 Research Objectives

The objectives of this research were to 1) assess the ability of graphene-coated sand to improve water quality, expressed in terms of turbidity, nutrients, chemical oxygen demand (COD), and bacteria removal, and 2) investigate the ability of graphene-coated sand to remove CECs. Results obtained were also discussed in terms of the grains’ size, shape, and mineralogical composition of three different raw materials used (Ottawa sand, Masonry sand, and Concrete.
sand). To highlight the novelty of the study, to the best of my knowledge, this is the first study assessing the ability of graphene-coated sand in removing CECs.

1.3 Thesis Layout

This thesis is divided into 4 chapters. Chapter 1 provides a brief introduction of water reuse, wastewater treatment methods implemented to assist with the use of recycled wastewater, human perception surrounding this concept, and standards that have been established to help with the human perception problem. Chapter 2 describes the materials and analytical methods used during the study such as the packing materials, feed water from the wastewater treatment plant, the experimental setup for the collection and measurement of the water quality, as well as the analytical methods and equipment used to quantify the water quality parameters in the samples. Chapter 3 presents the water quality results (e.g., COD, turbidity, pH/EC, CECs). Chapter 4 states the conclusions based on the obtained results as well as future research that can be conducted based on the findings from the experiment.
CHAPTER 2. MATERIALS AND METHODS

2.1 Packing materials

Three different types of sand were used: Ottawa sand, Masonry sand, and Concrete sand. The three types of sand were selected based on their geological classification, shape of the individual grain, and mineralogical composition (Table 4).

Table 4. Raw materials used during the study and their geological and physical properties.

<table>
<thead>
<tr>
<th>Geological Classification</th>
<th>Ottawa sand</th>
<th>Masonry sand</th>
<th>Concrete sand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fine/medium sand</td>
<td>Coarse/very coarse sand</td>
<td>Coarse/medium sand with gravel</td>
</tr>
<tr>
<td>Particle Shape</td>
<td>90% well rounded/rounded</td>
<td>Mixture of sub-rounded and sub-angular particles</td>
<td>5% rounded</td>
</tr>
<tr>
<td></td>
<td>10% sub-angular/angular</td>
<td></td>
<td>35% sub-rounded</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60% sub-angular</td>
</tr>
<tr>
<td>Composition</td>
<td>&gt;95% Quartz</td>
<td>99% Quartz</td>
<td>85% Quartz</td>
</tr>
<tr>
<td></td>
<td>&lt;5% Lithic fragments</td>
<td>1% Lithic fragments</td>
<td>15% Lithic fragments</td>
</tr>
</tbody>
</table>

Additionally, the three types of sand were exposed to different graphene-coated processes with and without an activation process. Table 5 summarizes the different packing materials used during the study. A detailed description of the different materials used as well as the production methods can be found elsewhere.16, 30.
Table 5. Raw materials used during the study and their abbreviations.

<table>
<thead>
<tr>
<th>Raw sand followed by activated graphene-coated sand</th>
<th>Ottawa sand</th>
<th>Masonry sand</th>
<th>Concrete sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sand</td>
<td>ROS_AS</td>
<td>RMS_AS</td>
<td>RCS_AS</td>
</tr>
<tr>
<td>Raw sand followed by activated graphene-coated sand</td>
<td>ROS_F</td>
<td>RMS_F</td>
<td>RCS_F</td>
</tr>
<tr>
<td>Graphene coated sand</td>
<td>N/A</td>
<td>GCMS</td>
<td>GCCS</td>
</tr>
<tr>
<td>Activated graphene coated sand</td>
<td>AGCOS</td>
<td>AGCMS</td>
<td>AGCCS</td>
</tr>
<tr>
<td>N/A: not applicable</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Feed water

As an activated sludge process, the UM wastewater treatment plant (WWTP) has a maximum influent flow of 3.0 MGD and uses UV light for disinfection. However, the estimated daily flow ranges between 0.2 and 0.5 MGD based on the absence and/or presence of students, faculty, and staff members on campus. Similarly, the population served ranges between 1,000 (summer) and 20,000 (spring and fall).

2.3 Experimental Setup

The experimental setup consisted of a 30-gallon water tank that acted as the reservoir for the collected wastewater. Eight tubes (Masterflex L/S 14, inner diameter: 1.6 mm) were passed from the reservoir through 4 Masterflex Easy-Load II double pump heads in parallel and into each of the eight columns filled with sand\textsuperscript{16}. Five of these columns were being run as single-stage filtration columns (AGCMS, AGCCS, AGCOS, GCMS, and GCCS) while the other three were run as two-stage filtration columns (ROS, RCS, and RMS). The two-stage filtration
columns were coupled in series with smaller columns filled with AGCOS, AGCCS, and AGCMS respectively. The smaller columns filled with AGCOS, AGCCS, and AGCMS as the filtration media were named O, C, and M respectively for easier differentiation during the data interpretation. The effluent from all eight columns discharged into 5-gallon buckets. Figure 1 illustrates the schematic of the eleven-column setup along with the tubing line connections.

![Figure 1: Experimental set-up used during the study](image)

All of the columns were made from polyvinyl chloride (PVC) pipes. The eight larger columns were 62 cm tall with an inner diameter of 52 mm. The three smaller columns were 13 cm tall with an inner diameter of 38 mm (Figure 1). All pipes were closed at both ends with adequate PVC rounded fittings that were drilled and tapered with 0.5-inch brass nozzles installed. The packing of each column was done in multiple stages. For the eight large columns, the first three layers from the bottom were gravel only starting with two 200 g layers of gravel,
then a third 100 g layer. A tampering rod was used to pack each layer three times and the whole column was placed on a shaker for 10 seconds after each layer. The height of the three layers of gravel differed from column to column due to random particle shape but was maintained in a range between 15 to 18 cm\textsuperscript{16}. The packing of the sand was done similarly, in increments of 200 g. Each of the columns took around eight to nine layers of sand before topping off until full for a total weight ranging between 1450 and 1800 g, and a total height ranging between 44 to 47 cm. The packing of the three smaller columns was done with the same procedure but with smaller increments of 100 g in two layers then topped off for a total weight of material around 225 g\textsuperscript{16}.

The experiment ran for 49 days total starting with a seven day acclimation period followed by a 42 day experiment time. Samples for water quality analysis were collected weekly and the system was fed continuously throughout the study. The average flow rate was 2.37 cm\textsuperscript{3}/min and the average empty bed contact time was approximately 555 min.

### 2.4 Water Quality Parameters & Analytical Methods

#### 2.4.1 Basic Water Quality Parameters

##### 2.4.1.1 Turbidity

Turbidity, or the measure of relative clarity of water\textsuperscript{31}, was measured using an Orion\textsuperscript{TM} AQ4500 Turbidimeter (ThermoFisher, St. Louis, MO, USA) shown in Figure 2. The percent removal after each column was obtained using Equation 1.

\[
\eta = \left(\frac{In - Out}{In}\right) \times 100 \quad \text{(Equation 1)}
\]

Where \( \eta = \% \text{ removal} \)

\( In = \text{turbidity in the influent (feed water)} \)

\( Out = \text{turbidity in the effluent (after each column)} \)
2.4.1.2 pH/Electrical Conductivity/TDS/Salinity

pH/Electrical Conductivity (EC)/TDS/Salinity were measured using an Oakton pH/Cond/TDS/Salinity Tester (Cole-Parmer, Vernon Hills, IL, USA) multiparameter probe (Figure 3) was used. The multiparameter probe was calibrated daily.
2.4.1.3 Chemical Oxygen Demand

The HACH Chemical Oxygen Demand (COD) TNTplus Vial Test kit, HR (Figure 4) was utilized for this analysis using the reactor digestion method. The vials containing the reagent were prepped by inserting 2.0 mL of sample and allowing the vials to digest in the DRB200 Digital Reactor Block HACH (Figure 4) (Loveland, CO, USA) for two hours then remove the test vials and let the temperature decrease for about 20 minutes to 120°C or less. After 20 minutes, the results were read from a DR6000 HACH spectrophotometer (Figure 5) (Loveland, CO, USA). The percent removal after each column was obtained using Equation 1.
Nitrate

To determine the nitrate concentrations in the samples for this experiment, the HACH Nitrate TNTplus Vial Test kit, LR (Figure 6) was used. To ensure that the levels were within the
detection limits, the samples were diluted using a dilution factor of 5. The test vials were prepped by slowly pipetting 1.0 mL of the diluted sample and 0.2 mL of the included “Solution A” containing 2-Propanol, 2,6-Dimethylphenol, Isoamyl acetate to the vials then allowed them to sit for 15 minutes. The nitrate concentrations were read after 15 minutes using a DR6000 HACH spectrophotometer (Figure 5) (Loveland, CO, USA). The percent removal after each column was obtained using Equation 1.

![Image of HACH Nitrate TNTplus Vial Test kit]

*Figure 6. HACH Nitrate TNTplus Vial Test kit*
2.4.1.5 Total Coliforms

The total coliform levels were quantified using a commercial Most Probable Number (MPN) test, Colilert 18, with a Quanti-Tray 2000 (Figure 7) from IDEXX Laboratories. Samples were collected aseptically and immediately after collection, 100 mL or an appropriate dilution of the sample was mixed with the reagent, poured into sterile trays, heat-sealed (Figure 8), and incubated at 35°C for 24 hours. Then the results were read. The percent removal after each column was obtained using Equation 1.

![Colilert Reagent and Sample of Results](image)

*Figure 7. Colilert Reagent and Sample of Results*
2.4.1.6  *E. coli*

*E. coli* in the water samples were also quantified using a commercial Most Probable Number (MPN) test, Colilert 18, with a Quanti-Tray 2000 (Figure X) from IDEXX Laboratories. Samples were collected aseptically and immediately after collection, 100 mL or an appropriate dilution of the sample was mixed with the reagent, poured into sterile trays, heat-sealed, and incubated at 35°C for 24 hours. After an incubation time of 24 hours had passed, an ultra-violet light (Figure 8) was used to read the results. The percent removal after each column was obtained using Equation 1.

2.4.1.7  Chemicals of Emerging Concern

In addition to this part of the experiment, there was also a setup for the solid phase extraction system. In order to extract the CECs from the samples, 100 mL of each influent and effluent samples were filtered and passed through a 200 mg Oasis HLB solid phase extraction
cartridge (Waters Corporation, Milford, MA, USA) preconditioned with 6 mL methanol, followed by 10 mL DI water (Figure 9).

![Solid Phase Extraction (SPE) setup for detecting CECs](image)

After that, the SPE cartridges were sealed with Parafilm, placed inside 50 mL centrifuge tubes and shipped to the Water Management and Conservation Research Unit at USDA-ARS, US Arid-Land Agricultural Research Center (Maricopa, AZ). 3 mL of HPLC grade methanol were added to the SPE cartridge reservoir and the eluate was collected under vacuum at 1 mL/minute in a clean graduated centrifuge tube. After that, 3 mL of HPLC grade acetonitrile were added to the SPE cartridge reservoir and the eluate was collected under vacuum at 1 mL/minute in the same graduated centrifuge tube. The two solvents were evaporated using a Labconco CentriVap concentrator at 35°C. After that, the evaporated residue was reconstituted with 1 mL of 10% acetonitrile solution, vortexed and sonicated to ensure the residue was
completely dissolved, and the sample was transferred sample into a new vial and run on the Xevo LCMS. The percent removal after each column was obtained using Equation 1.
CHAPTER 3. RESULTS & DISCUSSION

3.1 Basic Water Quality Parameters

3.1.1 Turbidity

Turbidity is an optical characteristic of water and the measurement of the amount of light that is scattered by material such as clay, silt, very tiny inorganic and organic matter, algae, dissolved colored organic compounds, plankton and other microscopic organisms in the water when a light is shined through the water sample\(^3\). Turbidity levels can act as an indicator of potential pollution in a water body because the particles provide attachment places for other pollutants, notably metals and bacteria. In drinking water, high turbidity is aesthetically unappealing and may also pose a concern to human health. It provides food and shelter for pathogens and if not removed the causes of high turbidity can promote the regrowth of pathogens in the water, leading to waterborne disease outbreaks\(^3\).

Throughout the study, the feed water was characterized by low turbidity (< 1.4 NTU, Figure 10). These low values were due to the nature of the feed water – treated municipal wastewater collected before the disinfection treatment but after undergoing preliminary, primary, and secondary treatment. Effluent samples collected after the different columns showed reduced turbidity, ranging from 0.12 and 1.05 NTU. These values are below the U.S. EPA standards for Agriculture Type 1 and 2 and Environmental Restoration in North Carolina (Table 3) and Landscaping Class A in Alabama (Table 2). Turbidity removal ranged between 7.25% and 85.71% (Figure 10). The lowest percent removal was achieved during week 2 after AGCMS and
it was most luckily related to the already low turbidity present in the feed water. During this time, all columns achieved the smallest percent removal in terms of turbidity (Figure 10). Overall, samples collected after activated graphene-coated sand showed a higher removal compared to those collected after the non-activated graphene-coated sand. Similarly, samples collected after the post-treatment (small columns packed with activated-graphene coated-sand) showed an increase in turbidity removal compared to those collected after the corresponding raw sand. Results obtained during the study were in line with previously published articles highlighting the ability of SSF to reduce turbidity in feed water having low-to medium levels of turbidity (0.6–20 NTU)\textsuperscript{32-34}.
3.1.2 pH

pH affects most chemical and biological processes in water, and it is one of the most important environmental factors limiting species distributions in aquatic habitats. Different species flourish within different ranges of pH, with the optima for most aquatic organisms falling
between a pH of 6.5 and 8. The United States Environmental Protection Agency water quality criteria for the pH in freshwater suggests a range of 6.5 to 9. pH values outside of this range can negatively impact many species, resulting in decreased growth, decreased reproduction, disease or even death ultimately leading to reduced biological diversity in streams. In addition to having a negative impact on many aquatic species, pH can alter the chemical state of many pollutants, thereby changing their solubility, transport, and bioavailability. These changes can increase exposure to and toxicity of metals and nutrients to aquatic plants and animals.

Throughout the study, pH ranged between 7.15 and 7.50 in the feed water and between 7.15 and 7.75 in the different effluent samples (Figure 11). The pH range in both the feed water and the effluent samples was appropriate and within a normal range for the nature of this water. Additionally, these values are below the U.S. EPA standards for Agriculture Type 1 and 2 and Environmental Restoration in North Carolina (Table 3) and Landscaping Class A and Agriculture in Alabama (Table 2). Overall, regardless of the coating process (activated vs. non-activated graphene-coated sand) as well as of the nature of the sand (Ottawa vs. Concrete vs. Masonry), the effluent samples had a slightly higher pH values (max: +0.4) than the influent samples. This trend can be related to the impact of the treated municipal wastewater on the packing materials.
3.1.3 Electrical Conductivity

EC is a general measure of water quality that measures the ability of water to pass an electrical current\textsuperscript{36}. It is important to evaluate conductivity because significant fluctuations could

Figure 11. pH (influent and effluent) throughout the study
be an indicator that a discharge or some other source of pollution has entered the water resource\textsuperscript{36}.

Throughout the study, EC ranged between 533 and 612 in the feed water and between 527 and 675 in the different effluent samples (Figure 11). Overall, with the exception of effluent collected after AGCOS during week 2, regardless of the coating process (activated vs. non-activated graphene-coated sand) as well as of the nature of the sand (Ottawa vs. Concrete vs. masonry), the difference in terms of EC between the influent and effluent samples was limited (± 40 mS/cm). A significant change in terms of EC can be anticipated in the presence of a poor coating process. However, the limited variation observed in terms EC suggested limited impact of the feed water (treated municipal wastewater) on the different packing materials and consequently the relative stability of the different packing materials. Similar with EC, TDS and salinity values obtained using the same multiparameter probe remained stable throughout the study suggesting limited to no impact of the feed water to the different packing materials.
Figure 12. EC (influent and effluent) throughout the study

3.1.4 Chemical Oxygen Demand

COD analysis is used as an indirect measure of organic pollutants in a water sample and is an important parameter in water quality analysis. The COD of a water body represents the capacity of water to consume oxygen during the decomposition of organic matter in the water\textsuperscript{17}.
COD measurement is an excellent way of monitoring the efficiency of water treatment plants and if the water is left untreated, or partially treated, then the water discharge contains effluent organics that can compete with downstream organisms for oxygen. This oxygen demand can kill or inhibit life downstream of the discharge area\textsuperscript{37}. COD is important to monitor because modern societies have a high demand for water to meet a wide range of personal, health, and commercial purposes. At the same time, the industrial society produces a wide range of pollutants and environmental challenges that can produce serious health and biodiversity outcomes if left untreated\textsuperscript{37}.

Throughout the study, COD in the feed water ranged between 39.8 and 70.6 mg/L (Figure 13). These values are typical for treated municipal wastewater and their fluctuations were related to the rainfall observed during the study with higher values occurring during strong rainfall. Effluent samples collected after the different columns showed reduced COD, ranging between 12.3 and 59.1 mg/L. COD removal ranged between 14.1\% and 69.1\% (Figure 10). Regardless of the types of sand, graphene-coated sand underperformed compared to activated graphene-coated sand as well as to the two stage-approach (Figure 13). Additionally, the results indicated that sand coating did not significantly improve the COD removal during SSF. These results were consistent with Verma et al. 2019\textsuperscript{38}. In fact, they observed limited COD removal (< 60\%) and no improvement while comparing uncoated and iron-coated fine sand to treat municipal wastewater\textsuperscript{38}. 

33
Figure 13. COD (influent values and percent removal achieved after the different columns) throughout the study

3.1.5 Nitrate

Nitrate, an oxidized form of nitrogen, is found in several different forms in aquatic and terrestrial ecosystems. Nitrates are essential plant nutrients, but in excess amounts they can cause
significant water quality problems and even impact the lives of both plants and animals. Nitrates, together with phosphorus, in excessive amounts can accelerate the eutrophication process resulting in the dramatic increase in aquatic plant growth and changes in the types of plants and animals that live in the affected stream. This also affects dissolved oxygen, temperature, and other indicators. Elevated nitrate levels in a water body can cause hypoxia or low levels of dissolved oxygen and can become toxic to warm-blooded animals at nitrate concentrations of 10 mg/L or higher under certain conditions\textsuperscript{39}.

Throughout the study, nitrate ranged between 25.8 and 37.9 mg/L in the feed water and between 21.4 and 30.7 mg/L in the different effluent samples (Figure 14). Overall, regardless of the coating process (activated vs. non-activated graphene-coated sand) as well as of the nature of the sand (Ottawa vs. Concrete vs. Masonry), nitrate removal was limited (< 30\%, Figure 14). While the removal of nitrate was low, results obtained during the study showed higher removal of nitrate compared to those available in the literature\textsuperscript{38,40,41}. For example, Verma et al. 2019 while comparing slow sand filters using uncoated and iron-coated fine sand in the presence of treated wastewater, not only observed no removal of nitrate after the different treatments, but higher levels of nitrate concentration were detected in the effluent compared to the influent\textsuperscript{38}. This was probably due to the nitrification occurring in the SSF units\textsuperscript{38,40,41}. The ability of the graphene-coated sand to partially remove nitrate reduced the impact related to the nitrification observed in the literature.
Figure 14. Nitrate (influent values and percent removal achieved after the different columns) throughout the study.
3.2 Bacteria

3.2.1 Total Coliforms

Total coliforms are a group of related bacteria that are (with a few exceptions) not harmful to humans. EPA considers total coliforms a useful indicator of other pathogens for drinking water. A variety of bacteria, parasites, and viruses are known as pathogens and can potentially cause health problems if humans ingest them. Monitoring total coliforms is important because they can be used to determine the adequacy of the water treatment and the integrity of the distribution system\textsuperscript{42}.

Throughout the study, the feed water was characterized by moderately high levels of total coliforms (68,930 – 129,970 MPN/100 mL, Figure 15). These values are typical for treated municipal wastewater collected before the disinfection treatment but after undergoing preliminary, primary, and secondary treatment. The variability of the feed water in terms of total coliforms can be related to storm events. Effluent samples collected after the different columns showed reduced levels of total coliforms, ranging between 96 and 5,475 MPN/100 mL. Total coliforms removal ranged between 64.90 and 99.91\% (Figure 15). The lowest percent removal was achieved during week 3 after ROS\_AS (Figure 15). However, by adding a post-treatment (small columns packed with activated-graphene coated-sand) the removal of total coliforms increased. Overall, samples collected after activated graphene-coated sand as well as after graphene-coated sand showed a higher removal compared to those collected after non-coated sand. In particular, activated graphene-coated sand consistently achieved at least 92\% removal in terms of total coliforms. Results obtained during the study were in line with previously published articles highlighting the ability of SSF to reduce total coliforms present in the feed water\textsuperscript{32-34, 38}. 
Figure 15. Total coliforms (influent values and percent removal achieved after the different columns) throughout the study

3.2.2 E. coli

E. coli are a large and diverse group of bacteria found in the environment, foods, and intestines of people and animals. Although most strains of E. coli are harmless, others can make you sick. It is important to measure E. coli to make sure water is safe for public recreation and
it is considered an indicator organism, used to identify fecal contamination in freshwater as well as the possible presence of disease-causing bacteria and viruses (pathogens).\footnote{44}

Results related to the \textit{E. coli} were similar to those related to the total coliforms even though the actual levels in the feed water were lower ($10^4$ \textit{vs.} $10^5$ MPN/100 mL). \textit{E. coli} in the effluent ranged between 25.9 and 476.4 MPN/100 mL. These values were sometimes below the U.S. EPA limit standards for Agriculture Type 1 and 2 and Environmental Restoration in North Carolina (Table 3) but consistently above the Landscaping Class A and Agriculture limits in Alabama (Table 2). The removal of \textit{E. coli} was constantly greater than 88\% (Figure 10). Results obtained during the study were similar to those observed elsewhere highlighting the ability of SSF to remove \textit{E. coli}\textsuperscript{32-34, 38}.\footnote{44}
Figure 16. *E. coli* (influent values and percent removal achieved after the different columns) throughout the study

3.3 Chemicals of Emerging Concern

Various CECs were measured in this experiment with 4 of them falling consistently below the analytical detection limit: Levodopa, Aciclovir, Diatrizoic acid, and Miconazole. However, 5 of the CECs measured had concentrations above 5 ppb and for the purpose of this
study these chemicals would be the focus. The CECs that the study focused on included: Lidocaine, Carbamazepine, Sulfamethoxazole, Losartan, and Irbesartan. Table 6 provides some of the chemical properties of the investigated CECs.

Among the different properties, the soil organic carbon-water partitioning coefficient, $K_{oc}$ (adsorption coefficient) can be expressed in terms of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon to its concentration in dilute aqueous solution at equilibrium. Its log value can be used to evaluate the mobility of the different CECs and consequently their environmental fate. In particular, compounds with a Log $K_{oc}$ less than one are characterized by high mobility, while compounds with a Log $K_{oc}$ greater than five are immobile. Among the five CECs investigated, sulfamethoxazole (Log $K_{oc} = 1.96$) is relatively mobile, while Irbesartan (Log $K_{oc} = 4.33$) and Losartan (Log $K_{oc} = 4.13$) are hardly mobile.
Table 6. Chemical properties of contaminants of interest

<table>
<thead>
<tr>
<th>CECs (class)</th>
<th>Chemical Formula</th>
<th>Chemical Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>Log K_{oc} (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lidocaine (anesthetic)</td>
<td>C_{14}H_{22}N_{2}O</td>
<td><img src="image" alt="Lidocaine Structure" /></td>
<td>234.343</td>
<td>2.51</td>
</tr>
<tr>
<td>Carbamazepine (anticonvulsant)</td>
<td>C_{15}H_{12}N_{2}O</td>
<td><img src="image" alt="Carbamazepine Structure" /></td>
<td>236.274</td>
<td>2.73</td>
</tr>
<tr>
<td>Sulfamethoxazole (antibiotic)</td>
<td>C_{10}H_{11}N_{3}O_{3}S</td>
<td><img src="image" alt="Sulfamethoxazole Structure" /></td>
<td>253.28</td>
<td>1.96</td>
</tr>
<tr>
<td>Losartan (Antihypertensive drug)</td>
<td>C_{22}H_{23}ClN_{6}O</td>
<td><img src="image" alt="Losartan Structure" /></td>
<td>422.92</td>
<td>4.13</td>
</tr>
<tr>
<td>Irbesartan (Antihypertensive drug)</td>
<td>C_{25}H_{28}N_{6}O</td>
<td><img src="image" alt="Irbesartan Structure" /></td>
<td>428.54</td>
<td>4.33</td>
</tr>
</tbody>
</table>

Overall, the different packing materials showed limited removal ability towards the different CECs (Figures 17-21). In fact, except for sulfamethoxazole in the presence of activated graphene-coated sand, regardless of the packing material used (activated graphene-coated sand vs. graphene-coated sand vs. raw sand), the percent removal for the different CECs was consistency less than 45% (Figures 17-21). However, among the different treatments, activated graphene-coated sand outperformed graphene-coated sand. This trend was consistent with the results obtained in terms of COD, nitrate, and bacteria removal.
The persistence of some of these CECs was anticipated. For example, carbamazepine acted like a tracer (no removal) in the presence of a SSF unit receiving stream water spiked with primary effluent\textsuperscript{46}. Additionally, numerous studies have shown the stability of carbamazepine under different environmental conditions during field and laboratory investigations\textsuperscript{46-48}. In contrast to carbamazepine, sulfamethoxazole was mostly removed (up to 80\%) in the presence of activated graphene-coated Ottawa sand. This is in contrast with the consistently low removal (< 28\%) achieved during SSF\textsuperscript{49}. To further increase the removal of the selected CECs, an enhanced contact time between the packing materials and the feed water combined with an extended acclimation time should be implemented.
Figure 17. Lidocaine (influent values and percent removal achieved after the different columns) throughout the study
Figure 18. Carbamazepine (influent values and percent removal achieved after the different columns) throughout the study
Figure 19. Sulfamethoxazole (influent values and percent removal achieved after the different columns) throughout the study
Figure 20. Losartan (influent values and percent removal achieved after the different columns) throughout the study
Figure 21. Irbesartan (influent values and percent removal achieved after the different columns) throughout the study
CHAPTER 4. Conclusions

Results from the study highlighted the ability of the proposed materials to successfully remove turbidity (> 85%), total coliforms (> 99%) and E. coli (> 99%), moderately remove COD (< 65%), and poor performance in terms of nitrate (< 30%) and CECs (< 20% with the exception of one type of sand, activated graphene-coated sand, and one CEC, sulfamethoxazole). Even though nitrate removal was limited, it was consistently higher compared to previously published results highlighting an increase in nitrate after slow sand filters due to nitrification occurring within the systems. Results from the study suggested that the ability of the graphene-coated sand to remove nitrate was partially able to overcompensate the nitrification process occurring within the different columns. Activated graphene-coated sand outperformed graphene-coated sand as well as columns packed with raw material. Graphene-coated sand without activation showed a limited enhanced removal in terms of water quality but increased the overall cost of the system. Therefore, instead of using a column entirely packed with graphene-coated sand, it would be more feasible, from an economic point of view, to use a combination of a traditional slow sand filter and a small post treatment containing activated graphene-coated sand. The cost of producing the graphene-coated sand can also be reduced by replacing commercially available sugar, used in the graphitization process, with waste that is rich in sugar content such as waste from a brewery. It is also important to consider that during the process of activating the graphene-coated sand, the addition of an acid (e.g., sulfuric acid) will further increase the cost of the manufacturing of the material.
Future Research

Research can be further conducted on how the system and packing materials can increase the removal efficiencies in terms of basic water quality parameters (e.g., COD, nitrate, etc.) as well as CECs as well as on the economic feasibility of the investigated approach. Some ideas to consider include:

- using different coating processes with reduced consumption of energy, enhanced sorption capacity/surface area, and more uniformity in the coating process;
- investigating the ability of graphene-coated sand to remove forever chemicals (PFAS). The regeneration process associated with graphene-coated sand (e.g., re-heating of the material) can further enhance the removal of CECs, including PFAS;
- implementing low-cost high carbon content alternatives such as agricultural or industrial by-products (e.g., brewery effluent, waste from meatpacking facility) as carbon source alternatives to obtain graphene-coated sand and consequently to further reduce the overall costs associated with the graphene-coated process;
- developing an economic feasibility assessment to estimate and compare the costs of different graphene-coated sand water treatments, evaluate the volumetric freshwater savings achievable under each treatment under the possible implementation scales at the farm or industry-levels, evaluate the implicit ecosystem services provided by these treatments and their merit as a potential sponsored conservation practice, and assess the scalability of these treatments based on the amount of water needed to be treated;
- studying the graphene coated material and the possibility of adding functional groups to enhance the removal of specific CECs using molecular dynamic simulations.
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