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INVESTIGATION OF ACETAMINOPHEN AND CAFFEINE REMOVAL USING MANGANESE OXIDES AND GRANULAR ACTIVATED CARBON IN COLUMN EXPERIMENTS

by

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B.S. CIVIL ENGINEERING
University of New Mexico, 2017

THESIS

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APPLICATION OF MANGANESE OXIDES AND GRANULAR ACTIVATED CARBON FOR EMERGING ORGANIC CONTAMINANT REMOVAL

by

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ABSTRACT

This study was conducted to investigate the application of manganese dioxide ($MnO_{x(s)}$) and granular activated carbon (GAC) media for the removal of the acetaminophen and caffeine. Treatment of emerging micropollutants has become a concern due to their effects on environmental health. Manganese oxides can be a viable alternative for water treatment due to their abundance in the environment. Laboratory scale flow through column experiments were performed using different combinations of commercial $MnO_{x(s)}$ and GAC to assess the removal of caffeine and acetaminophen, and the release of Mn due to the reductive dissolution of $MnO_{x(s)}$. Results from high performance liquid chromatography (HPLC) analyses indicate that the removal of acetaminophen was measured in all media combinations investigated. Removal of caffeine only occurred with columns containing combinations of GAC media. There was no removal of caffeine in columns containing $MnO_{x(s)}$ media. Effluent Mn concentrations analyzed with inductively coupled plasma - mass spectrometry (ICP-MS) increased in column experiments with $MnO_{x(s)}$ media, but effluent Mn were below secondary standard of 50 µg L^{-1} set by the US Environmental Protection Agency. The results of this investigation are relevant for implementation of $MnO_{x(s)}$ in combination with GAC for water treatment processes due to the commercial accessibility of these mineral oxides. The research contributes to a better understanding of alternative applications for the removal of micropollutants in water treatment.

Table of Contents

List of Figures

List of Tables

Chapter 1: Thesis Overview

This thesis consists of 3 chapters and 1 appendix. Chapter 2 contains a summary of the previous and current research and knowledge on the topics of emerging organic contaminants, manganese oxides, and granular activated carbon. It addresses the current research methods and then discusses the gaps within the research and the objective of the research conducted in the thesis. Chapter 3 contains the main portion of the thesis work. It is formatted in as a research journal article which will be submitted to the peer-reviewed journal *Water Research*. The main topic of the research in Chapter 3 is related to the investigation of the removal of emerging organic contaminants acetaminophen and caffeine with combinations of manganese oxide and granular activated carbon media using single stage columns and columns in series experiments. Chapter 3 discusses the results from the column in single stage and columns in series experiments including concentrations of organic compounds acetaminophen and caffeine, concentrations of reduced manganese in solution, and solid media analysis using scanning electron microscope and X-ray photoelectron spectroscopy. It also discusses the use of city of Albuquerque municipal drinking water in the columns in series experiments. Appendix A contains supplementary data and results obtained from the study in Chapter 3.

Chapter 2: Introduction and Literature Review

1 Background and Significance

Micropollutants have received considerable attention in recent years because of the harmful effects in the environment at trace concentrations in natural water sources. This includes pharmaceuticals and personal care products (PPCPs), and endocrine disrupting compounds (EDCs). They are diverse in type and there are various categories in which they can be classified. Aqueous concentrations can range from nanograms per liter (ng L^{-1}) to micrograms per liter (μg L^{-1}). Micropollutants are persistent and bioactive when present in natural surface waters. Endocrine disrupting compounds can cause great effects on the environment including hormonal imbalances of aquatic life. This includes the feminization and decreased reproductive success of aquatic species(De Rudder et al., 2004; Jobling et al., 1998). Although present in low concentrations, the long-term effects on the environment can be detrimental. These concentrations are known to cause negative impacts on the environment, including toxicity, and endocrine disrupting effects (Luo et al., 2014).

A variety of treatment processes in water/wastewater treatment plants can be used for removal of micropollutants from aqueous solutions. The successful application of these treatment processes is a function of the chemical properties of each micropollutant. These processes include coagulation-flocculation, activated carbon adsorption, oxidation processes including chlorination, ozonation, and UV, as well as membrane filtration (Snyder et al., 2003)The use of coagulation-flocculation for micropollutant removal was found to have varying removals from 0 to 50%. The high removals were considered to be from 20-50%. These removals were discerned for compounds with a log K_{ow} of 4 and at the pH range of 7-8 (Matamoros and Salvadó, 2013). As an overall, micropollutant removal with coagulation-flocculation has been inadequate (Luo et al., 2014). Activated carbon adsorption is a common process that has been proven to be successful in the removal of micropollutants (Katsigiannis et al., 2015; Kennedy et al., 2015; Luo et al., 2014; Sotelo et al., 2014). Granulated activated carbon (GAC) and/or powdered activated carbon (PAC) are commonly used to remove micropollutants, but there are problems that can occur if used for this purpose. The removal efficiency can be reduced if the source water has high levels of natural organic matter (NOM). Natural organic matter will compete for the adsorption sites on the surface of the GAC/PAC, which results in the sites being blocked and micropollutants not being able to sorb to the surface (Huguet et al., 2014; Luo et al., 2014; Snyder et al., 2003).

Chemical oxidation processes including chlorination, ozonation, and ultraviolet are commonly used for removal of organic micropollutants. The use of chlorination for micropollutant removal is challenging because Cl can react with the phenolic compounds through and undergo structural substitution in aromatic rings (Snyder et al., 2003). The use of ozonation can result in high removal rates. However, for ozonation to be viable in the removal of micropollutants, the use of advanced oxidation processes should be considered (Bo et al., 2016; Huber et al., 2003; Luo et al., 2014; Snyder et al., 2003). For instance, ultraviolet (UV) light has been found to be effective for removal of certain organic compounds, but it is not effective with all. UV would likely be effective when used in conjunction with other oxidation techniques. Chemical oxidation processes are known also to form disinfectant by-products. Disinfectant by-products formation is important because of their negative health effects. Chlorination disinfectant by-products include trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, and aldehydes.

Ozonation disinfectant by-products include aldehydes, carboxylic acids, ketoacids. Of these disinfectant by-products, the EPA regulates trihalomethanes, five haloacetic acids, bromate, and chlorite (Howe et al., 2012). These disinfectant by-products can form even at high concentrations of organic matter. The use of oxidation techniques for the removal of emerging organic contaminants causes oxidation by-products to form, which can cause harm to the environment as well (Luo et al., 2014; Pablos et al., 2013).

Membrane processes have been considered for removal of emerging organic contaminants. Membrane filtration utilizes microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO). MF and UF generally will not remove micropollutants because the pore sizes are too large. Using membrane filtration for micropollutant removal, it must be used in combination with other processes such as RO, or coagulation and filtration. This combination has seen very high removals ranging from 65% to 90% (Luo et al., 2014). The use of microfiltration requires substantial amounts of energy to overcome the osmotic pressure. Large scale membrane filtration may not be the most viable option for removal of micropollutants.

There are no drinking water regulations from the United States Environmental Protection Agency (EPA) for concentrations of most pharmaceuticals and personal care products (PPCPs) in water. The Safe Drinking Water Act under the EPA protects public drinking water supplies through regulations of constituents, but contaminants of emerging concern and not yet included in this. The EPA has established the *White Paper Aquatic Life Criteria for Contaminants of Emerging Concern: Part I Challenges and Recommendations* as a norm for water quality that includes about 150 pollutants. These standards are used as guidance for state and tribal governments to develop their own standards. The EPA defined the Contaminants of Emerging concern as pollutants that are not currently included in routine monitoring and could be regulated in the future depending on the toxicity to the environment, their potential health effects, public perception, etc. General classes of these contaminants listed in this document include persistent organic pollutants (polybrominated diphenyl ethers, perfluroinated organic acids), PPCPs (prescribed drugs, over-the-counter medicines, bactericides), veterinary medicines (antimicrobials, antibiotics, anti-fungal, hormones), EDCs (synthetic estrogens, androgens), and nanomaterials (carbon nanotubes or nano-scale particulate) (United States Environmental Protection Agency, 2008).

2 Applications of Granular Activated Carbon and Manganese Oxides for Water Treatment

Manganese oxides ($MnO_{x(s)}$) and Granulated Activated Carbon (GAC) are the two types of media selected as the focus of this study. Manganese is the second most abundant transition metal on earth and manganese dioxide (MnO_2) is a mineral that is commonly found in the environment (Hem, 1985). GAC is made of organic materials with high carbon contents. It is a common media that is used in water treatment because of its adsorption qualities.

2.1 Granulated Activated Carbon in Water Treatment

Granular Activated Carbon is most commonly used in drinking water treatment to remove organic constitutes. It is used as an adsorbent for natural and synthetic organic compounds. Granular activated carbon is made up of raw organic materials with high carbon contents. Wood, coal, coconut husk, bamboo, peat, and lignite are all examples of materials that can make up GAC (Çeçen and Aktaş, 2011; Hassler, 1974). Granular activated carbon is produced through two phases including carbonization and activation. The carbonization dries and heats the carbonaceous materials to remove any unwanted by-products. This material is then pyrolyzed and carbonized in a deoxygenated temperature ranging from 400-600°C. This causes the material to undergo the activation process. Activation is achieved thermally with oxidation gases above 800°C (Çeçen and Aktaş, 2011). Based on the particle size, GAC is normally used in a fixed-bed contactor. The basic uses of this in a fixed bed contactor is to control organic compounds, taste, odors, and natural organic matter (NOM).

Granular Activated Carbon is most commonly used in as an adsorbent media in a treatment train because of its non-selective adsorption sites. It is often applied with other types of media, such as sand and anthracite. Granular activated carbon contactors are normally classified through four types of characteristics. This includes: the driving force—pressure or gravity, the flow direction—downflow or upflow, the configuration—single stage, parallel, or in series, and the position—filter adsorber or postfilter adsorber (Summers et al., 2011). Although commonly used within water treatment plants, the cost of replacement and/or regeneration can be very expensive as discussed below (Howe et al., 2012)

2.1.1 Granular Activated Carbon Regeneration

GAC can be regenerated to be reused in water treatment, However, the regeneration is very expensive and difficult to achieve (Çeçen and Aktaş, 2011; Luo et al., 2014). Regeneration occurs when the contaminants are removed from the activated carbon through burning of the media at high temperatures, and the activated carbon is reactivated. If it is not practical to regenerate and reactivate the GAC, it must be disposed of. This can occur because the processes of regeneration and reactivation are challenging, or if the carbon is permanently contaminated (Çeçen and Aktaş, 2011).

The most common technique for carbon regeneration is through thermal processes. Thermal processes include the drying, thermal desorption, and heat treatment of the exhausted GAC. Oxidizing gases are used in limited amounts. The oxidizing gases most commonly used are water vapor and oxygen. When this process occurs, the organic matter that had be adsorbed will oxidize and be removed from the pores of the GAC. The regeneration of activated carbon has the advantage that it allows reuse of spent carbon and reduces the need to purchase new media. (Çeçen and Aktaş, 2011).

2.1.2 Granular Activated Carbon Adsorption Capacities

Although a good adsorbent, GAC does have its limits of how much organic constituents can be adsorbed. Because it is a non-selective adsorbent, it is more likely to be exhausted quicker when the amount of natural organic matter (NOM) is higher. NOM concentrations in water cannot be controlled due to the variability of the water matrix. Granular activated carbon adsorption is determined through the carbon usage rate (CUR). The CUR determines how often the activated carbon will become exhausted and when it needs to be replaced/regenerated. The carbon usage rate is also the "amount of carbon used to treat a volume of water". The CUR is dependent on constituents within the water matrix. The units of CUR are mass of carbon/volume of water (ex. kg/m^3) (Water Treatability Database, 2007; Howe et al., 2012).

2.2 Manganese Oxide in Water Treatment

Manganese oxides have been researched as an effective water treatment technology but have not been widely applied in large scale conventional treatment facilities, but in some smaller applications including the use of Mn-greensand filters (Cerrato et al., 2011). Manganese oxides are also used for removal of metals in solution including manganese and iron (Remucal and Ginder-Vogel, 2014; White et al., 1997). Manganese oxides could be applied to water treatment applications because it acts as an adsorbent and oxidant, although it is not as strong of an adsorbent such as GAC. Manganese oxides are abundant within the environment which leads to a potential inexpensive cost which could lead to less expensive alternatives for water treatment. Although this is the case, manganese oxides are not commonly used in large scale water treatment facilities. Reasons for limited use may be due to the successful application of treatment processes currently used in conventional treatment. For example, sand is currently used in filtration because of its low cost. Also, the use of strong oxidation techniques such as ozone, chlorine, and UV have successful. There is also the risk of soluble Mn(II) release into the water which can be a potential health hazard. (Aguiar et al., 2013; De Rudder et al., 2004; Huguet et al., 2014). The use of MnOx could be applied to smaller waste streams that contain select organic contaminants.

2.2.1 Manganese Oxides Regeneration/Reactivation

When used as a treatment technology for removal of micropollutants, a redox reaction occurs between MnO_2(s) and organic compounds. The reductive dissolution of the MnO_2. The $MnO_{2(s)}$ reduces to $Mn^{2+}_{(aq)}$. This occurs naturally in surface waters, as well as soil and sediments. The reduction reaction that takes place is as follows: $\frac{1}{2} MnO_{2(s)} + 2H^+ + e^- \leftrightarrow \frac{1}{2} Mn^{2+}_{(aq)} + H_2O$ (Morgan and Stumm, 1964; Stone, 1987; Stumm and Morgan, 1996). $MnO_{2(s)}$ has an oxidation state of +4 and the $Mn^{2+}_{(aq)}$ has an oxidation state of +2. This signifies that the manganese reduces from an oxidation state of +4 to +2 when the reaction occurs. If Mn(IV) is reduced, a corresponding oxidation reaction must occur which could consist of oxidation of an organic carbon molecule or oxidation of inorganic constituents such as As(III), Se(IV), or other redox active compounds. When oxygen is present, the MnO_2 acts as a catalyst to help reverse the reductive dissolution of the Mn^{2+}. The oxygen allows for re-oxidation of the Mn^{2+} and allows for the re-precipitation of the Mn^{2+} onto the MnO_2 solid (De Rudder et al., 2004). Therefore, the redeposited $Mn^{2+}_{(aq)}$ goes through another redox reaction and become the MnO_2. The ability for the MnO_2 to act as a catalyst allows for this to become a viable option for water reuse systems.

2.2.2 Manganese Oxide Adsorption Capacities and Oxidation

Manganese oxide media can be applied as an adsorptive medium that can successfully catalyze the oxidation and removal of micropollutants for water treatment applications. The adsorption of the micropollutants may be related to the pH of zero charge (pH_{zc}) of the MnO_2. The pH_{zc} can be directly related to adsorption by identifying the pH at which the charge of the surface is zero. Below the pH_{zc}, the surface of the media is positively charged, and above the pH_{zc} the media is negatively charged. The point of zero charge for the $MnO_{x(s)}$ solid has been investigated using different methods. As an overall, it has been determined that the pH_{zc} for $MnO_{x(s)}$ is about 2.25, which is relatively low on the pH scale. At lower pH values, the oxides can start to dissolve into solution (Tan et al., 2008). Therefore, at natural water pH values (pH range: 6-9) the $MnO_{x(s)}$ solid surface possess a net negative surface charge. The negative surface charge allows any positively charged ions to sorb to the surface of the $MnO_{x(s)}$. Although, most organics are not charged which means that the pH_{zc} will not apply to them. This means other factors discussed below become more important to determine oxidations.

Manganese oxides has also been known to oxidize amines, anilines, phenols, antibacterial agents, atrazine, aromatic N-oxides, and fluoroquinolonics (Huguet et al., 2014; Selig et al., 2003; Xiao et al., 2013; H. Zhang et al., 2008; Zhang and Huang, 2005, 2003) The oxidation of these compounds is thought to be because of the one electron transfer reaction that cause the reductive dissolution of the Mn and the organic compound (Grebel et al., 2016).

2.2.3 Synthetic and Commercial Manganese Oxides

Both synthetic and commercial manganese oxides have been researched as a treatment for emerging organic contaminants within a water treatment setting. Synthetic manganese oxides are commonly synthesized in a lab setting by reacting $KMnO_4$ and $MnCl_2$, usually resulting in an almost pure form of manganese oxides (Murray, 1974; Shaikh et al., 2016; Taujale and Zhang, 2012). Unlike synthetic manganese oxides, there are only a few instances in which commercial manganese oxides have been applied for removal of an organic contaminant (De Rudder et al., 2004; Grebel et al., 2016; Shaikh et al., 2018). Commercial manganese oxides can be purchased from distributors rather than synthesized. They often have other elemental impurities as well. A common commercial manganese oxide that is known is the LayneOx® from Layne Company. Previous research using x-ray fluorescence (XRF) has determined this commercial manganese oxides contains 29.1% impurities. These impurities include 10% Al, 9% Fe, and 7% Si (Shaikh et al., 2018).

The release of soluble Mn from both synthetic and commercial media does occur into solution. This is because of the reductive dissolution of $MnO_{x(s)}$. The process of Mn dissolution is discussed above in section 2.2.1. In a set of batch experiments completed with Bisphenol A as the emerging organic contaminant, the Mn release into solution was 14.2 mg L^{-1}, and 1.7 mg L^{-1} for the synthetic $MnO_{x(s)}$ and the commercial $MnO_{x(s)}$, respectively. This is thought to be due to the differences in surface properties including surface area. Upon normalization of Mn release with the surface area of each media, the release was within 2% for both (Shaikh et al., 2018). Impurities on the surface of the commercial media lowers the amount of surface binding sites. The amount of surface binding sites is vital for the oxidation of organic contaminants, for re-adsorption/re-oxidation of Mn in solution back onto the surface of the $MnO_{x(s)}$ (Shaikh et al., 2018, 2016; Stone, 1987).

3 Chemical Properties of Organic Micropollutants

3.1 Presence of Micropollutants in Water Systems

As discussed in the introduction, micropollutants are mostly found in wastewater as a result of wastes from human use and consumption/excretion of these compounds. They are most commonly found in wastewater effluents. Conventional wastewater treatment has varying degrees of effectiveness at removing these compounds from raw wastewater. The harmful effects of various micropollutants can cause harm to the environment and aquatic life when present in these systems. The following text will review the chemical properties of selected organic compounds that are relevant for water systems.

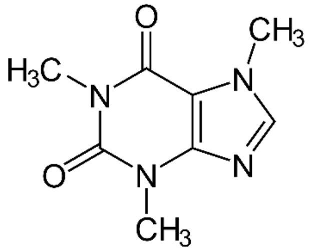
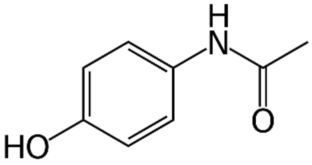
3.2 Caffeine and Acetaminophen Properties

Caffeine and acetaminophen are synthetic organic micropollutants studied in this research. The properties and structures are discussed below and can be found in Table 1. Caffeine is a naturally occurring central nervous stimulant that is the most common psychoactive drug that is consumed by humans. Caffeine can be found in coffee beans, tea leaves, seeds, etc.

In moderate dosages, it is used to aid with drowsiness and alertness. In large doses, it can cause sleep deprivation, reduction of fertility, risk of cardiovascular disease, etc. Caffeine can also be used as an anthropogenic marker for wastewater contamination. Caffeine also slow degrades within the environment. It is partly removed by wastewater treatment, but can still be used to indicate contamination (Gokulakrishnan et al., 2005). This means that caffeine can be input into the system before wastewater treatment and detected after to determine if the caffeine removal was efficient, indicating whether the process was efficient with the removal of other contaminants. Caffeine's water solubility is up to 2.61% at room temperature, with an octanol-water partition coefficient (log K_{ow}) of -0.07 and an acid dissociation constant (pKa) of 14 (Buerge et al., 2003; Dalmázio et al., 2005; Sotelo et al., 2011; Yalkowsky et al., 2010; Yu et al., 2010) .

Acetaminophen, also known as paracetamol, is a non-steroidal anti-inflammatory drug that is widely used as a pain and fever reducer. Acetaminophen can be found in the name brand drug, Tylenol. It is also combined with other ingredients to treat other illnesses such as allergies, cough, flu, etc. In excessive doses, acetaminophen is known to cause liver damage. Acetaminophen's water solubility is about 1.40% at room temperature, with an octanol-water partition coefficient (log K_{ow}) of 0.46, and an acid dissociation constant (pKa) of 9.7 (Huguet et al., 2014; Xiao et al., 2013; Yalkowsky et al., 2010; Yu et al., 2010).

Table 1: Properties and Structures of Caffeine and Acetaminophen

Chemical Name	**Therapeutic Class**	**Molecular Structure**	**Molecular Mass (g/mol)**	**Octanol-Water Partition Coefficient (log K_{ow})**	**Acid Dissociation Constant (pKa)**
Caffeine	Stimulant		194.2	-0.07[a,b]	14.0[b]
Acetaminophen	Non-steroidal anti-inflammatory drug		151.2	0.46[b]	9.7[b]

a. Sangster, J. *Octanol-Water Partition Coefficients: Fundamentals and Physical Chemistry*; John Wiley & Sons, 1997.

b. (Yu et al., 2010)

3.2.1 Reactivity and Degradation of Caffeine and Acetaminophen

When present in systems, micropollutant can degrade and transform into by-products. It is common for this to naturally occur. Oxidation of micropollutants normally occurs within the disinfection step of the treatment processes as mentioned above. This includes ozonation, advanced oxidation, and UV (Huber et al., 2003; Pablos et al., 2013; Zimmermann et al., 2011).

Caffeine degradation and by-product transformation has been studied using the disinfection technique of ozonation and UV. Caffeine is often quickly degraded by these techniques, but there are by-products that remain (Dalmázio et al., 2005). There are various by-products that are present after the oxidation of caffeine that are less likely to be oxidized again (Rosal et al., 2009). As mentioned above in section 4.3, caffeine can be used as an indication of general pollution within wastewater effluents and the sanitation of the source water (Buerge et al., 2003). It can specifically be used to determine any estrogenic activity within waters. Caffeine is often not completely removed in wastewater treatment. The use of caffeine as an indication for the presence of estrogenic micropollutants is strongly correlated, but it is based on the type of estrogenic micropollutant present (Montagner et al., 2014).

$MnO_{x(s)}$ is known to oxidize phenolic compounds. Oxidation by $MnO_{x(s)}$ causes the acetaminophen to be transformed with it interacts with media. $MnO_{x(s)}$ can partly degrade acetaminophen transforming it to 1,4-benzoquinone (Huguet et al., 2014; Xiao et al., 2013). Benzoquinone is a toxic by-product of acetaminophen that can cause damage to the liver and toxicity to the kidneys. Huguet et al, (2014) found that acetaminophen was oxidized into the 1,4-benzoquinone by-product in a $MnO_{x(s)}$ granulated bed filter. The $MnO_{x(s)}$ bed filter contained natural $MnO_{x(s)}$ that has been permitted as a drinking water treatment media. The introduction of a pH buffer (pH 7.0) helped reduce the oxidation of the acetaminophen into the toxic by-product (Huguet et al., 2014). The application of MnOx and GAC in different combinations are explored throughout this thesis to minimize the release of by-products into water.

4 Research Gaps

Research about the application of $MnO_{x(s)}$ as an adsorbent and oxidizing media for emerging organic compounds is still limited. Current literature is focusing on the use of GAC as the adsorption media within column experiments and understanding the mechanisms of $MnO_{x(s)}$ as a media within batch experiments. The next step within these areas would be to investigate the use of $MnO_{x(s)}$ as a water treatment technology for organic compounds. The oxidation of aromatic amines and phenols can occur after reaction with $MnO_{x(s)}$(Balgooyen et al., 2017; Shaikh et al., 2018, 2016) but the application of $MnO_{x(s)}$ as a water treatment technology has not been widely used. Additionally, the use of $MnO_{x(s)}$ and GAC medias in combination can provide further insight for the application of $MnO_{x(s)}$ to current water treatment systems for removal of micropollutants.

It is known that the $MnO_{x(s)}$ acts as a catalyst by allowing re-oxidation of reduced Mn in solution back onto the surface of the $MnO_{x(s)}$. However, the reductive dissolution of $MnO_{x(s)}$ can occur and cause the release of Mn. The use of GAC media in combination with the $MnO_{x(s)}$ media can aid with the remaining uptake of soluble Mn. Addressing these gaps will aid in a better understanding about the application of $MnO_{x(s)}$ media alone or in combination with GAC as a water treatment technology for micropollutants.

5 Research Objective

The objective of this study was to investigate the use of $MnO_{x(s)}$ and granular activated carbon to remove caffeine and acetaminophen in water treatment applications. Two separate column experiments using a single stage system and columns in series were conducted. A comparison and evaluation of organic compound removal with column experiments using different configurations of $MnO_{x(s)}$ and GAC was conducted. Single system columns allow for the comparison of removal efficiencies for commercial manganese oxides and granular activated carbon. Columns in series allow for comparison of removals of organic contaminants between one and two types of media. The use of granular activated carbon allows for the removal of Mn dissolution from the $MnO_{x(s)}$ media .

Chapter 3

Investigation of Caffeine and Acetaminophen removal using MnO_x(s) and GAC in Column Experiments

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ABSTRACT: The objective of this study is to investigate the water treatment applications of manganese dioxide ($MnO_{x(s)}$) and granular activated carbon (GAC) media for the removal of the organic compounds caffeine and acetaminophen. Organic compounds represent an important concern due to their effects on environmental and human health. Manganese oxides can be an accessible alternative for water treatment applications because of their abundance in the environment. Laboratory scale column experiments were performed using different combinations of commercial $MnO_{x(s)}$ and GAC for assessing the removal of caffeine and acetaminophen, and the release of Mn due to the reductive dissolution of $MnO_{x(s)}$. Results from high performance liquid chromatography (HPLC) analyses indicate that removal of acetaminophen was measured for all media combinations investigated in the column experiments. Removal of caffeine only occurred in columns containing combinations of GAC media. There was no removal of caffeine in columns containing only $MnO_{x(s)}$ media. Results from inductively coupled plasma - mass spectrometry (ICP-MS) indicate that Mn release occurred in the columns containing $MnO_{x(s)}$ media, but it below secondary standard of 50 μg L^{-1} set by the US

Environmental Protection Agency. The results of this investigation are relevant for implementation of $MnO_{x(s)}$ and GAC media combinations in water treatment applications due to the commercial accessibility of these mineral oxides. The research contributes to a better understanding of alternative applications for the removal of micropollutants in water treatment.

1 Introduction

Contaminants of emerging concern (CECs) have received substantial attention in recent years in part because of concerns regarding their ecological effects due to bioaccumulation. CECs (also known as micropollutants) include pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) at aqueous concentrations of nanograms per liter (ng L^{-1}) to micrograms per liter (μg L^{-1}) (Bernard et al., 1997; Luo et al., 2014; Pablos et al., 2013; Zearley and Summers, 2012). The presence of these compounds in natural waters are of concern for environmental health because of their persistence, accumulation and bioactivity (De Rudder et al., 2004; Fent et al., 2006; Laha and Luthy, 1990; Snyder et al., 2003). Endocrine disrupting compounds can cause hormonal imbalances in aquatic life, including feminization and decreased reproductive success of organisms. (De Rudder et al., 2004). The harmful ecological impacts present the need for the development of more applicative and efficient water treatment technologies aimed at targeting the treatment of CECs. Traditional water treatment processes are not effective for complete removal of CECs.

There are a variety of water treatment processes that have been studied for the removal of CECs. The successful removal of micropollutants is a function of the chemical properties of each micropollutant. The most common processes include activated carbon adsorption, membrane filtration, and oxidation processes such as chlorination, ozonation, and ultra violet (UV). (Snyder et al., 2003). Activated carbon adsorption has been thoroughly studied because of its ability to remove a wide range of organic compounds. Activated carbon removal efficiencies of micropollutants can be decreased if the water has a high concentration of dissolved organic matter which compete for sorption sites on the carbon (Katsigiannis et al., 2015; Kennedy et al., 2015; Luo et al., 2014; Sotelo et al., 2014). Micropollutants can undergo structural substitution with oxidation processes such as chlorination or must be used in conjunction with other physical-chemical processes. High dissolved organic carbon concentrations can also consume oxidants which causes ineffective removal (Bo et al., 2016; Huber et al., 2003; Luo et al., 2014; Snyder et al., 2003). The other oxidation techniques include UV, UV/H_2O_2, and ozonation. Advanced oxidation processes have been proposed to remove acetaminophen, caffeine, and other emerging organic contaminants using UV light and ozonation (Dalmázio et al., 2005; Devasagayam et al., 1996; Devasagayam and Kesavan, 1996), silica-gel enhanced oxidation (Manoli et al., 2017), among other technologies. More research is necessary to find feasible processes for the removal of emerging organic contaminants.

Acetaminophen and caffeine are two common organic contaminants that are often detected in water effluents. Acetaminophen (N-acetyl-para-aminophenol), also known as paracetamol, brand name drug Tylenol®, is a non-steroidal anti-inflammatory drug. Acetaminophen has a phenolic structure that can be oxidized by $MnO_{x(s)}$ (Huguet et al., 2014; Remucal and Ginder-Vogel, 2014; Xiao et al., 2013). In the presence of $MnO_{x(s)}$ al, acetaminophen transforms into 1,4-benzoquinone (Bedner and MacCrehan, 2006; Huguet et al., 2014). Benzoquinone is a toxic by-product of acetaminophen that can cause damage to the liver and toxicity to the kidneys. Caffeine is a naturally occurring central nervous stimulant that is the most consumed psychoactive drug by humans. Caffeine is a purine alkaloid from the methylxanthine compound (Buerge et al., 2003; Dalmázio et al., 2005; Sotelo et al., 2011). Caffeine scavenges highly reactive free radicals and has been shown to have antioxidant activity (Dalmázio et al., 2005; León-Carmona and Galano, 2011). Effectively attacking the C4=C5 double bond (Dalmázio et al., 2005; León-Carmona and Galano, 2011; Manoli et al., 2017) and the non-electrostatic interaction of H ring in its structure (Sotelo et al., 2011) are some of the challenges associated to degrading caffeine from water matrices.

Manganese oxides ($MnO_{x(s)}$) have been commercialized for use in water treatment systems as an adsorbent and oxidation catalyst for removal of inorganic and organic contaminants (Hua et al., 2011; Remucal and Ginder-Vogel, 2014; White et al., 1997). $MnO_{x(s)}$ are known to adsorb and oxidize various organic compounds including amines, anilines, phenols, antibacterial agents, atrazine, aromatic N-oxides, and fluoroquinolonics (Huguet et al., 2014; Selig et al., 2003; Xiao et al., 2013; H. Zhang et al., 2008; Zhang and Huang, 2005, 2003). Uses of $MnO_{x(s)}$ for water treatment of organic compounds is limited and requires more research in order to be applied effectively to larger scale systems. Additionally, the oxidation of organic compounds such as aromatic amines and phenols using $MnO_{x(s)}$ has been researched (Laha and Luthy, 1990; Remucal and Ginder-Vogel, 2014; L. Zhang et al., 2008), but the investigation of $MnO_{x(s)}$ to remove alkaloids like caffeine is limited. The use of $MnO_{x(s)}$ and GAC media in combination would provide further insight for the application of $MnO_{x(s)}$ for water treatment applications. Addressing these gaps will aid in providing a better understanding of the use and application of $MnO_{x(s)}$ media alone or in combination GAC as a water treatment technology for micropollutants.

The objective of this study was to investigate the application of $MnO_{x(s)}$ and GAC media for the removal of organic compounds acetaminophen and caffeine for water treatment using laboratory column experiments. The experimental approach included the use of single stage columns and columns operated in series with two separate steps of $MnO_{x(s)}$ and GAC media. The integration of aqueous chemistry, microscopy, and spectroscopy analyses were used for investigating the processes for the removal of acetaminophen and caffeine. Well water from the University of New Mexico (UNM) was used for the column experiments operated in series to evaluate the application of $MnO_{x(s)}$ and GAC media for the removal of organic compounds in a more realistic setting. The findings from this study provide new insights about the combined use of $MnO_{x(s)}$ and GAC for the removal of micropollutants for water treatment applications.

2 Materials and Methods

2.1 Materials

Acetaminophen (≥99%) was purchased from Sigma Aldrich. Caffeine (99%) was purchased from Alfa Aesar (Ward Hill, MA). Acetaminophen was selected because of the phenolic structure which is known to be adsorbed by GAC and also can be oxidized and adsorbed by $MnO_{x(s)}$. Caffeine was chosen because it has a purine alkaloid structure and has not been studied as a compound that can be removed with $MnO_{x(s).}$ Commercial manganese dioxides (LayneOx) were purchased from Layne (Woodlands, TX). The commercial manganese dioxide has a manganese dioxide content of 70-80% by weight throughout the media matrix. (Layne Water Treatment Technologies: LayneOx Systems).

Bed density of the $MnO_{x(s)}$ was measured to be 1.903 g mL^{-1}. Granular activated carbon (Norit® PK 3-5) was purchased from Sigma Aldrich. Manganese oxides and granular activated carbon media were crushed, washed with 18 mΩ ultrapure water, dried and sieved to particle sizes of 0.250-0.840mm (US sieve 20x60 mesh) to maintain a uniform size throughout the columns. Bed density of the GAC was measured to be 0.48 g mL^{-1}.

2.2 Analytical Methods

The analytical techniques used for these experiments included PerkinElmer Flexar 400 High Pressure Liquid Chromatography-Ultra Violet (HPLC-UV-VIS), PerkinElmer NexION 300D Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), x-ray photoelectron spectroscopy (XPS), and scanning electron microscope/energy dispersive x-ray spectroscopy (SEM/EDX). The HPLC analyses were used to determine concentrations (mg L^{-1}) of acetaminophen and caffeine from effluent samples taken directly from columns. Calibration of the HPLC-UV-VUS was done using stock solutions of acetaminophen and caffeine. The HPLC column used was TSKgel ODS-80Tm C-18 (4.6×250 mm, 5 µm) with a mobile phase of 40% methanol, 60% phosphate buffer at a flow rate of 0.8 mL min^{-1}. The peak for acetaminophen was obtained around 2.5 minutes retention time, and caffeine peak was obtained around 3 minutes retention time. The ICP-MS analyses determined the concentrations (µg L^{-1}) of soluble Mn effluent samples that were not filtered for the single state column experiment and filtered for columns performed in series experiment The ICP-MS instrument was a Perkin Elmer NexIon 300D inductively coupled plasma-mass spectrometer. X-ray photoelectron spectroscopy was used to characterize the solid $MnO_{x(s)}$ particles of unreacted and reacted media. XPS spectra were recorded using a Kratos Axis DLD Ultra X-ray photoelectron spectrometer with a non-monochromatic Mg

Kα source. Spectra were collected from three different areas on each sample. This was done for the experiments with samples taken from both the top and bottom of the columns. The SEM/EDX was used to determine the morphology and chemical composition of both GAC and $MnO_{x(s)}$ media.

2.3 Experimental Set Up

2.3.1 Single Stage System Columns

The first experiment consisted of a setup of single columns. $MnO_{x(s)}$ and GAC were used to pack the columns. Each column was made of acrylic with a ½ inch inner diameter and a length of 6 inches in three different combinations: 100% GAC, 100% $MnO_{x(s)}$, and 50% $MnO_{x(s)}$/50% GAC, and no media as a control. Each column contained 20g of glass fibers at each end to support the media and minimize dead volumes. The 100% $MnO_{x(s)}$ columns were packed completely with $MnO_{x(s)}$ media (mass of 24g), the 100% GAC columns were packed completely with GAC media (mass of 4.45g), and the 50%/50% combination was packed with $MnO_{x(s)}$ media on bottom and GAC media on top (mass of 12.g and 2.23g respectively). A Masterflex L/S cartridge peristaltic pump, model 7519-25 were used to feed the columns in an upward flow configuration.

A synthetic solution with concentration of 50 mg L^{-1} of acetaminophen and caffeine, 10 mM HEPES buffer, 18 megaohm (MΩ) and a volumetric flow rate of 2.0 ml min^{-1} was used. This concentration was used to ensure effluent concentrations would be within the detection limit of the HPLC-UV-VIS. The empty bed contact time was 8.04 minutes. The 10mM HEPES buffer kept pH of the solution at 7.5. Each column combination was performed in triplicate except for the control which contained no media. Effluent samples were collected at time intervals 0.5, 1, 2, 4, 24, 48, 72, 96, 120, 144, 168, and 192 hours. Effluent concentrations of acetaminophen and caffeine were determined with HPLC-UV.

2.3.2 University of New Mexico (UNM) Municipal Tap Water Testing

A batch experiment was performed using tap water from UNM municipal drinking water (Albuquerque, New Mexico) well. The batch experiment was performed to determine alkalinity and buffering of the source water. The UNM tap water source is supplied by the groundwater pumped from a well on the campus. This well supplied the university campus at a rate of 2000 gallons per minute and lie at a maximum depth of 720 feet below the ground surface. The groundwater is chlorinated before distribution to the campus. For the batch experiment, UNM tap water was stored in an open container for 7 days prior to use in experiment allow residual chlorine to a concentration of 0.1 mg L^{-1} or less. In order to reach this chlorine residual, the tap water was left out of for 7 days in an open container. After the 7 days, the chlorine residual was tested using a Hach Pocket Colorimeter™ II for total chlorine to verify that the chlorine residual would not affect the acetaminophen and caffeine.

A batch experiment was set up in beakers using 50 mL of tap water and 50 mg L^{-1} of acetaminophen and caffeine. This was performed in triplicates with one control of 50 mL of tap water. The pH of the samples was also measured to determine if the tap water solution would need a pH buffer, or if it contained a high enough concentration bicarbonate to be naturally buffered. Samples and pH measurements were taken at time intervals 0, 1, 4, 24, and 72 hours. The concentration of caffeine and acetaminophen were determined using HPLC-UV. Alkalinity was determined by alkalimetric titration. Cations (Ca, Mg, Al, Si) in the tap water were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES). Anions (sulfate, nitrate, chloride, phosphate…) were analyzed using ion chromatography (IC). Trace elements (As, Cu, Pb, Zn, Fe, Mn) were analyzed using ICP-MS.

2.3.3 Columns in Series using UNM Tap Water

The last experiment consisted of two columns in series. The first column in the series contained $MnO_{x(s)}$ media and the second column contained GAC media. Columns of the same dimensions were used. Columns were fed with upward flow to maintain saturation throughout the packed bed. The columns were set up in this configuration to determine if the use of GAC media as the second column in the series would remove the remainder of each constituent that were not removed by the $MnO_{x(s)}$ media.

The concentration of acetaminophen and caffeine in solution was 50 mg L^{-1} was used with the UNM tap water. No pH buffer was used due to the presence of bicarbonate which acts as a natural buffer. Dechlorinated tap water from the UNM water system was used. The tap water was left to sit for 7 days to dissipate the chlorine residual to make sure that the it would not affect the constituents in solution. Each of the series was performed in triplicate. Effluent samples were collected at the time intervals 0, 0.5, 1, 2, 3, 4, 5, 24, 48, 72, 96, 120, 144, 192, 216, and 240 hours. Effluent sample concentrations were also determined using HPLC-UV analysis.

3 Results and Discussion

3.1 Removal of Acetaminophen and Caffeine by $MnO_{x(s)}$ and GAC Single Stage Columns

Removal of both acetaminophen and caffeine was observed in columns reacted with 100% GAC and 50% $MnO_{x(s)}$/50% GAC combination (Figures 1a and 1b). However, only acetaminophen was removed in columns containing 100% $MnO_{x(s)}$ (Figure 1a). Limited or negligible removal of caffeine was observed in columns reacted with 100% $MnO_{x(s)}$ (Figure 1b). Each column combination reached exhaustion at about 1400 bed volumes (BV) or 168 hours.

Acetaminophen was efficiently removed from solution by all combinations of media. Removal with the 50% $MnO_{x(s)}$/50% GAC column combination was efficient, suggesting that both GAC and $MnO_{x(s)}$ aided in the removal of acetaminophen from solution. Acetaminophen has been shown to be removed by GAC (Nam et al., 2014; Sotelo et al., 2014). The removal of acetaminophen by $MnO_{x(s)}$ is caused by adsorption followed by oxidation. The oxidation of acetaminophen can result in the transformation to its by-product 1,4 benzoquinone (Huguet et al., 2014). Reductive dissolution of $MnO_{x(s)}$ after reaction with aniline, triclosan, BPA and other organic compounds has also been reported in other studies (Balgooyen et al., 2017; Remucal and Ginder-Vogel, 2014; Shaikh et al., 2018, 2016). The limited change in concentrations observed in the columns operated with no media (control) indicates that the HEPES buffer had limited reactivity with acetaminophen and caffeine (Figure #).

Caffeine was removed from solution by the 100% GAC and the 50% $MnO_{x(s)}$/50% GAC. The use of GAC alone or in combination with the $MnO_{x(s)}$ provided the best removal for both organic compounds. Granular activated carbon is well known to adsorb a large variety of compounds (Howe et al., 2012). Its high surface area to volume ratio allows adsorption to occur (Dwivedi et al., 2008; Howe et al., 2012; Katsigiannis et al., 2015). Caffeine has been previously shown to be removed by GAC (Kennedy et al., 2015; Sotelo et al., 2011, 2014). Granular Activated Carbon exhaustion was reached at similar times (between 120-160 hours) to the experiments conducted in previous research (Sotelo et al., 2011).There was limited removal of caffeine detected from the 100% $MnO_{x(s)}$ column. Caffeine is an purine alkaloid from the methylxanthine compound group (Buerge et al., 2003; Dalmázio et al., 2005; Sotelo et al., 2014). The pKa of caffeine ranges between 10.4 at 40 degrees C to 14.0 at room temperature (23 degrees C). Thus, the charge of caffeine is neutral and is not likely adsorbed by the MnOx (citation). It is also possible that caffeine was bound covalently to the GAC, but not with MnOx. Caffeine also has antioxidation properties that make it difficult to breakdown (Devasagayam et al., 1996; Devasagayam and Kesavan, 1996). Antioxidant properties of caffeine may explain why oxidation of caffeine by only $MnO_{x(s)}$ was limited. More research is necessary to understand the mechanisms of caffeine adsorption with GAC and its limited adsorption to MnOx.

Soluble Manganese was found in effluent from the 50% $MnO_{x(s)}$/50% GAC and 100% $MnO_{x(s)}$ columns at concentrations in the parts per billion (ppb) range (Supplementary Material- Figures 2a and 2b). Previous literature shows reductive dissolution does occur in which the $MnO_{x(s)}$ is reduced from the 3 to 4 oxidation state to an oxidation state of 2+ (De Rudder et al., 2004; Remucal and Ginder-Vogel, 2014; Shaikh et al., 2016). Dissolved Mn(II) can be adsorbed onto the surface of both the GAC and the $MnO_{x(s)}$. The $MnO_{x(s)}$ acts as a catalyst and redeposit the Mn^{2+} back onto the surface of the $MnO_{x(s)}$ in the presence of oxygen (Aguiar et al., 2013; De Rudder et al., 2004). Importantly, a secondary drinking water standard of 50 $\mu g\ L^{-1}$ has been established for manganese in water (United States Environmental Protection Agency, 1979). All Mn concentrations that were detected within the solution were below this secondary drinking water standard, with most concentrations in the range of 5 ppb.

Additional experiments were done using UNM tap water which is a more representative water matrix in order to better understand how acetaminophen and caffeine react with GAC and $MnO_{x(s)}$ media in columns operated in series.

3.2 Removal of Caffeine and Acetaminophen by $MnO_{x(s)}$ and GAC using UNM Tap Water

The chemistry of UNM tap water is shown in Table 2. A control experiment found no degradation of acetaminophen or caffeine in UNM tap water (Supplementary Material-Figure 3a). The limited changes in the concentration of indicate that the ions have little effect on the degradation of the organic contaminants. The pH of the solution also stayed between 7 and 8 (Supplementary Material- Figure 3b). A neutral pH throughout the 72 hours of the experiment indicates that the tap water is well buffered as indicated by the alkalinity range of 105-160 mg L^{-1} as $CaCo_3$ was obtained. At the pH of 7 and 8 obtained, it is likely that bicarbonate acts as the buffer for this water. The chemistry of UNM tap water is compared with the 2017 Drinking Water Quality Report results distributed yearly by UNM in Table 2. Ion concentrations for Ca, Mg, Al, Si, Fe, Mn, As, Cu, Pb, Zn, SO_4^{2-}, NO_3^-, Cl^- and PO_4^{3-} were measured. Some of the ions had concentrations comparable to the concentrations of organic compound in solution (i.e. SO_4^{2-} concentration was 58.50 mg L^{-1}). The presence of these ions at comparable concentrations indicates that they have little effect on the concentrations of acetaminophen and caffeine throughout the 72 hours of the batch experiment, as well as the media of the columns in series experiments.

The removal of acetaminophen was observed with $MnO_{x(s)}$ in the column experiments (Figure 2a). The outcomes were similar to the results from the column experiments done with synthetic water solution indicating that the effect of naturally occurring ions within the tap water had limited influence on the adsorption/reaction of acetaminophen and caffeine with the $MnO_{x(s)}$ or GAC. The $MnO_{x(s)}$ media column achieved removal of the acetaminophen throughout the first 1800 BV of the experiment, and breakthrough began between 200 and 400 BV. Removal was still occurring throughout this period, but as adsorption capacity was consumed, the acetaminophen concentration in the effluent increased. As reported in previous literature, the removal of acetaminophen with $MnO_{x(s)}$ likely occurs due to adsorption followed by rapid oxidation because it is a phenolic compound (De Rudder et al., 2004; Huguet et al., 2014; Klausen et al., 1997; Laha and Luthy, 1990; Lin et al., 2009; Remucal and Ginder-Vogel, 2014). Oxidation of phenolic compounds is triggered by the reactions that take place on the surface of the $MnO_{x(s)}$ media. A known byproduct of acetaminophen oxidation is 1,4-benzoquinone (Bedner and MacCrehan, 2006; Huguet et al., 2014). Oxidation of acetaminophen by $MnO_{x(s)}$ is considered to occur in two steps: (i) surface complex formation and (ii) electron transfer. These two steps occur at the interface of the acetaminophen and $MnO_{x(s)}$ before the formation of unstable by-products during oxidation. The complexation of acetaminophen to the surface of the $MnO_{x(s)}$ surface is a rate-limiting step (Xiao et al., 2013). The larger initial concentrations of $MnO_{x(s)}$ provides a greater amount of active sites for more complex formations to occur which causes an increase in the reaction rate (Xiao et al., 2013).

Other oxidation techniques, including ozonation, chlorine, UV and UV/H_2O_2 processes, have varying oxidation removals in comparison to $MnO_{x(s)}$. Ozonation at a 2.4 mg L^{-1} dose removes >95% of acetaminophen after 2 minutes of contact time and >80% removal of caffeine after a 24-minute contact time. Longer contact times of ozone causes higher percent removal of caffeine. Free chlorine has a removal of >80% of acetaminophen and <20% removal of caffeine at drinking water dosages. A UV dosage of 40 mJ cm^{-2} has a removal of 20-50% of acetaminophen, but <20% removal of caffeine. A UV/H_2O_2 treatment with a dosage of UV at 372 mJ cm^{-2} and a dosage of H_2O_2 of 5 mg L^{-1} removal >80% removal of acetaminophen and 50-80% removal of caffeine (Snyder et al., 2007). The removal rates of chlorine and UV do not have as high of removal rates as $MnO_{x(s)}$ media for acetaminophen when compared to the experimental data. The use of $MnO_{x(s)}$ could provide higher removal rates if used as a treatment technology in comparison to these other existing oxidation techniques.

Exhaustion of $MnO_{x(s)}$ media occurs in the presence of acetaminophen. This exhaustion is likely due to the acetaminophen occupying the adsorption sites on the surface of the $MnO_{x(s)}$. The by-product of acetaminophen oxidation, 1,4-benzoquinone, could be present in the surface sites but requires further investigation. $MnO_{x(s)}$ has the ability for regeneration in the presence of a strong oxidant. $MnO_{x(s)}$ cannot be regenerated with weaker oxidants such as oxygen at the pH 7-8 because the E_h value is too low (<0.8) (Xie et al., 2010). In parallel, chlorine is a stronger oxidant that can regenerate the $MnO_{x(s)}$ media. Studies have indicated that columns operated in the presence of chlorine aid in the removal of Mn(II) from solution due to the regeneration of the $MnO_{x(s)}$ (Cerrato et al., 2011). Because chlorine is absent from the solution with the column experiments, the $MnO_{x(s)}$ is not regenerated and the oxygen present in the reaction is not strong enough for favoring the regeneration.

As observed in the single stage experiments, limited removal of caffeine occurred after reaction with $MnO_{x(s)}$ media in the experiments conducted in series (Figure 2a). The results suggest that there is no adsorption or oxidation occurring in the $MnO_{x(s)}$ media. As suggested in the discussion for the single stage column experiments, caffeine has antioxidant properties (Dalmázio et al., 2005; Devasagayam et al., 1996; Devasagayam and Kesavan, 1996) as it can scavenge highly reactive free radicals. (Dalmázio et al., 2005; León-Carmona and Galano, 2011). Other research has shown that $MnO_{x(s)}$ can oxidize organic compounds such as phenols, amines, anilines, etc. However, cleavage of the C4=C5 double bond in the structure of the caffeine molecule provides a challenge towards the oxidation of caffeine (Dalmázio et al., 2005). It is possible that $MnO_{x(s)}$ is not capable of cleaving the C4=C5 double bond, which could explain why limited removal of caffeine was obtained after reaction with $MnO_{x(s)}$. This indicates that the $MnO_{x(s)}$ media can selectively react only with certain organic compounds based on their structure.

Acetaminophen and caffeine were both removed by the GAC (Figure 2b) . The GAC obtained consistent removals for the first 400 BV, and then breakthrough occurred between 600 and 800 BV. The concentration of caffeine in effluent samples reached the initial concentration around 120 hours. The limited removal of caffeine with the $MnO_{x(s)}$ media caused exhaustion of the GAC media and reached saturation within the first 1790 BV. Reaction with acetaminophen did result in complete saturation of the column after the 240 hours. This is likely due to the contribution of the $MnO_{x(s)}$ media column in the stage prior reaction with the GAC column that contributed to the removal of acetaminophen. Since both caffeine and acetaminophen adsorb readily with GAC, then the breakthrough of the media was observed during the 240-hour experiment duration. With a high initial concentration as high as 50 mg L^{-1} it is likely that the media reach saturation much quicker than would occur at lower environmentally relevant concentrations (ng L^{-1} or μg L^{-1}). In real situations, the initial concentrations of these CECs would be in the μg L^{-1} range and the amount of bed volumes needed before exhaustion would increase by 3-4 orders of magnitude (i.e. 1000 times). This is more realistic because the GAC adsorbs many compounds, inorganic and organic, as it is a non-selective media (Çeçen and Aktaş, 2011; Snyder et al., 2003; Westerhoff et al., 2005).

Adsorption capacities of the GAC media for the columns performed in series were calculated based on the experimental data obtained for the removal of acetaminophen and caffeine and compared with capacities based on the Polanyi equation and Freundlich parameters (Snyder et al., 2007). Adsorption capacity of the GAC for the constituents based on the experimental data from this study was 29.46 mg of acetaminophen per g of GAC and 32.80 mg caffeine per g of GAC. At the feed concentration of this study, the adsorption capacity for acetaminophen based on the Polanyi equation and Freundlich parameters was 34.06 mg of acetaminophen per g of GAC and 93.23 mg caffeine per g of GAC as reported in other studies (Snyder et al., 2007). The determination of the adsorption capacity was based on the Freundlich isotherm for a single solute (Howe et al., 2012). Comparable adsorption capacities for caffeine measured in other studies are within a similar range (150-250 mg g^{-1}) (Sotelo et al., 2011). The Polanyi theory describes adsorption by pore filling of micro porous adsorbents. It assumes that a thin layer of a fixed volume is present on the surface of the adsorbent and weak interactions on the surface with the adsorbed molecules hold them in place (Snyder et al., 2007). Freundlich parameters were obtained from Snyder et al., 2007 based on the Polanyi equation and a Calgon F-400 GAC. The Freundlich adsorption capacity parameter K (mg g^{-1})*(L mg^{-1})^(n^{-1}) for acetaminophen and caffeine were 1.84 and 10.8, respectively. The Freundlich adsorption intensity parameter n^{-1} for acetaminophen and caffeine were 0.746 and 0.551, respectively. Freundlich equation is as follows: $q_e=KC^{1/n}$, where q_e is the adsorption capacity in mg of adsorbate per g of adsorbent and C is the equilibrium concentration of adsorbate in solution as mg L^{-1} (Howe et al., 2012). Comparison of experimental data adsorption capacity obtained for this study and the model adsorption capacity based on parameters provided in the literature are similar (Snyder et al., 2007). Because these experiments were continuous flow through, experimental Freundlich isotherms were not determined in this study. The similarities of the experimental and modeled adsorption capacities indicate that the GAC used in this experiment is sufficient for the removal of acetaminophen and caffeine. At more realistic concentrations (μg L^{-1}) of constituents, the GAC would have a greater adsorption capacity and be used for longer periods of time before exhaustion occurred.

Results of the ICP-MS analysis indicated that the concentration of dissolved Mn in solution decreased after flowing water through the GAC media column as shown in Supplementary Material Figure S1c. The effluent concentrations were measured with the ICP-MS for total Mn. Mn in solution from the samples after the $MnO_{x(s)}$ media column were 4-5 times higher than the Mn concentrations that were detected after the GAC media column. Some of the effluent samples from the $MnO_{x(s)}$ media column exceed the EPA's secondary drinking water standard of 50 ppb for Mn (United States Environmental Protection Agency, 1979) in drinking water sources, reaching concentrations as high as 220 μg L^{-1}. However, after reaction with the GAC column, the concentrations dropped below the EPA secondary drinking water standard. These results indicate that the GAC aided in the removal of reduced Mn from solution through adsorption. Removal of Mn(II) from solution with GAC has been reported in previous studies (Bin Jusoh et al., 2005).

Future research should explore the integrated use of $MnO_{x(s)}$ and GAC in series for complex water matrices to investigate the removal of inorganic and organic compounds. Additional solid analyses were conducted to better investigate changes in Mn oxidation state in solid samples before and after the column experiments.

3.3 $MnO_{x(s)}$ and GAC Media Solid Analyses

Scanning electron microscope and energy dispersive X-ray spectroscopy (EDX) analyses indicate that both unreacted and reacted $MnO_{x(s)}$ from the column experiments operated in series have a similar morphology and chemical composition. For example, both unreacted and reacted $MnO_{x(s)}$ media (Supplementary Material- Figure S4a and S5a) have a porous surface with an average grain size ranging from 460-775 μm. The EDX results (Supplementary Material- Figure S4b and S5b) indicate that a majority of the MnOx media for unreacted and reacted are elements Mn and O (Supplementary Material- Table S1). The EDX also indicated the impurities on the surface of the $MnO_{x(s)}$ which include Al (5.69%), and Si (3.94%) (Supplementary Material- Table S1). The percent of impurities is comparable to that obtained in a previous study in which commercial $MnO_{x(s)}$ contained 29.1% impurities, including 10% Al, 9% Fe, and 7% Si (Shaikh et al., 2018). Interestingly, the EDX analyses of the reacted $MnO_{x(s)}$ detected the presence of K (1.35%). This could indicate levels of K from in the source tap water used for these experiments. The SEM/EDX analyses for unreacted GAC media (Supplementary Material- Figure S6a) showed a porous surface with various sizes and an average grain size ranging from 600-800 μm. The EDX results indicated that the chemical composition of the unreacted GAC was mostly C (94.17%) and a small amount of O (5.22%) (Supplementary Material- Table S3). This is consistent with literature because GAC is made from carbonaceous materials through oxygen deficient high temperature pyrolysis (Çeçen and Aktaş, 2011). As expected, the SEM images for reacted GAC analysis looked similar to those obtained for unreacted GAC (Supplementary Material- Figure S7a) with various pore and an average grain size raining from 370-730µm. Although imaging looked similar, EDX (Supplementary Material- Figure S7b) indicated that there were other constituents adsorbed on the surface of the GAC including Si (0.65%), Mg (0.43%), Al (0.35%), and Ca (0.26%) (Supplementary Material- Table S4). The presence of these constituents on the reacted GAC is likely due to the absorption of them from the UNM tap water solution. The analysis of concentrations of constituents in the tap water can be found in Table 2.

Analyses using XPS indicate that Mn reduction took place after reacting $MnO_{x(s)}$ media in the single stage column experiments. For example, fits of the Mn3p high resolution scans indicate an increase of 28.4% Mn(III) and 8.8% Mn(II) for the $MnO_{x(s)}$ media from the 50/50 media combination column compared to what was initially present in the in unreacted media (Supplementary Material- Figure S8a and S8b, Table S5). The increase of 33.3% Mn(III) and 8.5% Mn(II) for the $MnO_{x(s)}$ media from the 100% $MnO_{x(s)}$ media column (Supplementary Material- Figure S8a and S8c, Table S5).The presence of soluble Mn detected in these column experiments confirms that reductive dissolution occurred after the reaction of $MnO_{x(s)}$ in these experiments. Additionally, the presence of Mn(II) detected in the reacted media could be indicative of the re-adsorption of soluble Mn during these experiments. These results are consistent with previous research which report the reduction of synthetic and commercial $MnO_{x(s)}$ media with organic compounds such as phenol, aniline, triclosan, and BPA (Shaikh et al., 2018, 2016).

3.4 Implications for Water Treatment

The results from this study suggest that the application of $MnO_{x(s)}$ and GAC in series can remove organic compounds from UNM tap water with minimal release of soluble Mn. Acetaminophen and caffeine effectively adsorbed to GAC. The use of columns in series with the MnOx and GAC media columns could be advantageous. For example, $MnO_{x(s)}$ can be used selectively used to remove phenolic compounds such as acetaminophen, with limited reaction with alkaloid organics such as caffeine. The use of $MnO_{x(s)}$ and GAC media concurrently in a system may be used on a broader range of compounds that could adsorbed and oxidized by the $MnO_{x(s)}$ media in an initial stage, and then adsorbed by GAC in a second stage. This approach can facilitate the selective removal of phenols, anilines, and other compounds that are removed by $MnO_{x(s)}$ (Huguet et al., 2014; Selig et al., 2003; Xiao et al., 2013; H. Zhang et al., 2008; Zhang and Huang, 2005, 2003), slowing the exhaustion of available adsorption sites on GAC. Partial oxidation may also occur which increases the biodegradability of acetaminophen as seen similarly with partial oxidation by ozone (Bedner and MacCrehan, 2006). The application of this method has been evaluated in this study using UNM tap water. Experiments with waters that contain higher content of organic matter or other constituents are necessary to evaluate the removal constituents with different media combinations. Addressing these research gaps could provide further opportunities for the application of these media in treatment systems and determine the removal of emerging organic contaminants under these conditions.

The results of the tap water testing showed that co-occurring ions did not affect the removal organic compounds acetaminophen and caffeine . This suggests that the application of a treatment system with $MnO_{x(s)}$ and GAC media for the removal of organic compounds is promising. Future research with more complex waters including higher organic matter concentrations, and other organic compounds including the by-products produced from oxidation and other emerging organic contaminants present at trace concentrations is needed to further assess the use of $MnO_{x(s)}$ and GAC for removal of organic contaminants for water treatment applications.

4 Conclusions

- The removal of acetaminophen by $MnO_{x(s)}$ was observed with breakthrough occurring between 1700-2000 bed volumes. However, $MnO_{x(s)}$ did not remove caffeine. The application of GAC resulted in the removal of both acetaminophen and caffeine.
- The results presented in these experiments indicate that the combination of $MnO_{x(s)}$ and GAC resulted in the removal of acetaminophen and caffeine in synthetic and UNM tap waters.
- Reaction of $MnO_{x(s)}$ with organic compounds in the experiments conducted in this study resulted in the reductive dissolution of $MnO_{x(s)}$, causing the release of soluble Mn in column effluents. However, soluble Mn can be removed by GAC media after operation in series with $MnO_{x(s).}$

Table 2: Properties of UNM Municipal Tap Water

Ion	Detected Concentration	UNM Well Maximum Detected Concentration in 2017[e]	EPA Maximum Contaminants Level (MCL)	EPA Maximum Contaminants Level Goal (MCLG)	EPA Secondary Drinking Water Standard
Calcium (Ca)	43.50 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	n.a.[d]
Magnesium (Mg)	8.01 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	n.a.[d]
Sodium (Na)	33.53 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	20 mg L^{-1} [f]
Aluminum (Al)	2.17 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	0.05 to 0.2 mg L^{-1}
Silicon (Si)	27.9 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	n.a.[d]
Iron (Fe)	mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	0.3 mg L^{-1}
Manganese (Mn)	0.23 μg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	0.05 mg L^{-1}
Arsenic (As)	4.76 μg L^{-1}	7 μg L^{-1}	10 μg L^{-1}	0 μg L^{-1}	n.a.[d]
Copper (Cu)	0.08 mg L^{-1}	0.17 mg L^{-1}	TT[c]; Action Level= 1.3 mg L^{-1}	1.3 mg L^{-1}	n.a.[d]
Lead (Pb)	0.00 mg L^{-1}	0.003 mg L^{-1}	TT[c]; Action Level 0.015 mg L^{-1}	0 mg L^{-1}	n.a.[d]
Zinc (Zn)	3.475 μg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	5 mg L^{-1}
Sulfate (SO_4^{2-})	58.50 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	250 mg L^{-1}
Nitrate (NO_3^-)	2.42 mg L^{-1}	n.a.[a]	10 mg L^{-1}	10 mg L^{-1}	n.a.[d]
Chloride (Cl^-)	30.50 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	250 mg L^{-1}
Phosphate (PO_4^{3-})	0.00 mg L^{-1}	n.a.[a]	n.a.[b]	n.a.[b]	n.a.[d]

a. UNM measurements for parameter not present in 2017 Water Quality Report
b. No MCL or MCLG set for this parameter
c. TT- Treatment Technique; a process required to reduce the contaminant level in drinking water
d. No secondary drinking water standard set
e. (University of New Mexico, 2017)
f. (United States Environmental Protection Agency, 2003)

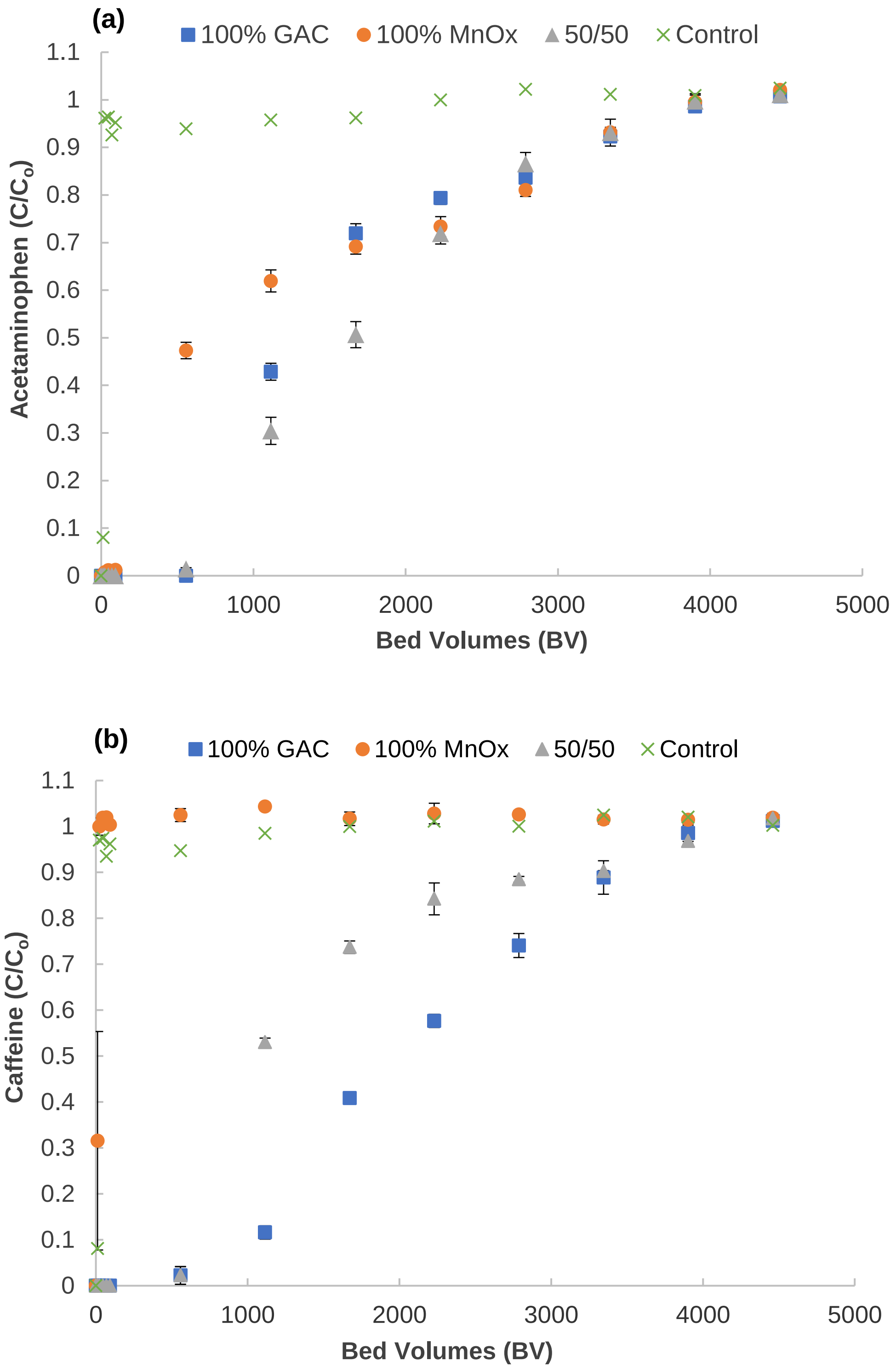

Figure 1: Effluent concentrations of (a) acetaminophen and (b) caffeine of bench-scale packed columns completed as single stage columns and fed with a synthetic water solution. The synthetic water solution consisted of an initial concentration (C_o) of 50 mg L^{-1}. Error bars represent standard deviation of triplicate data.

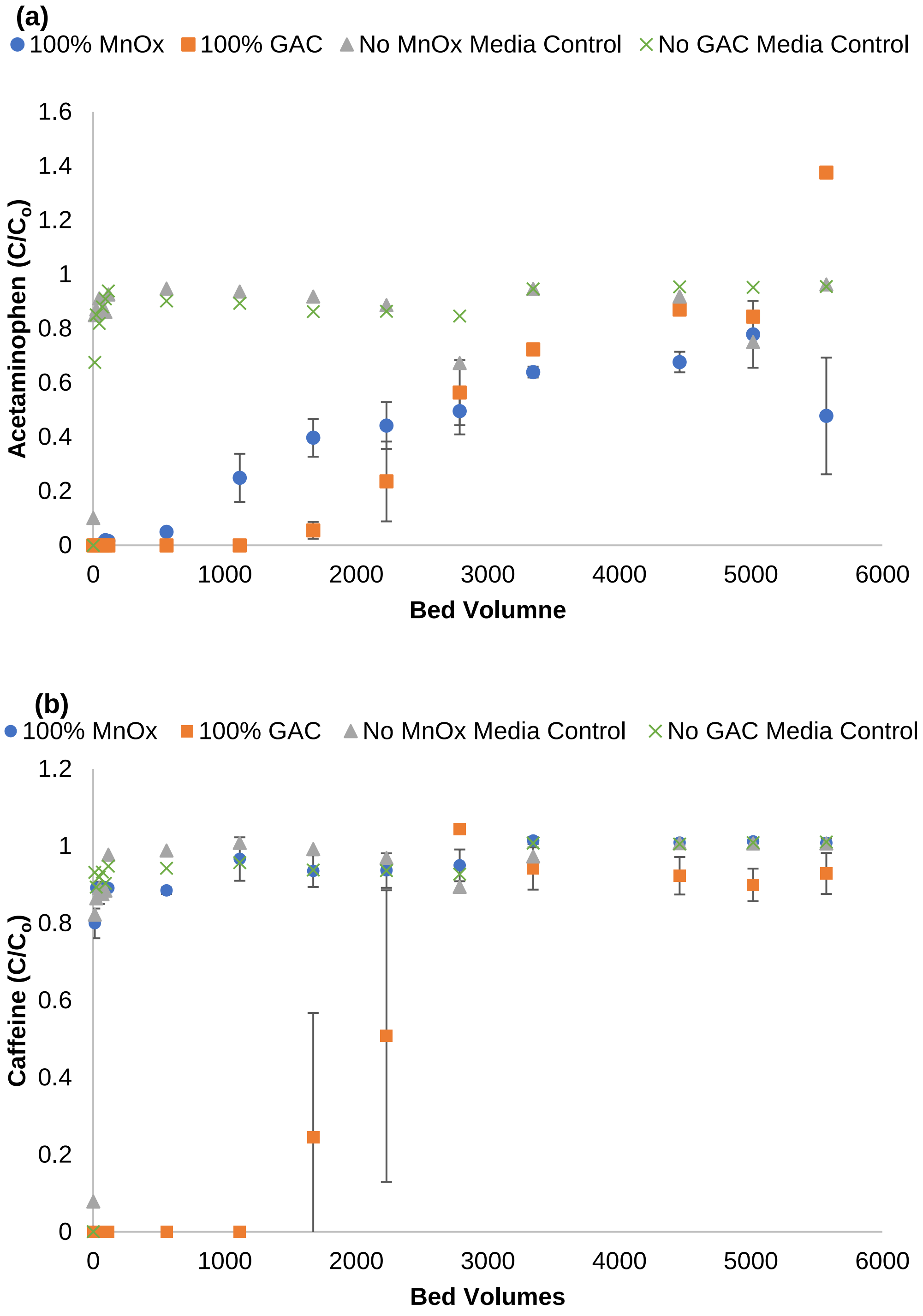

Figure 2: Effluent concentrations of (a) acetaminophen and (b) caffeine of bench-scale packed columns completed as single stage columns and fed with the UNM Tap water solution. The synthetic water solution consisted of an initial concentration (C_o) of 50 mg L^{-1} for MnOx effluent and C_o for GAC effluent samples is effluent MnOx concentrations . Error bars represent standard deviation of triplicate data.

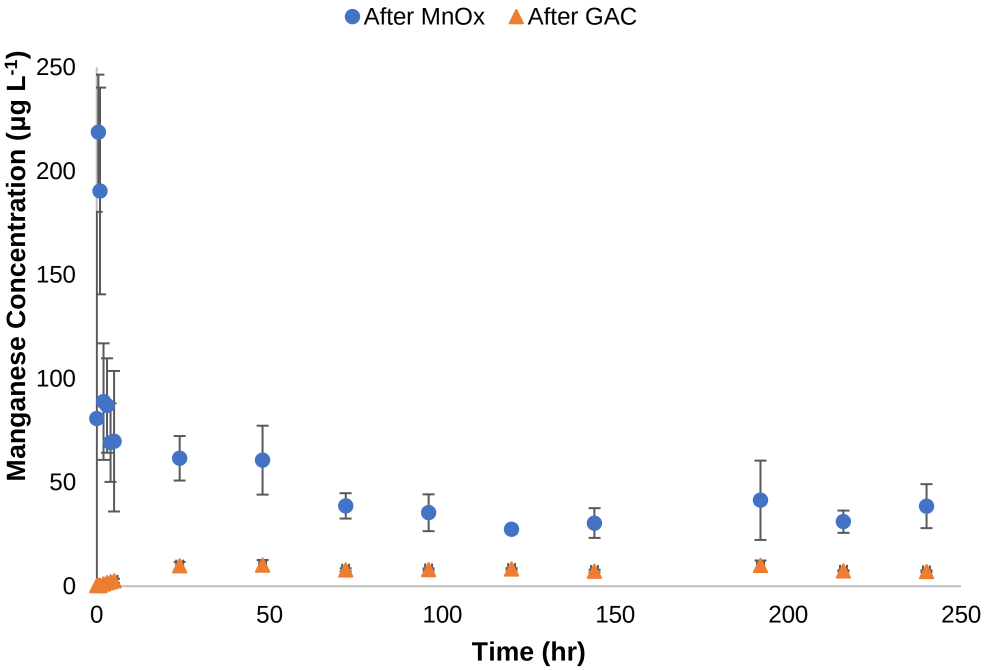

Figure 3: Manganese concentration from effluents of MnOx and GAC media columns.

Appendix A

Supplementary Material for Investigation of Caffeine and Acetaminophen removal using MnOx(s) and GAC in Column Experiments

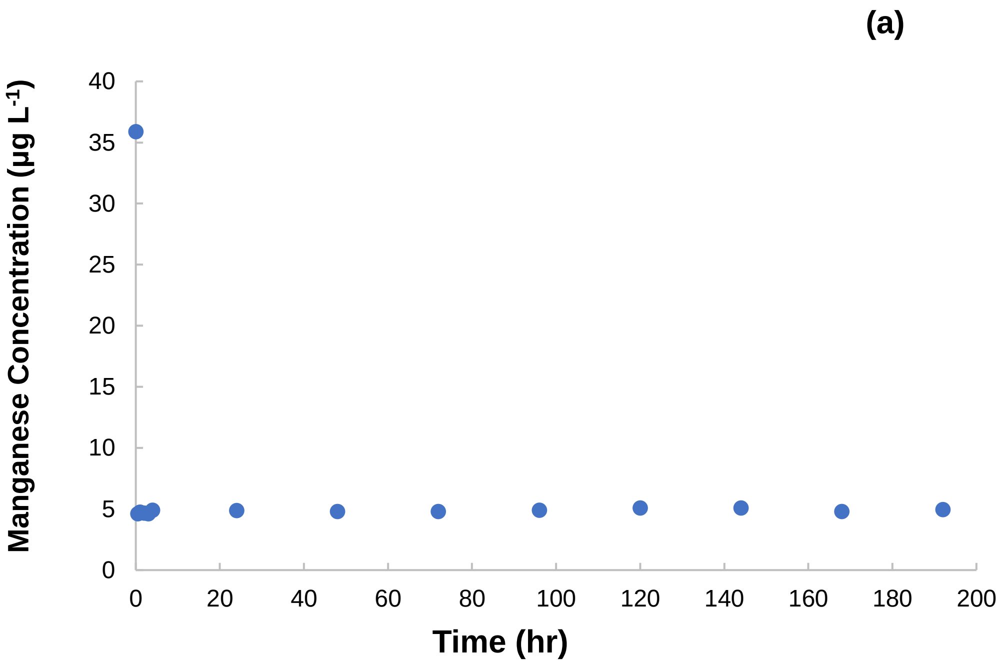

Figure S1a: Manganese effluent concentrations for 100% MnOx media column with a synthetic water solution. EPA has set a secondary drinking water standard of 50 µg L^{-1} for Mn in solution.

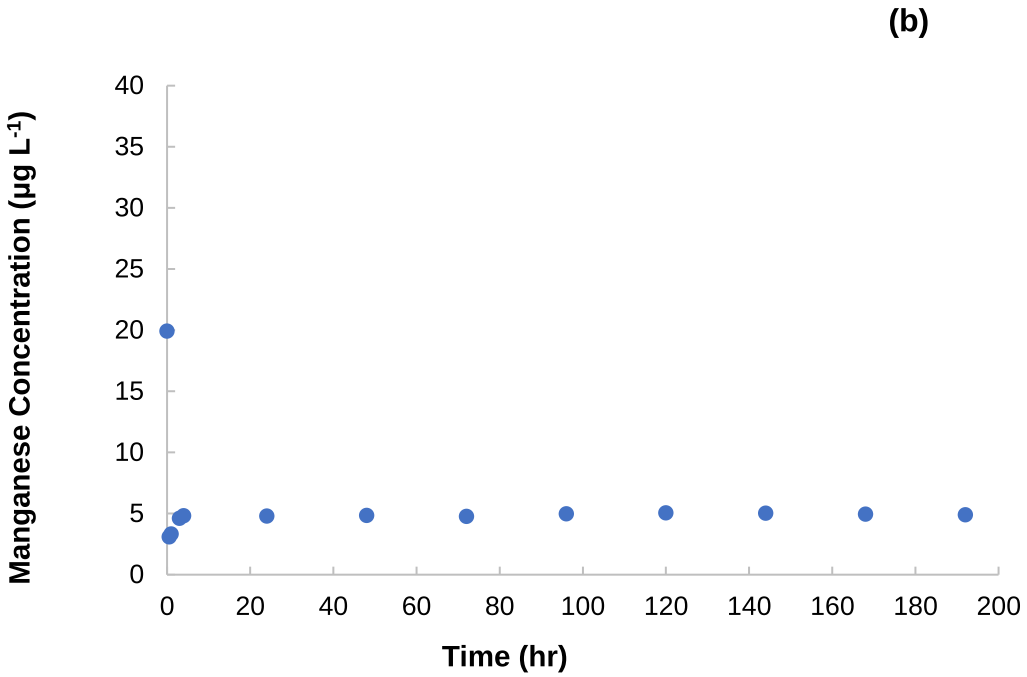

Figure S1b: Manganese effluent concentrations for 50% MnOx/50% GAC media columns with a synthetic water solution. EPA has set a secondary drinking water standard of 50 µg L^{-1} for Mn in solution.

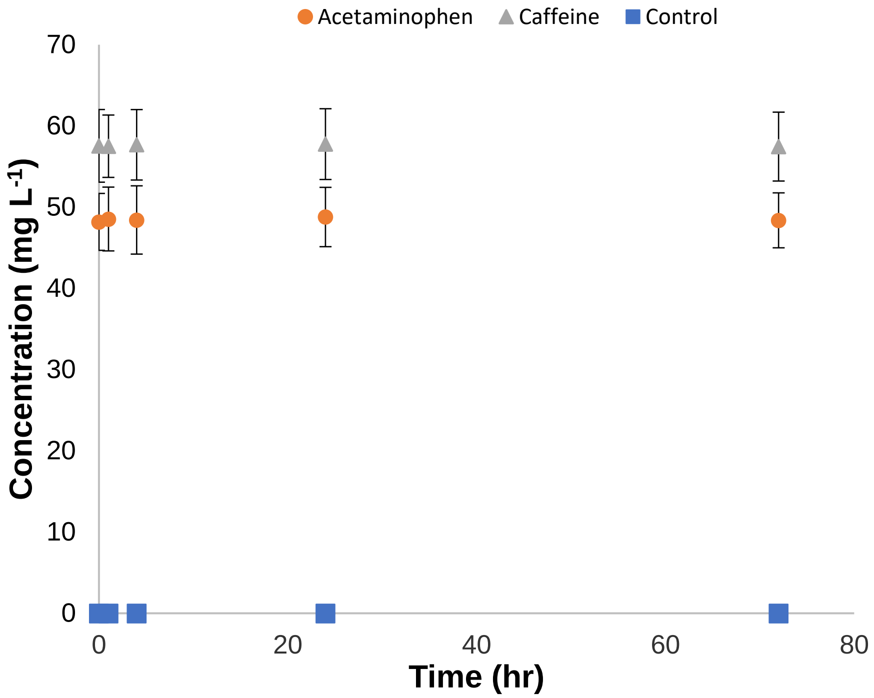

Figure S2: Albuquerque tap water batch experiment concentration of acetaminophen and caffeine results over 72 hours. The initial concentration of the acetaminophen and caffeine solution was 50 mg L^{-1}. The control was contained 50 mL of tap water with no acetaminophen and caffeine.

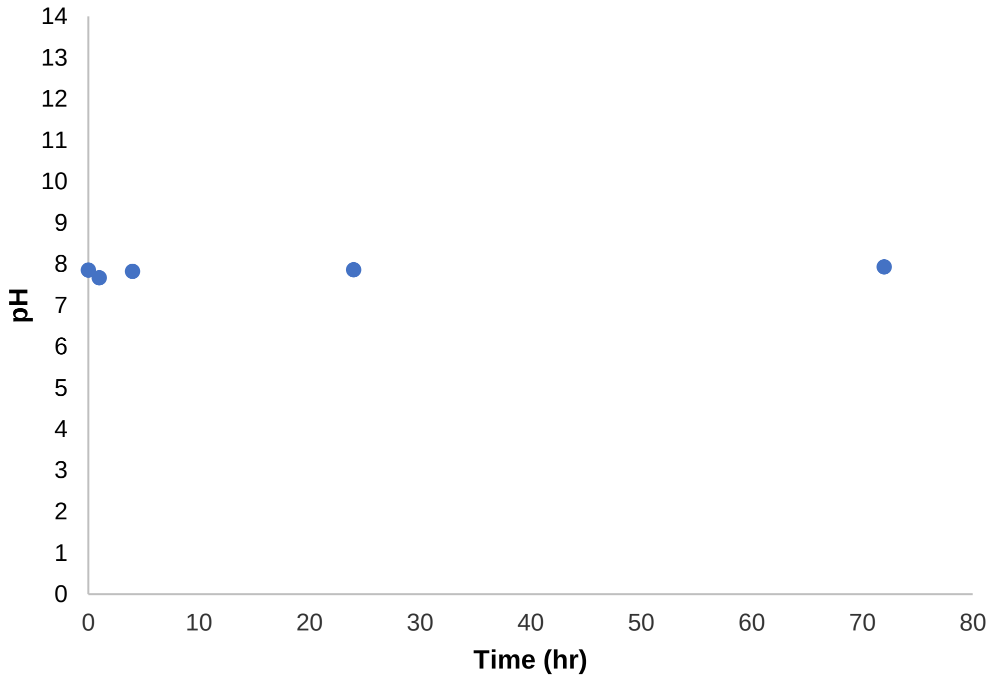

Figure S3: Albuquerque tap water batch experiment pH over 72 hours. Error bars represent the standard deviation of the average pH.

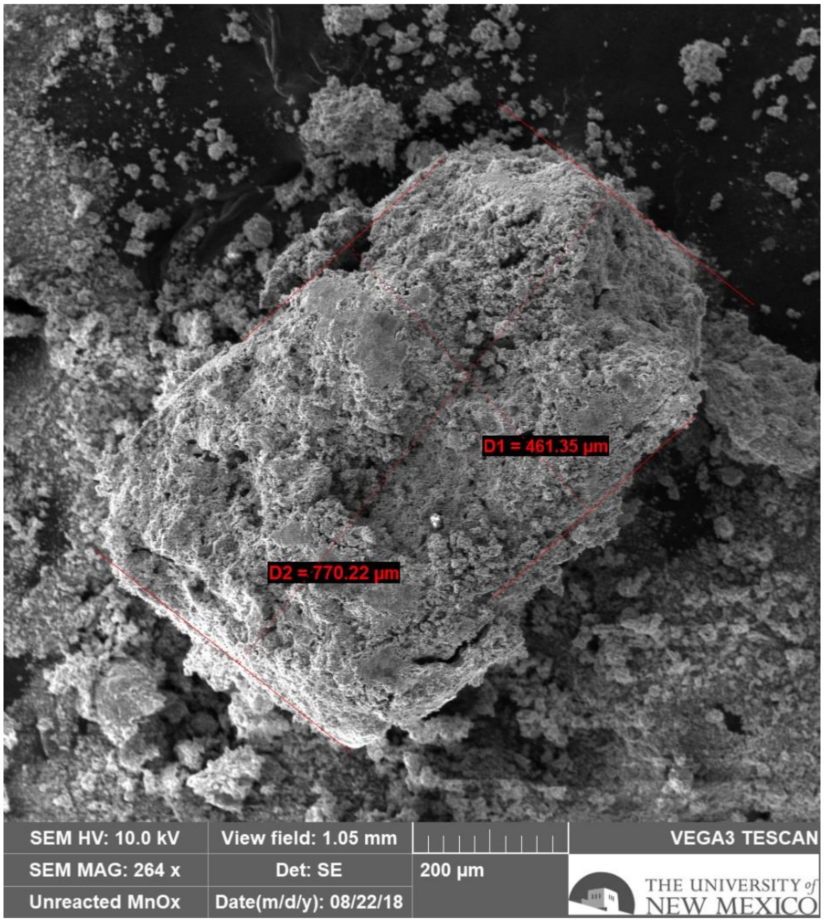

Figure S4a: Scanning electron microscope imaging of unreacted MnOx with particle size.

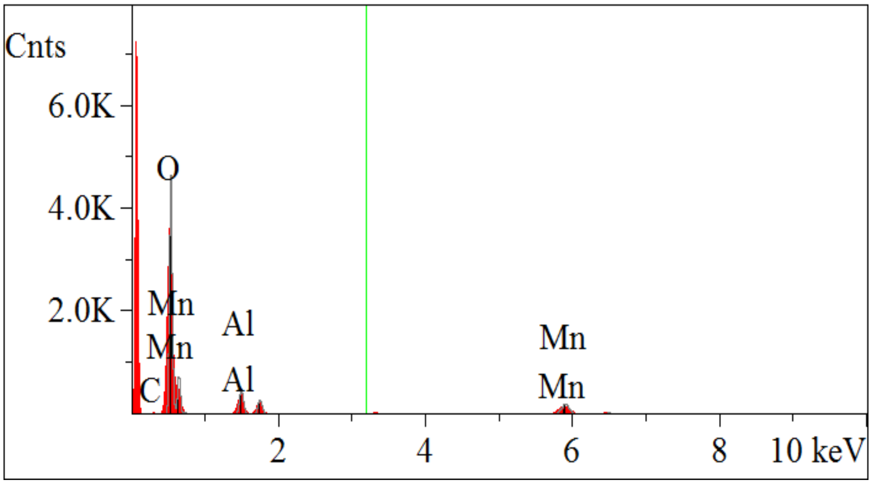

Figure S4b: Energy dispersive x-ray spectroscopy spectrum for unreacted MnOx.

Table S3: Energy dispersive x-ray spectroscopy components for unreacted MnOx.

Element	**Conc.**	**Units**	
C	0.236	wt.%	
O	42.272	wt.%	
Al	5.969	wt.%	
Si	3.941	wt.%	
Mn	47.582	wt.%	
	100.000	wt.%	Total

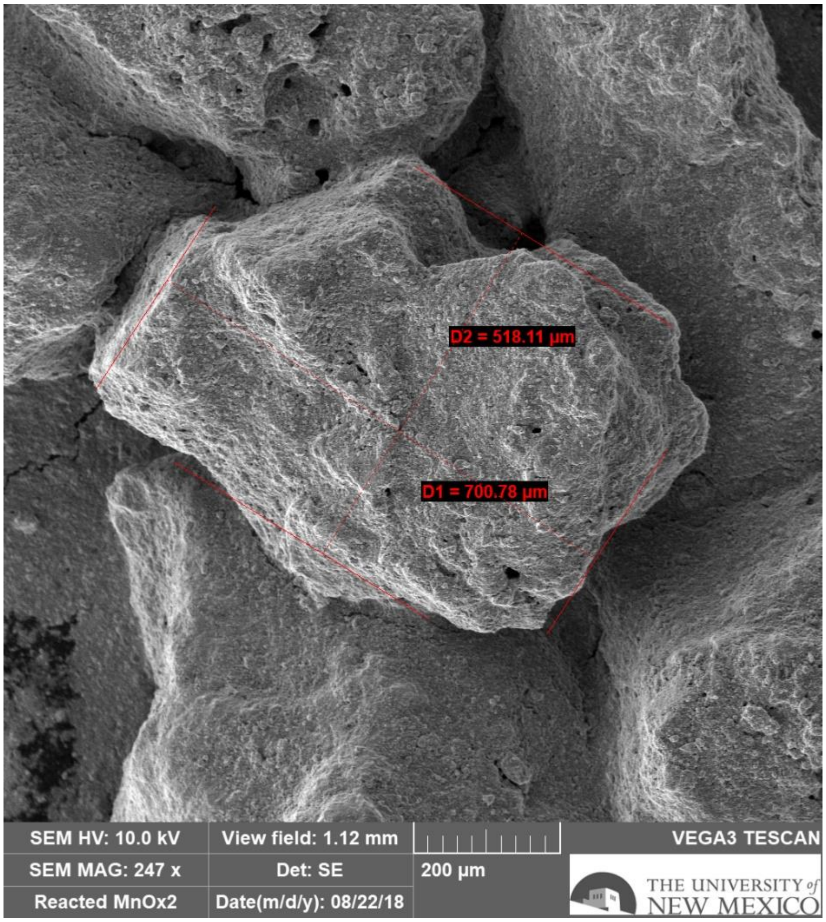

Figure S5a: Scanning electron microscope imaging of reacted MnOx with particle size.

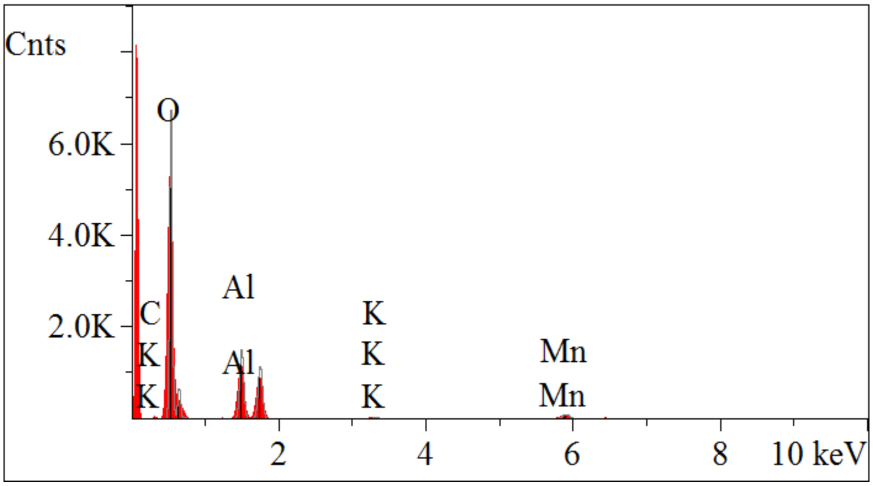

Figure S5b: Energy dispersive x-ray spectroscopy spectrum for reacted MnOx media.

Table S4: Energy dispersive x-ray spectroscopy components for reacted MnOx.

Element	**Conc**	**Units**	
C	0.379	wt.%	
O	52.132	wt.%	
Al	13.609	wt.%	
Si	12.248	wt.%	
K	1.353	wt.%	
Mn	20.279	wt.%	
	100.000	wt.%	Total

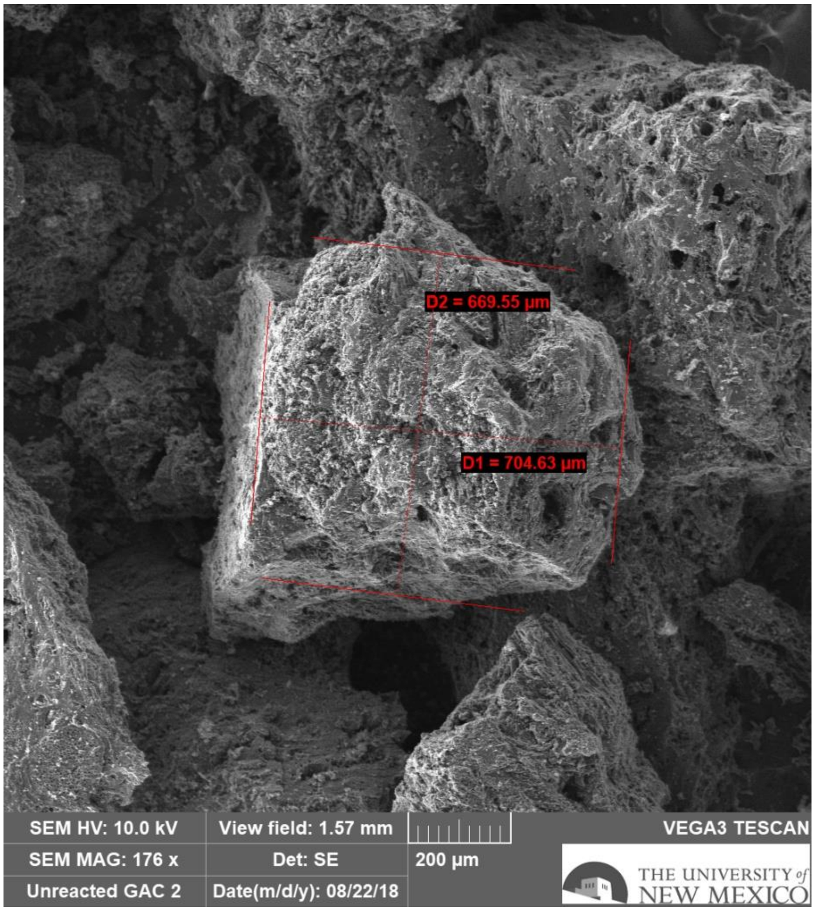

Figure S6a: Scanning electron microscope imaging of unreacted GAC with particle size.

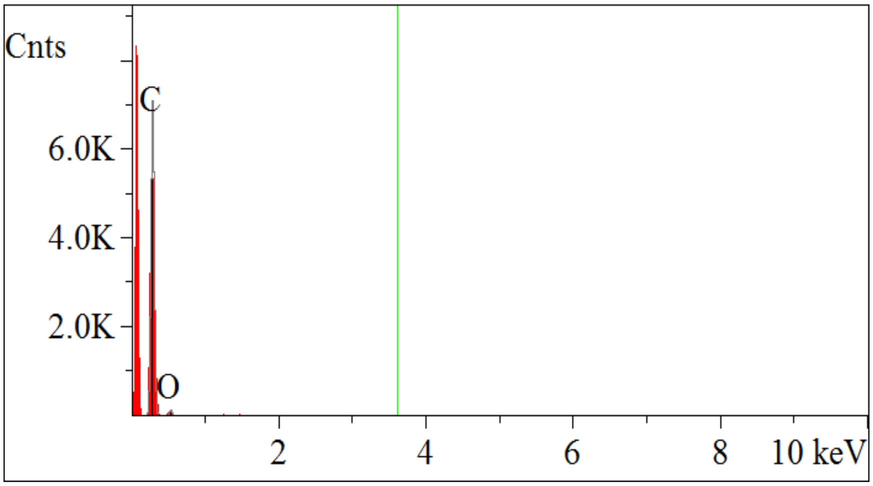

Figure S6b: Energy dispersive x-ray spectroscopy spectrum for unreacted GAC media.

Table S5: Energy dispersive x-ray spectroscopy components for unreacted GAC.

Element	**Mole Conc.**	**Conc.**	**Units**	
C	94.784	93.170	wt.%	
O	5.216	6.830	wt.%	
	100.000	100.000	wt.%	Total

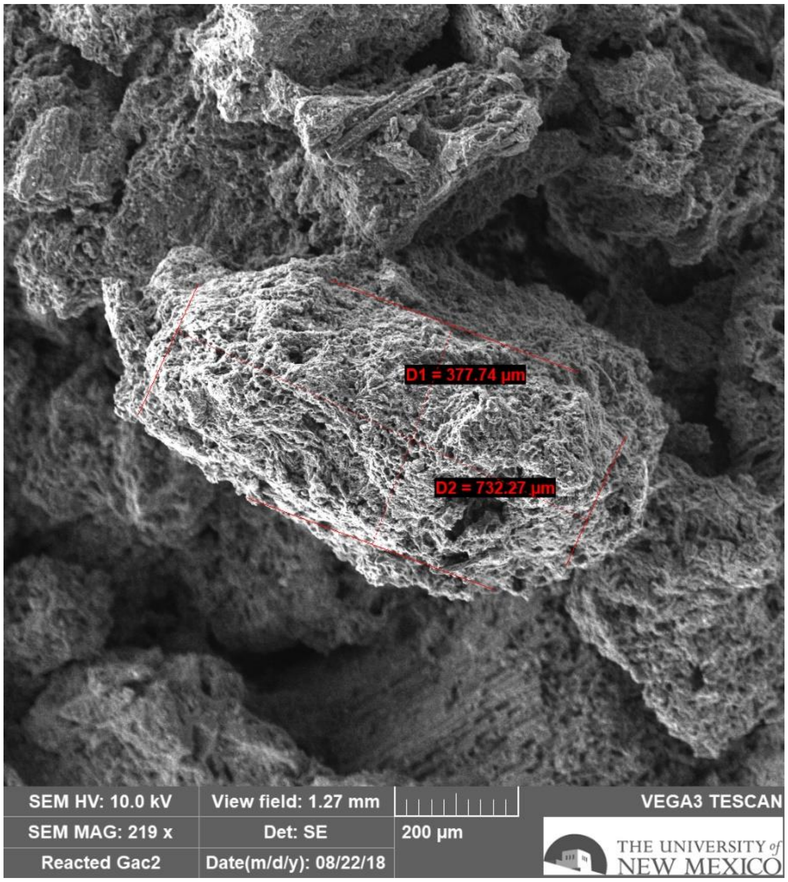

Figure S7a: Scanning electron microscope imaging of reacted GAC with particle size.

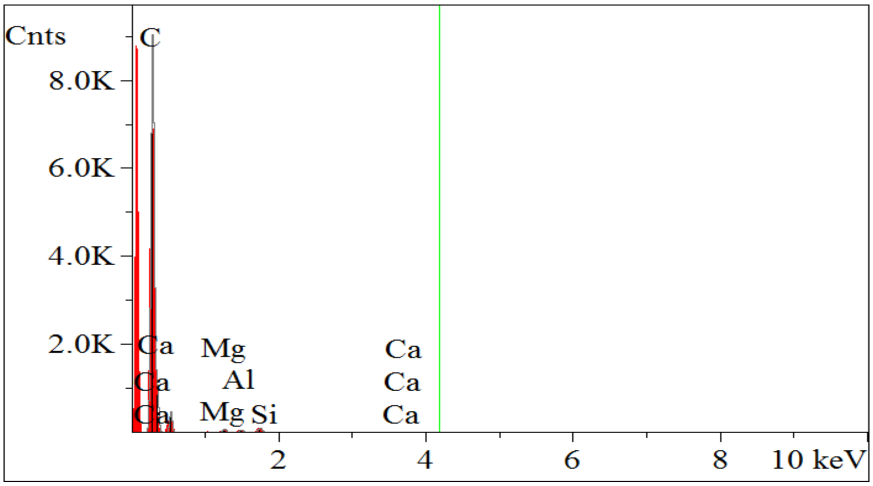

Figure S7b: Energy dispersive x-ray spectroscopy for reacted GAC media.

Table S6: Energy dispersive x-ray spectroscopy components for reacted GAC.

Element	**Mole Conc.**	**Conc.**	**Units**	
C	88.726	84.065	wt.%	
O	9.578	12.088	wt.%	
Mg	0.434	0.832	wt.%	
Al	0.347	0.739	wt.%	
Si	0.654	1.449	wt.%	
Ca	0.262	0.828	wt.%	
	100.000	100.000	wt.%	Total

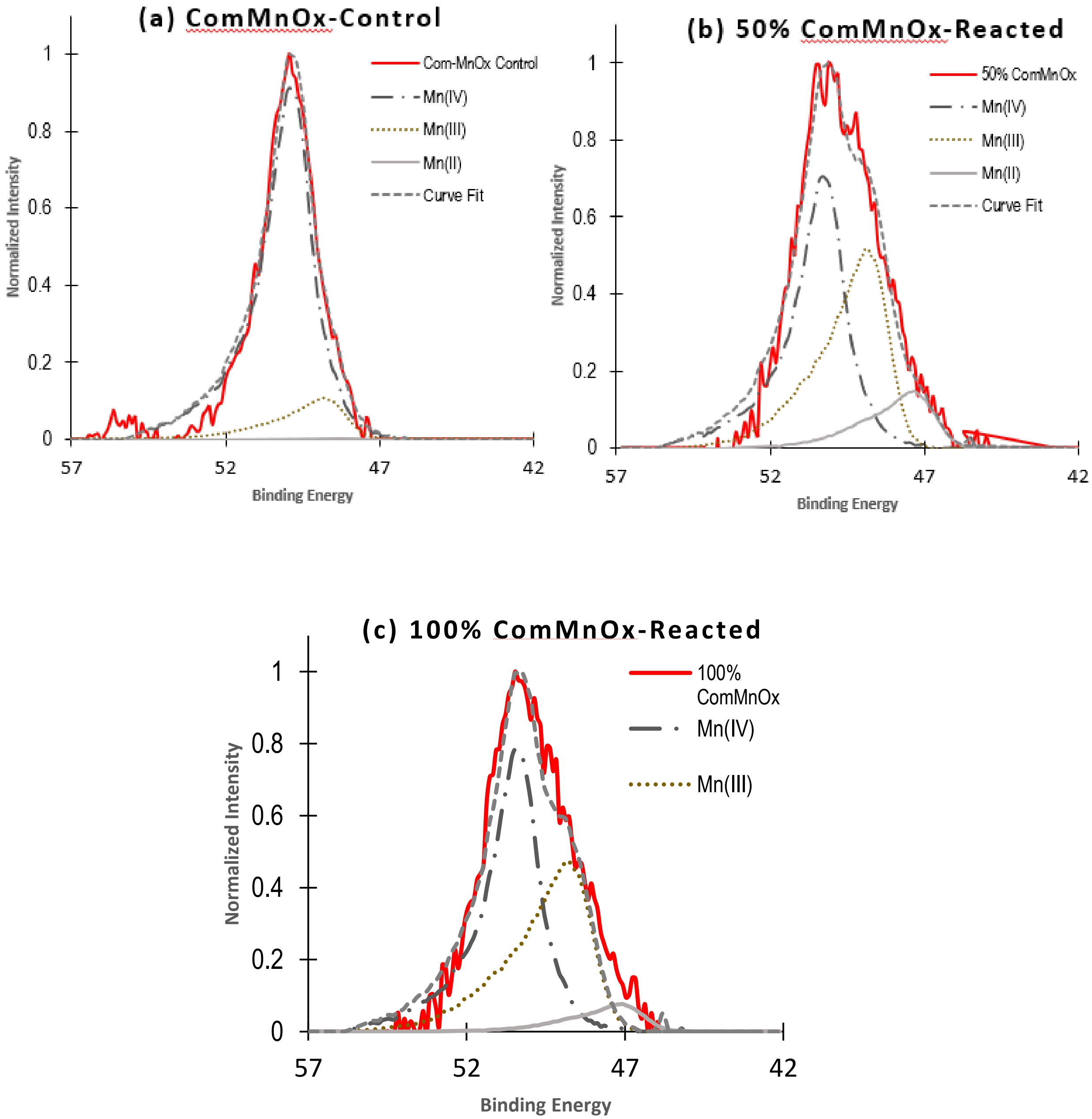

Figure S8: XPS figures for the single stage column experiments. (a) Unreacted commercial MnOx media before experiments were conducted. (b) Reacted MnOx sample from 50/50 media combination column after experiment completion. (c) Reacted MnOx media sample from 100% MnOx media column after experiment completion.

Table S7: Near surface elemental composition of Commercial MnOx (Com-MnOx) media before and after reaction with acetaminophen and caffeine. Uncertainty shown is standard deviation for triplicate data.

Sample	% Mn IV	% Mn III	% Mn II	Oxidation state
Com-MnO_x Control	88 ± 2	12 ± 2.4	0 ± 0.2	3.9
50% Com-MnO_x column	50.9 ± 6.1	40.4 ± 5.6	8.8 ± 1.8	3.4
100% Com-MnO_x column	46.1±11.8	45.3±9.5	8.5±3.4	3.4

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