Organic/Inorganic Interfacial Interactions Affecting Metal Reactivity: Water Treatment and Sensor Applications

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ORGANIC/INORGANIC INTERFACIAL INTERACTIONS AFFECTING METAL REACTIVITY: WATER TREATMENT AND SENSOR APPLICATIONS

by

MOHAMED NABIL SHAIKH

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ORGANIC/INORGANIC INTERFACIAL INTERACTIONS AFFECTING METAL REACTIVITY: WATER TREATMENT AND SENSOR APPLICATIONS

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Abstract

The aim of this dissertation was to investigate the interactions occurring at the organic – inorganic interface between solid media and aqueous contaminants for water treatment and sensor applications. The gaps in current literature on these interfacial organic-inorganic interactions must be bridged in order to develop advanced water treatment and monitoring technologies for improving water quality and thus, restore and protect the contaminated water resources. As a part of this dissertation, manganese oxides-based composites and electrospun polymer mats were developed and investigated for gaining mechanistic insights of organic (bisphenol A and acetaminophen) and inorganic (uranium) contaminants removal, respectively. These reactions were studied for (i) surficial changes on the solid media (ii) removal mechanism of aqueous contaminant and (iii) processes affecting the removal kinetics using multiple techniques such as spectroscopy, chromatography, electrochemistry and kinetic modelling.

The specific research objectives for the first study was to evaluate the removal of Bisphenol A by commercial MnO\textsubscript{x} and synthesized MnO\textsubscript{x} using spectroscopic and aqueous chemistry techniques. The removal of 99.7% BPA was observed by applying synthesized MnO\textsubscript{x}, while 71.2% BPA removal was observed by applying commercial MnO\textsubscript{x} after 44 hours of reaction of 10 mM MnO\textsubscript{x(s)} media with 1mM BPA at pH 5.5. The reduction of Mn was detected in the surface of both BPA reacted media, but a higher content of reduced Mn was observed in synthesized MnO\textsubscript{x}. The reaction of BPA with synthesized MnO\textsubscript{x} fit the
electron transfer-limited model, while the reaction of BPA with Com-MnO₅ had a better fit for surface complex formation-limited model. These results suggest that BPA removal and the reactivity of MnOₓ(5) are affected by the differences in surface area and impurities present in these media. Thus, this study has relevant implications for the reaction of MnOₓ(5) with phenolic contaminants in natural systems and for water treatment applications.

The objective of the second study was to determine the binding mechanism of U with phosphonate functionalized groups in electrospun polymer to understand U uptake with different co-occurring ions such as calcium and carbonate. A HDPA (hexadecyl phosphonate) functionalized electrospun polymer was developed in order to study the U-surface association. The U uptake was similar in control solutions containing no Ca²⁺ and HCO₃⁻ (resulting in 19% U uptake), and in those containing only 5 mM Ca²⁺ (resulting in 20% U uptake). A decrease in U uptake (13% U uptake) was observed in experiments with HCO₃⁻, indicating that UO₂-CO₃ complexes may increase uranium solubility. Almost negligible U uptake (3% U uptake) was observed in experiments with U, Ca, and HCO₃ likely due to the formation of neutral and negatively charged U-Ca-CO₃ ternary complexes as indicated by chemical equilibrium modelling. Results from shell-by-shell EXAFS fitting and aqueous extractions indicate that U is bound to phosphonate as a monodentate inner sphere surface complex to one of the hydroxyls in the phosphonate functional groups. The main finding from this study was that the aqueous speciation of U influenced the uptake on the phosphonate. This U binding information for in-situ sensor application by integrating spectroscopy microscopy and solution chemistry.

The third study involved development of electrochemically active MnOₓ/C media for application towards removal of acetaminophen in environmentally relevant conditions. The reaction mechanism of MnOₓ/C composites for treating phenolic micropollutants in water systems was investigated to obtain information on interfacial interactions occurring at organic-inorganic interface by integrating aqueous chemistry and electrochemistry measurements. Improved electrochemical activity was measured for the MnOₓ/C composite compared to pure undoped carbon and MnOₓ oxide media tested individually.
The enhanced electrochemical activity of the MnO\textsubscript{x}/C composite resulted in the faster oxidation of acetaminophen when compared to individual effects of just oxidation with pure MnO\textsubscript{x} and adsorption on undoped carbon. The findings from this study are relevant as using a cost efficient and ubiquitous manganese oxide on carbon composites for acetaminophen oxidation is promising towards development of efficient water treatment technologies.

This Ph.D. research contributes to the body of knowledge by improving the understanding of processes at the solid – liquid interface which affect the organic-inorganic reactions, contaminant removal and reactive media performance. The goal of this dissertation was to provide essential insights on the effect of surface and structure of solid media on the reaction with aqueous contaminants by using advanced spectroscopy, microscopy and analytical chemistry tools. The scientific information obtained from this dissertation, such as the identification of the contaminant associated with the solid surface and contaminant removal rate limiting step, is crucial towards proposing appropriate detection and remediation strategies for contaminated sites with similar water chemistry especially in rural communities with non-centralized potable water treatment system.
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Chapter 1

1. Introduction

The research performed in this dissertation was to understand the underlying solid-liquid interfacial dynamics influencing metal reactivity by investigating the effect of surface morphology, surface chemistry and composite-contaminant interaction. This dissertation has been divided into 5 chapters and 3 appendixes. Chapter 2 is a summarized literature review on the topics covered by this dissertation, including a background on organic and inorganic contaminants (bisphenol-A BPA, acetaminophen and uranium), their occurrence in the environment and ill-effects, interaction with surfaces (Manganese oxides and functionalized electrospun polymers) and ending with a review of fundamental theory and research gaps in the proposed field of study. Chapter 3, 4 and 5 are the main body of work of the dissertation, formatted as a research paper.

Chapter 3 has been published in Environmental Science: Processes and Impact (https://doi.org/10.1039/C8EM00121A) and relates to the investigation of the removal of Bisphenol A by commercial-MnO$_x$ and lab synthesized-MnO$_x$ using spectroscopic and aqueous chemistry techniques to identify the reaction pathway. Chapter 3 includes a discussion of the observed spectroscopy and aqueous chemistry results and provides potential kinetic explanations on the reaction between MnO$_x$ and BPA.

Chapter 4 of this study focuses on two aspects of U interaction with electrospun polymers namely (i) identification of the U binding mechanism onto electrospun polymers under controlled laboratory conditions; and (ii) influence co-occurring constituent ions such as Calcium and carbonate on U uptake by electrospun polymers.
The objective of the study presented in Chapter 5 was to develop electrochemically active MnO$_x$/C composite media and investigate the acetaminophen removal mechanism by these MnO$_x$/C composites. Electrochemical analysis was conducted to obtain information on interfacial interactions occurring at organic-inorganic interface. Appendices A, B and C contain supplementary information for the chapters 3, 4 and 5 respectively.

The interfacial interactions influence the performance of solid media, which are currently not well understood. Thus, the fundamental knowledge gained from this dissertation will lay the foundations for innovative water and sensor technologies integrating material sciences and environmental chemistry.
Chapter 2

2. Literature Review

2.1. Background and Significance

Surfaces play a critical role in interfacial processes such as redox reactions, mineralization, and catalysis. A surface is the interface between the bulk material and its surrounding as these surficial molecules have different chemical environment compared to the rest of the material resulting in different thermodynamic conditions and higher chemical reactivity. Thus, the surface behaves as nucleation sites which influences the start of the reaction as well the kinetics. The interfacial reaction can stop if the surface has been exhausted. Hence, the investigation of surface chemistry is essential to understand the interfacial reactions which dictate environmental fate of contaminants. The inorganic surface chemistry e.g. metal-metal interaction has been well documented in current body of knowledge with use of surficial characterization techniques such electron microscopy and X-ray spectroscopy. However, the gaps in current literature on interfacial organic-inorganic interactions must be bridged in order to develop advanced water treatment and monitoring technologies for improving water quality and thus, restore and protect the contaminated water resources. The aim of this dissertation is to investigate the interactions occurring at the organic – inorganic interface between solid media and aqueous contaminants for water treatment and sensor applications.

2.2. Phenolic micropollutants in natural and engineered systems

The presence of micropollutants in natural and engineered water systems is a concerning issue due to their chronic toxicity and endocrine disrupting activity. These contaminants, even in trace
levels, have been shown to have adverse health effects on local wildlife and communities. Bisphenol A (BPA) and Acetaminophen are examples of phenolic micropollutants that are widely used in personal care products. Incomplete removal of phenolic micropollutants in water treatment facilities have been documented\textsuperscript{2,3} resulting in contamination of many aquatic systems\textsuperscript{4}.

Acetaminophen and BPA are discharged in the waste water systems due to disposal of pharmaceuticals and personal care products.\textsuperscript{4-7} It was estimated that 109 tons of BPA was reported as releases to air, surface water or wastewater treatment plants in 1993.\textsuperscript{8,9} Apart from the releases, the leaching of chemical from products such as bottles containing BPA has been well reported.\textsuperscript{10,11} A survey of data published for pharmaceuticals and personal care products in natural water sources show that acetaminophen was most frequently detected in 80\% of the source waters, with a maximum concentration of 11 μg/l, Bisphenol A was detected in 41.2\% of the streams (maximum concentration was 12 μg/l).\textsuperscript{4,12} Acetaminophen has been found in concentrations upto 10 ng/l in groundwater samples as well as widely observed in natural and engineered water systems.\textsuperscript{3,4,12,13}

Bisphenol A (IUPAC name: 4,4′-(propane-2,2-diyl)diphenol is a widely used phenolic chemical for the production of plastics like polycarbonates.\textsuperscript{10} BPA has also been used for manufacturing flame retardants, paper and paint coatings, adhesives and epoxy resins. It was widely used from the 1930’s to the 1990’s. In ambient conditions, BPA is a solid crystal with melting point 150°C and solubility of 120-300 mg/l. It has two acid dissociation constants, pKa\textsubscript{1} at 9.6 and pKa\textsubscript{2} at 10.2. The octanol water partition coefficient (log K\textsubscript{ow}) for BPA measure under ambient pH conditions was 3.40.\textsuperscript{5,8,9,14}

Acetaminophen (IUPAC name: N-acetyl-para-aminophenol) is also commonly known as paracetamol. It is a non-steroidal anti-inflammatory drug that is widely used as a pain reliver and fever reducer as an active ingredient of over-the-counter pharmaceutical such as Panadol and
Tylenol. Excessive doses of acetaminophen can result in acute liver trauma which can be fatal. Chronic effects of acetaminophen intake include increase. Acetaminophen 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.$^{15,16}$

The structure and properties of the micropollutants discussed above are illustrated in Table 1.

### Table 1. Structure and a few properties of the micropollutants used in this study

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Structure</th>
<th>Molecular mass (g/mol)</th>
<th>Octanol–water Partition Coefficient (log $K_{ow}$)</th>
<th>Acid dissociation constant (pKa)</th>
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<tr>
<td>Bisphenol A</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>228.29</td>
<td>3.40</td>
<td>$9.6^a$ $10.2^b$</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>151.16</td>
<td>0.46</td>
<td>9.7</td>
</tr>
</tbody>
</table>

$a \ldots$ pKa$_1$$^8$

$b \ldots$ pKa$_2$$^9,14$

### 2.3. Mechanistic insights of MnO$_x$ reactivity with phenolic micropollutants

The reactivity between various organics and MnO$_x$(s) has been extensively reported in literature.$^{17-19}$ While a few studies suggest towards auto-catalytic behavior of Mn(IV)/Mn(III) in MnO$_x$(s) during the reaction with organics,$^{20,21}$ most studies have identified the dissolution of Mn taking place due to reduction of Mn(IV) to Mn(II).$^{17,19,22,23}$ There are multiple chemical pathways suggested such as free radical oxidation, addition of substrate to quinones, complete oxidation to carbon dioxide, sorption onto MnO$_x$(s) surface and microbial driven redox mechanism.$^{24-26}$ The
micropollutants, after getting sorbed onto the MnO\textsubscript{x}(s) surface, get degraded due to formation of a radical which can either react with other formed radicals to produce polymeric products.\textsuperscript{25-27} Alternatively, a second electron transfer can take place, resulting in formation of quinones.\textsuperscript{25}

The reaction of MnO\textsubscript{x}(s) with phenolic micropollutants causes the reductive dissolution of Mn in the solid phase; the dissolution of MnO\textsubscript{x}(s) depends on the substituted group on the phenol ring due to electrophilic and steric effects.\textsuperscript{19} Similar studies on the oxidation of BPA and BPF (respectively) by MnO\textsubscript{x}(s) with change in pH, humic acid concentration and cations (Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Mn\textsuperscript{2+}) suggests that metal cations inhibited the reaction with Mn\textsuperscript{2+} being the most suppressive.\textsuperscript{11,28} Humic acid had negligible inhibition on BPA reaction with MnO\textsubscript{x}(s), but it showed significant inhibition for BPF removal by MnO\textsubscript{x}(s) at lower pH (<5.5). Studies identified the major product as hydroquinone along with other intermediates which were formed by radical coupling, substitution, fragmentation and elimination. Acetaminophen oxidation by MnO\textsubscript{x}(s) causes the transformation of acetaminophen to 1,4-benzoquinone.\textsuperscript{15,29} Recent studies have also shown the prospective use of MnO\textsubscript{x}(s) granulated bed filter for acetaminophen removal for stormwater treatment applications.

2.4. Limitations of using MnO\textsubscript{x} for water treatment applications

MnO\textsubscript{x}(s) have traditionally been used in water treatment plants for inorganic contaminant removal. However, recent studies have shown promising results in the application of MnO\textsubscript{x}(s) in columns and bed filters for removal of organic micropollutants via biotic and abiotic mechanisms. However, the reductive dissolution of Mn during the reaction of MnO\textsubscript{x} with organic micropollutants represents a limitation for the application of MnO\textsubscript{x} media in water treatment. Previous work has shown release of as much as 10% Mn from the MnO\textsubscript{x} media during the reaction with phenolic compounds \textsuperscript{30}. The relationship between physicochemical properties and interfacial
chemistry is not well demonstrated. This forms an important foundation for the research in chapter 3 to obtain information on interfacial interactions occurring at organic-inorganic interface. Additionally, our research show that the reaction of phenols with MnO$_x$(s) is electron transfer limited in the absence of chemical impurities. Thus, improving the MnO$_x$(s) stability and increasing the surface area should improve the MnO$_x$ media’s performance in the removal of organic micropollutant.

2.5. Application of electrochemistry concepts for water treatment

Carbon based support materials such as carbon nano-fibers (Cnf), powdered activated carbon (PAC) and carbon black (Vulcan) are physically-chemically stable and electrochemically active materials. These carbons are used in electrochemistry with enhancement by doping with metal (and oxides) such Ti, Au, Pt and Pd. as catalyst for batteries and fuel cells due to its improved stability and catalytic activity. These noble metal-based catalysts are very expensive and can be deactivated due to poisoning or leach out of the composite material. Hence, the Pt, Pd, and Au based composites cannot be applied to large scale water treatment systems.

Increasing amounts of studies over the past 15 years are using MnO$_x$ doped carbon as an alternative to expensive Pt, Pd or Au based carbon electro-catalysts due to the lower costs as well as ease of synthesis. MnO$_x$/C composites have been widely studied for supercapacitors for battery applications and oxygen reduction reaction catalysts for fuel cell applications. However, most of these studies are conducted at extremely acidic or basic conditions. Thus, the application of MnO$_x$/C composite to environmental systems has not been well explored, with limited information on catalytic performance, kinetics and feasibility for water treatment application.
Figure 1 is a schematic diagram of a reaction occurring at an electrode interface with the electrolyte containing the redox species $R \rightleftharpoons O + ne^-$. In our system, the parent phenolic micropollutants is the reduced species as it gets oxidized by $\text{MnO}_x$. Briefly, the parent species will need to be transported from the bulk solution into the electrode surface boundary layer. This reduced species would be adsorbed transiently onto the electrode surface. An electron transfer occurs between the reduced species and electrode through a faradaic process resulting in oxidized species produced at the surface. The oxidized species must desorb the surface to regenerate the surface site and be transported from the surface region to the bulk solution. The transfer between bulk solution and electrode surface region is determined by mass-transfer processes such as diffusion, migration and convection.\textsuperscript{43,44}

![Figure 1. Schematic diagram of a redox reaction on an electrode.](image)
Cyclic voltammetry (CV) is a popular and useful electrochemistry technique for initial electrochemical analysis of new systems. It can provide useful information about complicated reactions and qualitative data on catalytic activity of materials during the electrochemical reactions. In particular, the onset potential and peak current is used to show electrocatalytic activity of an electrode. CV involves reversal sweep of linear scan voltammetry by switching the direction of the scan at the end of a set potential window. Reversal of the potential sweep helps understand the faradaic response of the redox reactions occurring at the electrode.

2.6. Environmental chemistry of Uranium

Uranium (U) is micropollutant which can cause cancer, kidney toxicity, miscarriages, birth defects and heart diseases at very low concentrations (μg/kg). The U.S.EPA has established maximum contaminant limit for U at 0.03 mg/l in drinking water. Elevated U concentrations have been observed in ground and surface water near mine waste sites, ranging from 67 to 135 μg/l. Additionally, U contamination was found in 13% of tested water sources in the Navajo Nation.

U speciation information is important to identify source of U contamination and recommend remediation strategies as Uranium is a redox active element with multiple oxidation states. The most common state in oxic conditions is the hexavalent uranium U(VI), such as uranyl (UO$_2^{2+}$) ion which can form various aqueous complexes and solid compounds through interaction with other constituents. Uranyl exists as a linear molecule, with two strongly bound oxygen atoms located in the axial positions to form the dioxo cation. An addition of four to five bonds can occur between the uranyl cation and ligands in the equatorial plane resulting in square, pentagonal, or hexagonal bipyramidal geometry. The uranyl can readily hydrolyze through olation and
oxolation reactions, causing polymerization of the uranyl coordination complex to form dimeric, trimeric or larger uranyl colloidal species.\textsuperscript{53,54}

While removal of U in engineered system is well established, its presence in groundwater and surface water because of mining and geochemical processes is concern for surrounding communities and ecosystem. The uptake of uranium is possible by extracting U with scavenging organic groups such as phosphonates and quaternary ammonium salts. However, these organic groups must be integrated onto solid material for reliable U uptake, while overcoming the challenges of complex water matrices and U speciation.

Extensive studies have been conducted on the interaction of U with phosphonate ligands in solution but the specific mechanisms affecting the binding of U in functionalized solid surfaces are not well understood.\textsuperscript{55–57} Computational chemistry studies using thermodynamics and quantum mechanical calculations show that binding of uranyl with aqueous phosphonate functional groups can occur as monodentate (UO$_2$-PO$_2$-) or binuclear bidentate (-PO-UO$_2$-PO-) surface complexes, even in the presence of competing ligands such as carbonates and phosphates.\textsuperscript{56,58–60} However, most U-phosphonate characterization were carried out using precipitated solids and under highly acidic conditions. Additionally, these studies do not consider the effect of pH and co-occurring ions influencing the uptake of U in functionalized solids and limited experimental studies have been conducted complimenting theoretical studies.

2.7. Application of electrospun polymers for U uptake

Highly porous materials such as polymeric nanofibers provide easy surface modification and large surface-to-volume ratio improves performance for many interfacial reactions. Electrospinning makes it possible to produce these nanofibers into various structural-aligned, functionalized electrospun polymers for U uptake. Recent studies have shown that organic
functional groups such as phosphonates, amidoximes and aliquats are incorporated into these nanofibers to enhance the U extraction from contaminated water sources. An innovative and safe method of near real-time monitoring of uranium in contaminated water sources is by using functionalized electrospun polymer mats to uptake the U followed by detection using surface enhanced Raman scattering (SERS).

The electrospinning process involves dissolving a polymer powder into an appropriate solvent and mixed thoroughly to produce a sol gel. After the sol-gel is formed, Electrospinning is carried out using a syringe pump to slowly push the sol gel out through a small blunt needle with a high applied positive voltage (~10-25 kV). This high applied potential disrupts the surface tension of the sol gel and creates a whipping jet known as Taylor cone that deposits the sol gel into the electrospun nanofibers on a grounded collector surface. A non-woven nanofiber mat structure is produced while the solvent evaporates. Various polymers can be used as the backbone of the electrospun polymer such as either hydrophobic (polyvinylidene fluoride (PVDF) and polystyrene (PS)) or hydrophilic polymers (polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA)).

2.8. Gaps in the Literature

2.8.1. Differences in commercially available MnO$_x$ vs. MnO$_x$ used in literature

The effect of surface area and surface impurities on reactivity of MnO$_x$(s) with organic micropollutants is not well understood as most studies utilize pure synthesized media that are not completely representative of naturally occurring manganese oxides. The use of commercially available MnO$_x$(s) derived from natural MnO$_x$(s) minerals is well documented in water treatment for inorganic contaminant removal such as As, Fe and Mn. However, only a few studies have
been done to evaluate the feasibility of using these commercial MnO$_x$(s) for the removal of organic compounds.\textsuperscript{72,73} The effect of MnO$_x$(s) surface physicochemical properties on the media performance and contaminant removal kinetics is of utmost importance to determine the fate and transport of these contaminants in natural and engineered systems.\textsuperscript{74} However, limited investigations have compared the differences in reaction of organic micropollutants with commercial versus synthetic MnO$_x$(s).\textsuperscript{72,75} Thus, the relationship between MnO$_x$ surface physicochemical properties and interfacial chemistry is not well established. This forms the basis for our research objective 1 that is studied in chapter 3.

2.8.2. Uranium – phosphonate surface binding in environmental relevant conditions

Extensive studies have been conducted on the interaction of U with phosphonate ligands in solution but the specific mechanisms affecting the binding of U in functionalized solid surfaces are not well understood.\textsuperscript{55–57} Computational chemistry studies using thermodynamics and quantum mechanical calculations show that binding of uranyl with aqueous phosphonate functional groups can occur as monodentate (UO$_2$PO-) or binuclear bidentate (-PO-UO$_2$PO-) surface complexes, even in the presence of competing ligands such as carbonates and phosphates.\textsuperscript{58–60} However, most U-phosphonate characterization were carried out using precipitated solids, under highly acidic conditions and using bulk characterization techniques that are not surface specific.\textsuperscript{53,54,56} Additionally, these studies do not consider the effect of co-occurring ions in environmental relevant conditions influencing the uptake of U in functionalized solids and limited experimental studies have been conducted complimentary theoretical studies. Carbonate is an important natural complexant that react with U to form stable UO$_2$-CO$_3$ aqueous complexes while calcium can provide some cationic competition with uranyl cations.\textsuperscript{76,77,48,59} Additionally, the presence of ternary complexes of U involving uranyl cation, carbonate anion, and calcium can influence the
aqueous U(VI) speciation under circumneutral to alkaline pH conditions.\textsuperscript{51,60,78} There is limited understanding about the effect of major ions such as Ca and carbonate on the uptake of U in functionalized polymers in complex environmental water matrixes.\textsuperscript{56,79–81} Hence, the study of the mechanism of U uptake on phosphonate surface and identification of U surface binding forms the framework for the research objective 2 and demonstrated in the chapter 4 of this dissertation.

2.8.3. Electrochemically active MnOx/C catalysts for water treatment

Acetaminophen is reported in literature to be electroactive towards oxidation to N-acetyl-p-benzoquinone imine using a variety of carbon composites electrodes modified with organic functional groups such as carbon nanotubes, glassy carbon and graphene.\textsuperscript{82–85} Recent studies have shown improved acetaminophen electrochemical oxidation using metal oxide such as TiO\textsubscript{2}, CoO, CuO, MgO – carbon composites for electrochemical sensor applications across a wide pH range.\textsuperscript{86–89} However, limited information is available for acetaminophen electro-oxidation using low cost and environmental friendly MnOx carbon composites for water treatment applications.\textsuperscript{90} Pure manganese oxides are poor conductors of electricity but it can improved by doping with conductive material such as carbon.\textsuperscript{91,92} These MnO\textsubscript{x} doped carbon are used in electrochemistry as catalyst for batteries and fuel cells due to its increased capacitance, improved stability and catalytic activity.\textsuperscript{36,37,41,93} Additionally, the accumulation of reduced Mn and oxidized organics on the surface of MnO\textsubscript{x}(s) results in surface passivation and the reductive dissolution of Mn represents a limitation for the application of MnO\textsubscript{x} media in water treatment.\textsuperscript{25,67,94} Although these previous studies use MnOx/C composites in catalysis for batteries and fuel cells, the application in water treatment systems is still limited. Thus, the investigation of MnOx/C composite as electrocatalyst for acetaminophen oxidation in environmentally relevant conditions is performed as chapter 5.
3. Reaction of Bisphenol A with Synthetic and Commercial MnO$_x$(s): Spectroscopic and Kinetic Study

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Abstract

The reaction of bisphenol A (BPA) using laboratory synthesized (Syn-MnO$_x$) and commercially available (Com-MnO$_x$) MnO$_x$(s) media was investigated using spectroscopic and aqueous chemistry methods. The surface area of Syn-MnO$_x$ (128 $\text{m}^2/\text{g}$) and Com-MnO$_x$ (13.6 $\text{m}^2/\text{g}$) differed by an order of magnitude. The impurities were less than 1% by weight for Syn-MnO$_x$ while Com-MnO$_x$ contained 29% impurity by weight, mainly Al, Si and Fe. The removal of 99.7% BPA was observed applying Syn-MnO$_x$, while 71.2% BPA removal was observed applying Com-MnO$_x$. 

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after 44 hours of reaction of 10 mM MnO\textsubscript{x(s)} media with 1mM BPA at pH 5.5. The reduction of Mn was detected in the surface of both BPA reacted media, but a higher content of reduced Mn was observed in Syn-MnO\textsubscript{x} (52% in Syn-MnO\textsubscript{x} compared to 29% in Com-MnO\textsubscript{x}). The release of soluble Mn was an order of magnitude higher in batch experiments reacting BPA with Syn-MnO\textsubscript{x} compared with Com-MnO\textsubscript{x}. The C 1s and O 1s XPS high resolution spectral analyses identified the presence of functional groups that likely correspond to BPA oxidation products, such as dimers and quinones associated with MnO\textsubscript{x(s)} surfaces on both reacted media. The reaction of BPA with Syn-MnO\textsubscript{x} fit the electron transfer-limited model ($R^2$=0.96), while the reaction of BPA with Com-MnO\textsubscript{x} had a better fit for surface complex formation-limited model ($R^2$=0.95). These results suggest that BPA removal and the reactivity of MnO\textsubscript{x(s)} are affected by the differences in surface area and impurities present in these media. Thus, this study has relevant implications for the reaction of MnO\textsubscript{x(s)} with emerging organic contaminants in natural biogeochemical processes and water treatment applications.

### 3.1. Introduction

Compounds classified as endocrine disruptors such as organic micropollutants are a major concern in natural and engineered water systems. These contaminants, even in trace levels, have been shown to have adverse effects on aquatic communities.\textsuperscript{95,96} Bisphenol A (BPA) is an example of a micropollutant that was widely used as a plasticizer in the polymer production industries and has been found to be estogenically active.\textsuperscript{97} The incomplete removal of BPA at existing wastewater and drinking water treatment plants is a concerning issue due to its estrogenic activity.\textsuperscript{2,3} Thus, the identification of geochemical processes affecting the reaction of these micropollutants is necessary to understand the fate of these chemicals and develop economically efficient treatment technologies.
Previous studies \(^{19,22,98}\) have shown that organic micropollutants react with MnO\(_x(s)\) resulting in reductive dissolution of Mn and oxidation of organic groups. Recent studies \(^{11,99–101}\) have shown that the oxidation rate of organic micropollutants reacted with MnO\(_x(s)\) decreases in the presence of secondary metal oxides, metal cations and natural organic matter. The use of commercially available MnO\(_x(s)\) derived from natural MnO\(_x(s)\) minerals is well documented in water treatment for inorganic contaminant removal.\(^{68–70,102}\) However, only a few studies have been done to evaluate the feasibility of using these commercial MnO\(_x(s)\) for the removal of organic compounds.\(^{72,73}\) Recent studies have shown promising results in the application of MnO\(_x(s)\) in columns and bed filters for removal of pharmaceuticals such as diclofenac and estradiols via biotic and abiotic mechanisms.\(^{74,103–105}\) Additionally, the effect of surface area and surface impurities on reactivity of MnO\(_x(s)\) with organic micropollutants is not well understood as most studies utilize pure synthesized media that are not completely representative of naturally occurring manganese oxides.\(^{30,67,100}\) The effect of MnO\(_x(s)\) surface physicochemical properties on the media performance and contaminant removal kinetics is of utmost importance to determine the fate and transport of these contaminants in natural and engineered systems.\(^{74}\) However, limited investigations have compared the differences in reaction of organic micropollutants with commercial versus synthetic MnO\(_x(s)\).

The objective of this study was to evaluate the reaction of BPA by laboratory synthesized (Syn-MnO\(_x\)) and commercially available (Com-MnO\(_x\)) MnO\(_x(s)\) media using spectroscopic and aqueous chemistry techniques. We monitored solid phase changes based on the Mn oxidation state of MnO\(_x(s)\), C1s and O1s bonding using X-ray photoelectron spectroscopy (XPS), while residual BPA and soluble Mn were evaluated to obtain the kinetics of BPA removal. The physicochemical difference in Syn-MnO\(_x\) and Com-MnO\(_x\) media employed in this study provided an interesting
basis for comparison of the reactivity of each media with BPA. Given that commercially available media are economically affordable, the results from this study provide insights into the practical application of MnO$_x$(s) for treatment of organic micropollutants in engineered systems.

3.2. Materials and methods

3.2.1. Materials

Bisphenol A (>99% purity) was purchased from Sigma Aldrich (St. Louis, MO). Commercial MnO$_x$ (Com-MnO$_x$, LayneOx® media purchased from Layne Co., TX) is a MnO$_x$(s) filter media, which is used to remove inorganics from drinking water such as Mn and Fe.$^{69,106,107}$ Pure (>99%) manganese oxides (MnO, Mn$_2$O$_3$, MnO$_2$ and Mn(III,IV) oxide) were purchased from Strem Chemicals (Newburyport, MA) and Sigma Aldrich (St. Louis, MO) to be used as XPS references. All other chemicals where bought from VWR or Thermo Fisher with >90% purity and used without further purification. The Syn-MnO$_x$ was synthesized as described by Taujale and Zhang$^{100,101}$ reacting KMnO$_4$ and MnCl$_2$ in basic conditions to precipitate as Mn(III)-rich δ-MnO$_x$(s).

3.2.2. Batch experiments

The reaction of BPA with MnO$_x$(s) was studied to examine the impacts of solutes and impurities on the removal of BPA and net release of manganese into solution. First, batch experiments were conducted with 1 mM BPA reacting with 10 mM Syn-MnO$_x$ or 10 mM Com-MnO$_x$ (in separate reactors) in ultrapure water at pH 5.5 (buffered using 50 mM phosphate buffer). A concentration of 0.01 M NaCl was added to the reactors to maintain ionic strength. The pH 5.5 was chosen to keep the study at conditions relevant for engineered systems while remaining low enough for the reaction to be appreciably completed within the experimental time-frame. Elevated concentrations of BPA and MnO$_x$(s) were used to have appreciable amounts of BPA reacted solids collected for
analyses during the experimental time-frame. The reactor setup is shown in supporting information (Figure A16). A volume of 10 ml of liquid samples were filtered through 0.45 μm and taken at timed intervals (5, 15, 30, 45, 90, 180 minutes and 44 hours) to evaluate the dissolved Mn and residual BPA. The MnO$_x$(s) media in the reactors were used for solid phase analysis.

### 3.2.3. Adsorption/oxidation experiments

The reactors for kinetic experiments were set up in 60 ml screw-cap amber bottles with Teflon caps. The reaction was carried out under similar reactor conditions to the batch experiment described above. Reactors with 100 µM of Syn-MnO$_x$ or Com-MnO$_x$ were setup and 10 µM of BPA was added to the reactors to initiate the reaction at pH 5.0 using 25mM acetate buffer. Samples were taken at predetermined time intervals with two different approaches to quench the reaction. The first approach was to centrifuge and filter through a 0.22 μm filter and the second approach was using NaOH in order to increase pH to above 10.0 followed by centrifuging and filtering the sample. Although we did not show the results in this work, in our separate research on BPA oxidation by MnO$_x$(s), ascorbic acid was used to quench the reaction and comparable kinetics were observed using both quenching methods. Previous work has shown that phenolic compounds stop oxidizing and completely desorb from MnO$_x$(s) surface at high pH values.$^{100,101,108}$ The aliquots were analyzed for residual BPA using high performance liquid chromatography (HPLC).

### 3.2.4. Solid phase analysis

The surface area was calculated using N$_2$ adsorption (Brunauer–Emmett–Teller) on a Micrometrics 2360 Gemini Analyzer. The bulk elemental composition of the MnO$_x$(s) media were analyzed using X-ray fluorescence (XRF) on a Rigaku ZSX Primus II Wavelength Dispersive XRF...
Spectrometer and Energy-dispersive X-ray spectroscopy (EDS) on an EDAX Genesis system. A Kratos Axis DLD Ultra X-ray photoelectron spectrometer with a monochromatic Al Kα source was used to acquire the XPS spectra at 225W from three different areas on each sample. Elemental survey spectra were acquired at 80 eV and high resolution at 20 eV pass energy. The software CasaXPS was used to perform curve fitting and quantification. XPS spectra were processed using Shirley background subtraction and a Gaussian-Lorentzian line shape for the curve fitting. Oxidation states of Mn were determined using the Mn 3s multiplet splitting method and by examination of the shape and position of the Mn 3p region as described by Cerrato et al. Analyses of O 1s and C 1s spectra were done based on results obtained from other studies.

3.2.5. Liquid phase analysis

A reverse phase HPLC with an electro-chemical detector was used to analyze BPA in liquid samples of batch experiments. A TSKgel ODS-80Tm C-18 column (4.6×250 mm, 5 µm) was used with a mobile phase of 50% methanol, 50% phosphate buffer at pH 6 and a flowrate of 0.8 ml/min. The peak for BPA was obtained at around 10 min retention time. A PerkinElmer Nexion 300D inductively coupled plasma-mass spectrometer (ICP-MS) system was used to analyze the metal concentration in liquid samples from the reactor.

3.2.6. Kinetic analysis

The reaction between MnO$_x$(s) and BPA is assumed to follow the kinetic models developed in a previous study:

$$
\text{MnO}_x(s) + \text{BPA} \rightleftharpoons \text{[MnO}_x - \text{BPA]} \rightleftharpoons (> \text{Mn}^{III}, \text{BPA}^*) \overset{\text{fast}}{\rightarrow} \text{Mn}^{2+} + \text{BPAO}^*
$$
Briefly, the reaction initiates with formation of an organic reactant - oxide surface precursor complex (MnOₓ-BPA), followed by electron transfer in the complex resulting in organic radical formation and surficial Mn reduction (>Mn<sup>III</sup>, BPA•). The reaction proceeds with rapid transformation of the unstable organic radical resulting in formation of BPA oxidation products (BPAO*) and further reduction of surficial Mn to soluble Mn<sup>2+</sup>. The kinetic model equation varies based on the rate limiting step: (i) limited by electron transfer, and (ii) limited by precursor surface complex formation. The analytical solution for each scenario is as follows:

(i) Electron transfer limited:

\[
C = C_e + S_{rxn} \cdot e^{-k'_t \cdot t} \quad ; \quad k' = k_2
\]

(ii) Surface complex formation limited:

\[
1 - \frac{C_e}{C} = \frac{S_{rxn}}{C_0} \cdot e^{-k''e \cdot t} \quad ; \quad k'' = \frac{k_1 \cdot k_2}{k_1 + k_2}
\]

Where, \(C\) is the molar concentration of the BPA in the reactor with subscripts ‘0’ and ‘e’ representing initial and equilibrium concentration respectively, \(t\) is time in hours, \(k' (h^{-1})\) and \(k'' (h^{-1} M^{-1})\) are the rate constants, and \(S_{rxn}\) is the total reactive surface sites that can be oxidized by BPA, calculated as \(S_{rxn} = C_0 - C_e\).

### 3.3. Results and discussion

#### 3.3.1. Physical and chemical characterization of MnOₓ(s)

The surface area measured by BET was one order of magnitude higher for Syn-MnOₓ (128.3 m²/g) compared to Com-MnOₓ (13.6 m²/g). Bulk elemental analyses conducted on the unreacted Com-MnOₓ media using XRF show that Al (10%), Fe (9%) and Si (7%) are the most abundant impurities in the which had an Mn content of 71% (Table A7). A content of 99.9% Mn and no detectable metal impurities were observed for Syn-MnOₓ based on the XRF and EDS analyses.
**Near surface elemental composition.** The presence of impurities was observed in the top 5-10 nm (near surface) by XPS survey scans for unreacted (control) and BPA-reacted media (Com-MnOₓ and Syn-MnOₓ) (Table 2). The carbon content (C 1s) for control Com-MnOₓ was 50.8% and for control Syn-MnOₓ was 39.1%, likely due to the contribution of adventitious carbon. In contrast, there was an increase in C 1s for both reacted Com-MnOₓ (60.9%) and reacted Syn-MnOₓ (60.4%), suggesting the possible association of organic compounds to the MnOₓ(s) surface. The presence of Al and Si was detected in the surface of control and reacted Com-MnOₓ samples, confirming the presence of impurities in these media as indicated by the XRF and EDS analyses. A decrease in Al 2p in the surface of reacted Com-MnOₓ samples (2.8%) compared to 4.2% in control Com-MnOₓ samples was observed, which also suggests a decrease on the Al signal due to the presence of organic compounds in the surface of MnOₓ(s). A decrease in Mn 2p signal is observed in Syn-MnOₓ, from 11.7% in control Syn-MnOₓ to 6.2% for reacted Syn-MnOₓ. The Mn 2p content in the control Com-MnOₓ sample (1.9%) showed a minor decrease when reacted with BPA, 1.4% for the reacted Com-MnOₓ samples. Additional aqueous samples from the batch experiments of BPA reaction with MnOₓ(s) media were analyzed to obtain information on BPA removal and Mn dissolution.

### 3.3.2. Residual BPA

Higher amount of residual BPA was observed when reacted with Com-MnOₓ (0.228 mM BPA) compared to Syn-MnOₓ (0.002 mM BPA) in the batch experiments (Figure 2). No BPA removal was observed for control experiments conducted in the presence of BPA and absence of MnOₓ(s). Rapid initial BPA removal was observed for Syn-MnOₓ (67% removal) and Com-MnOₓ (61% removal) during the first 15 mins. As the reaction proceeded from 15 mins onwards, BPA removal followed first order kinetics with rates of 0.096 hr⁻¹ for Syn-MnOₓ and 0.0054 hr⁻¹ for Com-MnOₓ.
Faster removal of BPA was observed for Syn-MnO$_x$ while slower for Com-MnO$_x$. The residual BPA data was used in the kinetic analyses presented later.

Our data from adsorption/oxidation experiments suggest that removal of BPA was mainly due to oxidation in the case of Com-MnO$_x$, while Syn-MnO$_x$ had retained un-oxidized BPA on its surface, which was released by addition of excess NaOH (Figure 3). Thus, removal of BPA was likely due to adsorption followed by rapid oxidation on the MnO$_x(s)$ media. The maximum amount of BPA removed solely by adsorption on MnO$_x(s)$ was calculated to be 32 μM BPA per mM MnO$_x$ for Syn-MnO$_x$ and 3.3 μM BPA per mM MnO$_x$ for Com-MnO$_x$. This maximum amount was calculated by extrapolating the data of total BPA removed subtracted from BPA removed solely by oxidation (Figure A17). As the reaction proceeded, the amount of BPA removed by adsorption onto the media decreased linearly with respect to time and residual BPA concentration, most likely due to the continuous oxidation of the adsorbed BPA. The concentration of adsorbed BPA at the end of 4 hours was 0.44 μM for Syn-MnO$_x$ and 0.08 μM for Com-MnO$_x$.

Differences in the BPA removal and BPA adsorption kinetics can be attributed to the differences in surficial properties, as the presence of impurities results in fewer reactive sites available for BPA oxidation. For instance, the Syn-MnO$_x$ has 99.9% purity. However, Com-MnO$_x$ has 29.1% impurities which likely occupy surface sites with elements such as Al and Si as indicated by XPS survey scans (Table 2). The release of soluble Mn during the reaction was studied to further understand the influence of surface chemistry and differences in the reactivity between the MnO$_x(s)$ media.

### 3.3.3. Soluble Mn release to solution

The soluble Mn released to solution due to Mn dissolution after 44 hours of reaction of MnO$_x(s)$ with BPA in the batch experiments was one order of magnitude higher for Syn-MnO$_x$ (14.2 mg/l)
than Com-MnO\textsubscript{x} (1.7 mg/l). Both Syn-MnO\textsubscript{x} and Com-MnO\textsubscript{x} media that reacted with BPA showed a similar initial soluble Mn concentration of 0.25 mg/l at 5 mins. After 44 hours of reaction, the final Mn release value of 14.2 mg/l was obtained for Syn-MnO\textsubscript{x}, compared to 1.1 mg/l for Com-MnO\textsubscript{x} (Figure 4). It is likely that the differences in surficial properties, such as lower surface area influenced the limited Mn dissolution observed in Com-MnO\textsubscript{x} when compared to Syn-MnO\textsubscript{x}. As the reaction proceeds, the MnO\textsubscript{x(s)} surface sites are occupied by oxidation products and consumed due to Mn reduction. Thus, we observed two distinct and opposite trends in the BPA removal and soluble Mn release: a) an initial rapid BPA removal corresponding with low soluble Mn release; and b) later, a slower BPA removal and high Mn release.

The order of magnitude difference in Mn release for the two media is comparable to the order of magnitude difference in the surface area of the two media. On normalizing the Mn release to respective surface area, the amount of Mn released was within 2% for both media (0.11 mg/l Mn per unit surface area for Syn-MnO\textsubscript{x} and 0.13 mg/l Mn per unit surface area for Com-MnO\textsubscript{x}). Thus, these data suggest that the availability of surface binding sites is essential for the oxidation of BPA and subsequently, for re-adsorption/re-oxidation of aqueous Mn onto MnO\textsubscript{x(s)}, as suggested in other studies.\textsuperscript{30,100,111} Additional analyses were carried out to understand the influence of interfacial processes at the MnO\textsubscript{x(s)} surface on the reaction with BPA, such as change in Mn oxidation state and carbon/oxygen bonding in the near surface of MnO\textsubscript{x(s)}.

### 3.3.4. Oxidation state of Mn

The presence of more than 75% Mn(IV) and less than 25% Mn(III) was observed in the near surface region of unreacted MnO\textsubscript{x(s)}, and the reduction of Mn after reaction with BPA was determined by XPS analyses of Mn 3s multiplet splitting and Mn 3p spectra. The data shows an increase in Mn 3s multiplet splitting values for reacted Syn-MnO\textsubscript{x} (4.82) compared to 4.63 for
control Syn-MnOₓ, and a similar increase for reacted Com-MnOₓ (4.68) compared to 4.47 for control Com-MnOₓ (Table A8). The value of 4.82 for reacted Syn-MnOₓ is within 0.08 eV of the Mn(III, IV) reference and the value of 4.47 for control Com-MnOₓ is within 0.09 eV of the Mn(IV) reference. The increase in multiplet splitting for the reacted samples suggests reduction in the Mn oxidation state of MnOₓ(s) occurred after reaction with BPA. On comparison with the Mn reference data, the average surface Mn oxidation state for control Syn-MnOₓ was 3.7 and for control Com-MnOₓ was 3.9, consistent with data from other studies of 3.6 to 3.9 for unreacted birnessite.⁷,²⁴,³⁰ The average Mn oxidation state for reacted Syn-MnOₓ was 3.5 (compared to 3.7 for unreacted Syn-MnOₓ) and for reacted Com-MnOₓ was 3.7 (compared to 3.9 for unreacted Com-MnOₓ), which indicated reduction of Mn on the surface.

The presence of reduced Mn is confirmed by the change of the shape of the Mn 3p spectra, which show more pronounced shoulders that correspond with the reduced Mn references (Figure 5). The contribution of Mn(IV) to Mn 3p spectra decreased in reacted samples, while the shoulder features that correspond to reduced Mn increased. For example, the control Syn-MnOₓ (73%) had more Mn(IV) than the reacted Syn-MnOₓ (48%); a similar trend was observed for the control Com-MnOₓ (88%) compared to the reacted Com-MnOₓ reacted (71%). An increase in reduced Mn features was observed in the Mn 3p spectra of reacted MnOₓ(s) samples, with 22% increase in Mn(III) characteristics for reacted Syn-MnOₓ compared to control Syn-MnOₓ and 14% increase in Mn(III) characteristics for reacted Com-MnOₓ compared to control Com-MnOₓ. Negligible Mn(II) was observed in the control samples; but a minor presence of Mn(II) in the reacted MnOₓ(s) samples was identified in both media [reacted Syn-MnOₓ had 4% Mn(II) and reacted Com-MnOₓ had 3% Mn(II)]. The average oxidation states calculated from Mn 3p were similar to the oxidation state calculated from Mn 3s multiplet splitting values. Thus, the presence of reduced Mn in MnOₓ(s)
from XPS analyses and the increasing presence of soluble Mn in solution confirm that the reductive
dissolution of MnO$_x$(s) occurred in these experiments. Additional XPS analyses were conducted to
assess changes in the C 1s and O 1s high resolution spectra after reaction with BPA.

### 3.3.5. Oxygen and carbon surface bonding

The changes in the shapes of the O 1s and C 1s high resolution XPS scans for both Syn-MnO$_x$
and Com-MnO$_x$ suggest that the binding environments of oxygen and carbon changed after the
reaction with BPA. The analysis and fitting of O 1s spectra for unreacted and reacted MnO$_x$(s)
media are illustrated in Figure 6 and the relative percentage composition of corresponding oxygen
bonds are summarized in Table A9. The presence of peaks associated with organic oxygen bonds
on the surface of control samples can be attributed to adventitious contamination. There is a
decrease in the peak at 529.6 eV which corresponds to oxygen species attached to metal, from
59.4% in the Syn-MnO$_x$ control to 33.0% in reacted Syn-MnO$_x$. A decrease in the same peak
(529.6 eV) is observed from 17.2% in control Com-MnO$_x$ to 13.7% in reacted Com-MnO$_x$. An
approximate 10% increase in O 1s component at 533.7 eV, associated with oxygen from
esters/carboxylates (C-O-C/COOH), was observed in the reacted MnO$_x$ samples for both media,
with reacted Syn-MnO$_x$ 17.7% compared to control Syn-MnO$_x$ 7.9% and reacted Com-MnO$_x$
30.0% compared to control Com-MnO$_x$ 22.1%. Additionally, presence of a noticeable peak at 535
eV was observed on reacted MnO$_x$ media, which is attributed to the presence of C-O-O-C bonds.
Fits to the O 1s spectra for reacted Syn-MnO$_x$ suggest the presence of 5.3% C-O-O-C bonds; the
reacted Com-MnO$_x$ contained 21.6% C-O-O-C bonds compared to 12.5% in the control Com-
MnO$_x$. No features characteristic to C-O-O-C bonds were observed in the control Syn-MnO$_x$. The
increase in peaks associated with other oxygen bonds, such as C−O−O−C, and C−O−C, indicates
association of organic groups with the MnO$_x$(s) surface such as dimers and quinones, which are
formed due to radical coupling during the oxidation of phenolic compounds by MnO$_x$(s).$^{11,67}$ The increased contribution of peaks associated with these organic groups suggests that adsorbed BPA oxidation products are present in the MnO$_x$(s) surface even after completion of the reaction.

The changes in C1s spectra after the reaction of MnO$_x$(s) with BPA suggest that aromatic organic reaction products are associated with the solid surface. The C1s spectral analyses are illustrated in Figure 6 and the fitting of these spectra to identify features that correspond to different carbon bonds is shown in Table A10. The C-C/C=C bonds (characteristic binding energy 284.8 eV) are associated with adventitious carbon$^{22,30}$ and were present in similar amounts at 63.4% for reacted Syn-MnO$_x$ vs. 65.2% for control Syn-MnO$_x$, and 26.4% for reacted Com-MnO$_x$ vs. 34.7% for control Com-MnO$_x$. Similarly, the peaks at the binding energy 288.5 eV, associated with C=O bonds, were within 2% of each other for reacted and control samples (reacted Syn-MnO$_x$ has 9.7% C=O bonds compared to 9.2% control Syn-MnO$_x$, and reacted Com-MnO$_x$ has 31.5% C=O bonds compared to 29.1% control Com-MnO$_x$). An increase was observed in the peak at 287.2 eV associated with C-OH bonds, (reacted Syn-MnO$_x$ has 26.6% compared to 21.2% control Syn-MnO$_x$; and reacted Com-MnO$_x$ has 40.9% compared to 33.0% control Com-MnO$_x$). Both reacted Syn-MnO$_x$ and reacted Com-MnO$_x$ show a decrease (4%) in C 1s component at binding energy 285.6 eV which are associated with secondary carbon carboxylates when compared to the control. This decrease in -COOH and increase in -COH indicates decarboxylation of BPA and retention of aromatic compounds on the surface of MnO$_x$(s), as observed in other studies.$^{104,112}$ The formation of dimers and decarboxylation can explain sorption onto the media due to reduced electrostatic repulsion with the MnO$_x$(s) surface.$^{104}$ Additional kinetic analyses were conducted to evaluate possible pathways that affect BPA removal by Syn-MnO$_x$ and Com-MnO$_x$. 

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3.3.6. Kinetic analyses

The results of fitting the kinetic data (illustrated in Figure 7) for (i) electron transfer limited model ($k'$) and (ii) surface complex formation limited model ($k''$), show that the rate limiting step in the reaction of BPA with Syn-MnO$_x$ is most likely electron transfer. This finding is similar to previous studies between pure MnO$_x$(s) and phenolic compounds.$^{19,67,110}$ The data for BPA reaction with Syn-MnO$_x$ adequately fit to the electron transfer-limited model ($R^2=0.96$), with the calculated rate constant of $k' = 1.25$ h$^{-1}$ for the electron transfer limited transformation of BPA by MnO$_x$(s).

The prescribed model for surface complex formation limited reaction yielded a better fit for Com-MnO$_x$ ($k'' = 0.45$ mM$^{-1}$ h$^{-1}$, $R^2 = 0.95$) compared to the electron transfer limited model ($R^2=0.86$). The poor fit for Com-MnO$_x$ electron transfer limited model could be due to the presence of impurities (e.g., Al, Si, Fe) on the solid surface which may influence the kinetics of the reaction. For instance, oxides of Al and Fe have a strong inhibitory effect on MnO$_x$(s) reactivity due to higher points of zero charge ($\text{pH}_{\text{pzc}}$ 6 to 9 compared to 2.4 for MnO$_x$) and hetero-aggregation on MnO$_x$(s) surface.$^{72,100}$ Thus, the presence of these impurities in the commercial media could occupy sites in the Com-MnO$_x$, inhibiting the precursor complex formation. Further investigations are necessary to elucidate the influence of the Al, Fe and Si impurities and co-occurring oxides in commercial MnO$_x$.

The kinetic results from this study report similar trends of decreased oxidation of BPA by MnO$_x$(s) over time, as seen in previous studies.$^{67,110,113}$ The increase in reduced Mn on the surface of MnO$_x$(s), observed from XPS analyses and soluble Mn in solution, contributed largely to the decreasing BPA removal rate by MnO$_x$(s) due to lower Mn oxidation states and competition for reactive sites.$^{61,67,100}$ Additionally, the accumulation of oxidation by-products bound on the surface
as seen from the C1s, O1s and adsorption/oxidation experiment affected the surface binding which could influence the long-term reactivity of MnOx(s).22,114,115

3.4. Conclusions

The removal of BPA occurred using both synthesized (Syn-MnOx) and commercial (Com-MnOx) MnOx(s) media, but a higher BPA removal and higher Mn release to solution was observed for Syn-MnOx. The lower surface area and impurities (Al, Fe, and Si) in Com-MnOx possibly caused a lower effective removal of BPA compared to Syn-MnOx. The results of surface analysis and kinetic modelling indicate that the surface chemistry strongly influences the results of the reaction. Findings from our kinetic modeling suggest that the rate limiting step for BPA removal for Syn-MnOx is most likely electron transfer while BPA reaction with Com-MnOx fit the surface complex formation limited model. Integration of solution chemistry and solid chemistry data suggested that the presence of Mn(III), Mn(II), and adsorbed organic compounds (e.g., BPA parent and product compounds) on the MnOx(s) surface contributed to the decrease in long term BPA removal rates when compared to rapid initial oxidation rates. As most studies utilize pure lab synthesized MnOx(s) for removal of emerging organic micropollutants such as BPA, the results of this research suggest that differences exist in the reaction mechanism between synthesized and commercial MnOx(s) media. Further investigations are necessary to elucidate the influence of mineral impurities and long-term reactivity of MnOx(s) media with environmental relevant organic concentrations to understand the fate and transport of these micropollutants and develop effective water treatment processes.
3.5. Environmental Significance:

The reactivity of manganese oxides [MnO$_x$(s)] is relevant to the fate and transport of emerging micropollutants in natural and engineered systems. The limited current knowledge on the reaction of bisphenol-A (BPA) with synthetic-MnO$_x$ and commercial-MnO$_x$ motivates this study. The results from this research suggest that the reaction of BPA with synthetic-MnO$_x$ fit the electron transfer limited model, while the reaction of BPA with commercial-MnO$_x$ had a better fit with the surface complex formation limited model. The physicochemical differences between synthetic-MnO$_x$ and commercial-MnO$_x$ affect the observed variations in the interfacial interaction of these solids with BPA. The findings from this study are relevant to better understand biogeochemical processes affecting the reaction of emerging organic micropollutants with MnO$_x$(s) in natural systems, and potential applications for water treatment.

3.6. Acknowledgements

The authors would like to thank Diana Perales and Enrique Argeñal for their help with experiments performed for this study. Funding for this research was provided by the University of New Mexico School of Engineering Startup Fund, the National Science Foundation under New Mexico EPSCoR (Grant Number #IIA-1301346) and CREST (Grant Number #HRD-1345169). Huichun Zhang acknowledges financial support from the National Science Foundation through grant number #CBET 1236517. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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Table 2. Near surface elemental composition of synthetic (Syn-MnO$_x$) and commercial (Com-MnO$_x$) manganese oxide media after reaction with BPA. Uncertainty shown is standard deviation for triplicate data.

<table>
<thead>
<tr>
<th></th>
<th>C 1s %</th>
<th>O 1s %</th>
<th>Mn 2p%</th>
<th>Si 2p %</th>
<th>Al 2p %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn-MnO$_x$ Control</td>
<td>39.1 ± 4.3</td>
<td>49.2 ± 3.1</td>
<td>11.7 ± 1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Syn-MnO$_x$ Reacted</td>
<td>60.4 ± 0.3</td>
<td>33.4 ± 0.2</td>
<td>6.2 ± 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Com-MnO$_x$ Control</td>
<td>50.8 ± 3.0</td>
<td>40.0 ± 1.5</td>
<td>1.9 ± 0.2</td>
<td>3.1 ± 0.7</td>
<td>4.2 ± 0.6</td>
</tr>
<tr>
<td>Com-MnO$_x$ Reacted</td>
<td>60.9 ± 5.2</td>
<td>31.7 ± 3.9</td>
<td>1.4 ± 0.4</td>
<td>3.2 ± 0.3</td>
<td>2.8 ± 1.0</td>
</tr>
</tbody>
</table>
Figure 2. Residual BPA concentrations in aliquots from batch experiments of solutions reacted with Commercial MnO$_x$ (circle) and Synthesized MnO$_x$ (triangle) taken at times 0.1, 5, 15, 30, 45, 90, 180 and 2640 mins. Reaction conditions were 10 mM MnO$_x$, 1 mM BPA, 10 mM NaCl and pH 5.5, vertical error bars represent standard deviation for triplicate reactors.
Figure 3. Residual BPA in the reactors after reaction with MnO_x(s) media; Syn-MnO_x (blue) and Com-MnO_x (orange). The samples were treated in two ways, by only filtering to get removal by oxidation and adsorption (solid triangle), or by adding NaOH to get BPA removed by oxidation alone (hollow circle). Reaction conditions: 100 μM MnO_x, 10 μM BPA, 10 mM NaCl, pH 5.0, vertical error bars represent standard deviation for duplicate reactors.
Figure 4. (a) Concentration of Mn released into solution from batch experiments (n=3) and (b) Mn release normalized to surface area of respective media for Syn-MnO$_x$ (triangle) and Com-MnO$_x$ (circle). Reaction conditions were 10 mM MnO$_x$, 1 mM BPA, 10 mM NaCl and pH 5.5, vertical error bars represent standard deviation for triplicate reactors.
Figure 5. High resolution Mn 3p fitted spectra for MnO$_x$ media (a) unreacted Syn-MnO$_x$ (b) Syn-MnO$_x$ reacted with BPA (c) unreacted Com-MnO$_x$ (d) Com-MnO$_x$ reacted with BPA; (e) Percent composition of Mn 3p spectra by fitting Mn(II), Mn(III), and Mn(IV) reference spectra, uncertainty shown is standard deviation for triplicate data. Note that the spectra for unknown samples are shown in red, and for the Mn(II), Mn(III), and Mn(IV) references are shown in grayscale.
Figure 6. High resolution XPS O 1s (left) and C 1s (right) fitted spectra with corresponding types of oxygen and carbon bonds based on their binding energy for (a) Syn-MnO$_x$-control, (b) Syn-MnO$_x$-reacted, (c) Com-MnO$_x$-control, and (d) Com-MnO$_x$-reacted. The XPS data are shown as black dotted lines, solid green lines represent the composite curves of these bonds, and the different component oxygen or carbon bonds are shown as inset lines.
Figure 7. Results from kinetic modelling for (a) the electron transfer limited model and (b) the surface complex formation limited model. The data points for Syn-MnO$_x$ (triangle) and Com-MnO$_x$ (circle) are calculated based on the experimental data; the model fits equation and corresponding R$^2$ values are shown with each fit.
Chapter 4

4. U(VI) Binding onto Phosphonate Functionalized Electrospun Polymers

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Abstract:

The objective of this study is to investigate the mechanism affecting U(VI) binding onto phosphonate functionalized electrospun polymers under the influence of environmentally relevant ions (e.g., Ca and CO₃) using spectroscopy and aqueous chemistry techniques. Previous studies show high U uptake on functionalized polymers, but the specific mechanisms affecting the solid-liquid interfacial interactions are not well understood. Uptake experiments were carried out using 5 mg of Hexadecyl Phosphonic Acid (HDPA) functionalized mats with 10 uM U at pH 6.8 in 4 different reactors using different combinations of solutions containing 5mM calcium (Ca²⁺) and 5mM bicarbonate (HCO₃⁻). The U uptake was similar in control solutions containing no Ca²⁺ and HCO₃⁻ (resulting in 19% U uptake), and in those containing only 5 mM Ca²⁺ (resulting in 20% U uptake). A decrease in U uptake to 13% was observed in experiments with HCO₃⁻, indicating that UO₂-CO₃ complexes may increase uranium solubility. Almost negligible U uptake (3%) was observed in experiments with U, Ca, and HCO₃ likely due to the formation of neutral and negatively charged U-Ca-CO₃ ternary complexes as indicated by chemical equilibrium modelling. Results from shell-by-shell EXAFS fitting and aqueous extractions indicate that U is bound to phosphonate as a monodentate inner sphere surface complex to one of the hydroxyls in the phosphonate functional groups. The knowledge from this study is relevant for the advancement of technologies for in-situ detection and treatment of U in water.
4.1. Introduction:

Understanding U binding in carbon-based functionalized materials is necessary for environmental sensing and remediation applications. The transport of U(VI) caused by geochemical processes can be concerning for surrounding communities and ecosystems\textsuperscript{46,116} due to the toxicological effects of U in humans, such as cancer and kidney failure.\textsuperscript{45,46} Selective U uptake is possible by U chelation with organic functional groups (e.g. phosphonate, quaternary ammonia, etc.) embedded in the surface of solid substrates.\textsuperscript{55,117} Previous studies show high U uptake on phosphonate functionalized resins, but the specific mechanisms affecting the solid-liquid interfacial interactions are not well understood.\textsuperscript{79,118,119}

Electrospun polymers are advantageous due to their high surface to volume ratio, ease of synthesis and high porosity. Recent applications of electrospun polymers include passive samplers, solid phase extractions, filter media, and sensing devices.\textsuperscript{61,66,120–122} Although PAN (polyacrylonitrile) based electrospun polymers have shown metal binding affinity due to the nitrile group\textsuperscript{62,123–126}, further enhancement of U uptake is possible by incorporating U scavenging functional groups. In particular, phosphonates have been considered as an important chelating
agent for U uptake due to the strong U bonding with the three oxygen atoms ligands which are stable over a wide pH range. The nanofibers produced by electrospinning can incorporate the phosphonate ligand by using a sol-gel synthesis. Thus, the identification of surface associated U complexes is essential for the application of phosphonate functionalized electrospun polymers for enhanced U uptake towards development of rapid U sensors and point-of-use water remediation.

Extensive studies have been conducted on the interaction of U with phosphonate ligands in solution but the specific mechanisms affecting the binding of U in functionalized solid surfaces are not well understood. Computational chemistry studies using thermodynamics and quantum mechanical calculations show that binding of uranyl with aqueous phosphonate functional groups can occur as monodentate (UO$_2$PO-) or binuclear bidentate (-PO-UO$_2$PO-) surface complexes, even in the presence of competing ligands such as carbonates and phosphates. However, most U-phosphonate characterizations were carried out using precipitated solids and under highly acidic conditions. Additionally, these studies do not consider the effect of pH and co-occurring ions influencing the uptake of U in functionalized solids and limited experimental studies have been conducted complimenting theoretical studies. The presence of soluble calcium in the mM range enhanced adsorption of phosphonate onto a model solid surface. Carbonate is an important natural complexant that react with U to form stable UO$_2$CO$_3$ aqueous complexes. Additionally, the presence of ternary complexes of U involving uranyl cation, carbonate anion, and alkaline earth metals can influence the aqueous U(VI) speciation under circumneutral to alkaline pH conditions. There is limited understanding about the effect of major ions such as Ca and carbonate on the uptake of U in functionalized polymers in complex environmental water matrixes. Hence, the determination of the mechanism of U uptake will provide the necessary
framework for electrospun polymers to be applied as versatile U sensors in waters of various characteristics. 64,129

The objective of this study is to investigate the mechanisms affecting the binding of U onto phosphonate functionalized electrospun polymers in solutions containing Ca and CO₃ using spectroscopy (X-ray Photoelectron Spectroscopy, X-ray Absorption Spectroscopy, Raman Spectroscopy) and aqueous chemistry techniques. The novel aspect of this study is the identification of specific processes that influence the U binding in electrospun polymer mats under environmentally relevant reactants such as Ca and carbonate. The results are relevant for the advancement of water sensor technologies for in-situ detection of U.

4.2. Methods:

4.2.1. Materials.

The phosphonate functionalized mats where made using an electrospinner, using sol-gel synthesis. Sol-gel method is used to synthesize the electrospun polymers, which involves dissolving the parent polymer (Polyacrylonitrile PAN) and surfactant (HDPA) into an appropriate solvent. The HDPA solgel was prepared by dissolving 0.031 g of HDPA and 0.36 g of PAN into 5 mL DMSO (dimethyl sulfoxide), by shaking for 12 hours at 700rpm and 60C on a Thermomixer (Eppendorf). This sol-gel is fed using a syringe pump at 0.5 ml/hr and 16-20% humidity to an electrospinner needle at 15 kV applied potential resulting in electrospun nanofibers deposited on a ground collector surface rotating at 550 rpm.
4.2.2. Uptake experiments.

Batch experiment were performed to investigate the mechanism of uranium uptake on the polymer mat. Previous studies measured pH ranging from 6.8 to 8.2, alkalinity ranging from 100 to 430 mg/l as CaCO₃, Ca concentration between 30 to 280 mg/l and U concentration between 50 to 700 μg/l in spring and surface waters near mine waste sites in New Mexico and Arizona.⁴⁸,⁴⁹,¹¹⁶ Thus, based on these conditions measured in the field we conducted batch uptake experiments reacting solutions with 10 μM uranyl nitrate [UO₂(NO₃)₂•6H₂O] at pH 7.0 (buffered with 0.1 M HEPES) with 5 mg HDPA electrospun polymer mat in a centrifuge tube for 16 hours referred as U reactor. Additional experiments were conducted with 10 μM U, (i) 5 mM Ca (as CaCl₂) referred as U+Ca reactor (ii) 5 mM CO₃ (as NaHCO₃) referred as U+CO₃ reactor and (iii) 5 mM each of Ca and CO₃ referred as U+Ca+CO₃ reactor, together at pH 7.0 (Adjusted with HCl). Upon completion of reaction, the electrospun polymer mat were taken out of the reactor, rinsed with deionized water, and prepared for solid analyses.

4.2.3. Extraction experiments.

A set of experiments were conducted to evaluate the effect of different reactants on U release from the polymer mats after the uptake experiments. We used the 5mg of reacted mats from the uptake experiment reactors, referred to as U+HDPA reacted, U+Ca+HDPA reacted, U+CO₃+HDPA reacted and U+Ca+CO₃+HDPA reacted mats from this point on. These mats were reacted with 15 ml of the following solutions:

a) 1 M MgCl₂ reacted with electrospun polymer mats at room temperature for 1 hour to extract ion exchangeable species bound to the surface through ionic interactions or outer-sphere complexes.¹³⁰,¹³¹
b) 50 mM HCO$_3^-$, an environmentally relevant complexant, reacted with electrospun polymer mats to extract inner sphere surface complexed U. The extraction was done in a centrifuge tube with 100 mM of NaHCO$_3$ at pH 8.7 tube rotating at 60 rpm.

**4.2.4. Spectroscopy.**

The top 5 nm (near surface) of reacted and control polymer mats was analyzed using survey and high resolution XPS scans for the spectroscopic features of U, C, O, P and N. This provides insights on the binding chemistry of organic groups with U. The changes in binding environment of U was observed using the U 4f narrow scan. XPS high resolution spectra was collected for U 4f, C 1s, N 1s, O 1s, and P 2p using step size of 0.1 eV and pass energy of 20.

X-ray Absorption Spectroscopy (XAS) analyses were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) at beam line 11-2 to identify changes in oxidation state (XANES) and molecular coordination (EXAFS) of U during these batch experiments. The EXAFS provides coordination number, and atomic distances (eg. U-U, U-N and U-C) in the local molecular environment and help identify the surface complexes when compared to reference values. These references (U adsorbed ferrihydrite, liebigite and carnotite) were also analyzed. At least six scans were collected for each sample, and 3 scans for the references.

**4.2.5. Aqueous chemistry analysis.**

A PerkinElmer Nexion 300D inductively coupled plasma-mass spectrometer (ICP-MS) system with Dynamic Reaction Cell (DRC) and a method detection limit (MDL) of <0.5 μg/L was used to analyze the uranium concentration in liquid samples from the reactor. The aqueous samples were filtered through 0.22 μm syringe filter and acidified with ultra-pure HNO$_3$. 

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4.3. Results and Discussion

4.3.1. Electrospun polymer characterization.

The electrospun polymers have a polymeric backbone with the surfactant present on the surface as ligands as confirmed by XPS survey scans (Table 3) and ATR-FTIR spectra (appendix B, Figure B21). The XPS survey scans for the synthesized HDPA electrospun polymers exhibited 1.0% P on the surface and the presence of a peak at 134 eV region representing XPS P2p confirms the presence of phosphonate on the near surface of the electrospun polymer. The dimensions of the nanofibers were similar for all the control and reacted mats with the width of each nanofibers at 120 nm indicating that similar swelling of the

4.3.2. Uptake experiment.

The results from the uptake experiments indicate that the reaction of U with carbonate and with a mixture of calcium and carbonate causes the inhibition of U uptake on the HDPA electrospun polymer. For example, lower U uptake was observed in the U+CO$_3$ and U+Ca+CO$_3$ reactors when compared to the reactors without CO$_3$ (Figure 8). Comparable U uptake was observed in the U reactor (1.98 ± 0.07 μg U/mg mat) and in the U+Ca reactors (1.96 ± 0.37 μg U/mg mat). This similarity in U uptake can be attributed to highly preferential sorption of U on HDPA resulting in limited cationic competition from Ca.$^{63,119}$ The uptake in the U+CO$_3$ reactors was 1.14 ± 0.22 μgU/mg mat, corresponding to 39.4% decrease in U uptake compared to the U reactor. The U+Ca+CO$_3$ reactors had the least U uptake (0.35 ± 0.24 μg U/mg mat) which corresponds to 82% decrease when compared to the U reactor. This decrease is similar to recent studies showing 70% decrease in U sorption on solids when Ca and CO$_3$ are present.$^{132,133}$ Thus, the presence of co-
occurring ions influences the U uptake into the HDPA mats, which may be attributed to changes in U aqueous complexation.

The formation of uranyl-carbonate or ternary calcium-uranyl-carbonate aqueous complexes, which have neutral or negative charge, decreases the binding of U in the mats. Chemical equilibrium modelling was used to further interpret the results from the uptake experiments (Figure B23). Simulations at pH 7 suggest that the cationic U aqueous species are prevalent in the U reactors and in the U+Ca reactors, with 70% (UO$_2$)$_3$(OH)$_5^+$, 20% (UO$_2$)$_5$(OH)$_7^+$ and 6% UO$_2$OH$^+$. Anionic U aqueous species are prevalent in the U+CO$_3$ reactors, with 75% UO$_2$(CO$_3$)$_3^4$ and 21% UO$_2$(CO$_3$)$_2^{2-}$. For the U+Ca+CO$_3$ reactors, 67% Ca$_2$UO$_2$(CO$_3$)$_3$ neutral U species and 31% CaUO$_2$(CO$_3$)$_3^{2-}$ anionic U species were present. The presence of these ternary calcium-uranyl-carbonate aqueous complexes has also been reported in other studies. $^{78,79,81}$ As our experiments are conducted at pH 7 > pK$_a$=2.6 for HDPA, the surface is negatively charged, causing electrostatic repulsion with the negative and neutral aqueous complexes, thereby preventing U binding with the HDPA surface. Thus, lower uptake is observed for U+CO$_3$ and U+Ca+CO$_3$ reactors. Additional extraction experiments with targeted reactants were pursued to better understand the U release to solution from surface associated U species on the reacted mats.

4.3.3. Extractions experiments.

Higher U release from the HDPA reacted mats was observed after extractions with HCO$_3$ compared to MgCl$_2$, indicating that the U associated to these mats is more amenable to complexation rather than ion exchange. This result suggests that U is initially complexed to the surface of the HDPA reacted mats after the uptake experiments, but removed from the surface and released to solution after complexation with bicarbonate in the extraction experiments. (Figure 9) The U+HDPA reacted mats had 70% higher U release (3.0 µg HCO$_3$ extractable U) with
extractions using HCO$_3^-$ when compared to MgCl$_2$ extractions (0.9 μg MgCl$_2$ extractable U). A similar trend was observed for the U+Ca+HDPA reacted mats, given that 78% higher HCO$_3^-$ extractable U (3.9 μg) was released when compared to MgCl$_2$ extractable U (0.8 μg). An order of magnitude higher HCO$_3^-$ extractable U was obtained for the U+CO$_3^-$+HDPA reacted mats (1.7 μg U) and U+Ca+CO$_3^-$+HDPA reacted mats (0.6 μg U) in contrast to that released from MgCl$_2$ extractions (0.02 μg for U+CO$_3^-$+HDPA reacted mats and 0.06 μg for U+Ca+CO$_3^-$+HDPA reacted mats).

Although the U+CO$_3^-$ and U+Ca+CO$_3^-$ reactors had a lower U uptake, most extractable U was amenable to complexation after HCO$_3^-$ addition. The low U released after extractions with MgCl$_2$ indicates limited ion exchangeable U in these mats. Strong complexing agents like HCO$_3^-$ would bind and solubilize most surface associated U complexes$^{49,130}$ resulting in release of both the inner sphere and outer sphere surface U complexes into solution. Thus, a higher HCO$_3^-$ and low MgCl$_2$ extractible U indicate the presence of inner-sphere U surface complex on all the reacted mats. Further analyses of the reacted mats were carried out to understand the binding structure of surface associated U using XAS and XPS.

4.3.4. Solid analyses.

The EXAFS U L-III shell-by-shell fitting (Figure 10) for HDPA+U reacted mat indicates that U is coordinated as an eight (as UO$_2$O$_6^-$) inner-sphere complex with the HDPA mat. The fitting of peaks observed in the Fourier Transformed (FT peaks, Figure 10b) EXAFS spectra around 1.8 Å corresponds to the 2 U=O dioxo bonds and 6 U-O bonds with atomic distances of 1.79 Å and 2.31 Å respectively. The FT peaks at 2.3 Å is likely due to shell of neighboring atoms, which in our system is nitrate ligands, at atomic distance of 2.9 Å. The FT peaks observed at 2.9 to 3.1 Å can be attributed to a second neighbor shell of U-P coordination on HDPA, which suggests inner-
sphere complexation through one of the hydroxyls of the phosphonic acid functional group (≡P-O-U, atomic distance U-P 3.72 Å). Similar atomic distances for surface associated U have been reported in literature.\textsuperscript{51,134,135}

Additionally, the presence of FT peak at 3.69 Å is characteristic of a U-U linking, most likely as an edge-sharing U-O-U coordination complex.\textsuperscript{51,80} This suggests presence of a dimeric uranyl surface complex on the same phosphonate surface site (dimeric mononuclear surface complex) or a neighboring phosphonate surface site (binuclear surface complex) forming a UO\textsubscript{2}-phosphonate-UO\textsubscript{2} framework as reported in other studies using DFT and vibrational spectra.\textsuperscript{56,136} All other reacted mats (U+Ca+HDPA, U+CO\textsubscript{3}+HDPA, U+Ca+CO\textsubscript{3}+HDPA) showed similar EXAFS spectra, indicating that the U binding on surface was consistent to the U only shell-by-shell fitting.

The XPS survey and high-resolution spectra detected the presence of U in the near surface of all the reacted mats (survey scan table). The U 4f high resolution spectra for all mats had similar shapes which indicates similar U(VI) binding in the near surface (Figure 11). Fitting of the U 4f 7/2 spectra indicates the presence of two components with binding energy at 381.6 eV and 379.6 eV. A U4f satellite peak is observed at 384.4 eV. The U4f 5/2 spectra imitates the shape of the components of U4f 7/2 with exactly 10.9 eV lower binding energy and 1/3\textsuperscript{rd} the intensity. Since these two components are present for all the reacted mats, the surface associated uranyl species is likely the same. Analysis of high-resolution P 2p spectra indicates that there are no noticeable changes in shape for all the reacted mats. The lack of changes in the EXAFS U L-III spectra and XPS U 4f high resolution spectra in all the reacted mats suggests that similar binding environment on the surface reacted HDPA mats in all reaction conditions.
4.4. Mechanistic insights.

The results from this study indicate that the U(VI) binding occurs primarily on the deprotonated oxygen of the phosphonate (≡P-O\textsuperscript{−}). As the cationic U aqueous species would easily bind to the negatively charged ≡P-O\textsuperscript{−} surface site, a higher U uptake was observed for the U only and U+Ca reactors. The lower U uptake in the U+CO\textsubscript{3} and U+Ca+CO\textsubscript{3} reacted mats is due to the repulsion between anionic and neutral aqueous U species with the negatively charge phosphonate surface. This limited U-uptake was confirmed by the limited ion-exchangeable surface complexes. The surface associated U is predominantly an inner-sphere surface complex, as observed from the \( \text{HCO}_3^− \) strongly complexed and EXAFS solid analyses. The formation of U-U multimers on the surface may strengthen the U-phosphonate surface interaction and increase the U uptake as reported in uranium-phosphonates literature\textsuperscript{53,60,77}. Thus, the surficial interaction of aqueous U species strongly influences the U uptake on the solid electrospun polymer as similar surface associated U species are present for all the reaction conditions.

4.5. Conclusion

The presence of environmentally relevant concentrations of Ca and CO\textsubscript{3} inhibits U uptake in phosphonate functionalized electrospun polymers. The mechanism of U uptake is identified as inner-sphere complexation with U-phosphonate monodentate surface complexes observed on all the reacted mats. Similar U-surface binding characteristics was observed on all the reacted mats despite differences in aqueous U speciation. The results from this research are relevant for future applications of phosphonate functionalized electrospun polymers towards U sensing or water treatment applications given the stability of inner-sphere complexation as a binding mechanism.
4.6. Acknowledgements

Funding for this research was provided by the U.S. National Institutes of Health under award number R01ES027145, UNM METALS Superfund Research Program Center P42ES025589 and National Science Foundation CAREER Award 1652619. Use of the SSRL Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.
**Figures & tables**

**Figure 8.** Uptake of U (μgU / mg mat) on HDPA-PAN electrospun mats reacted with 10 μM [U], 50 mM [HEPES] and in the presence of either 5 mM [Ca] (orange), 5 mM [CO$_3$] (gray) or both 5 mM [Ca] and [CO$_3$] (yellow). The experiments were conducted using 5 mg mat in 20 ml solution reacted for 16 hours. Error bars represent the standard deviation of triplicate reactors.
Figure 9. Results from reactivity experiments indicating U released from the reacted mats after the addition of extractants (a)MgCl$_2$ (b) HCO$_3$. Reaction conditions involved taking the reacted mats from U uptake experiments and reacting with extracted for 12 hours.
Figure 10. U L_{III}-edge EXAFS spectra from beamline 11-2 in (a) real-part (b) Fourier transformed (c) shell-by-shell fits for reacted HDPA+U mats compared to references autunite and carnotite minerals. Reaction conditions \([U] = 10 \, \mu M\), Mat = 5 mg, volume = 20 ml, pH = 6.8 buffered HEPES = 10mM. Numbers in parentheses represent the standard deviations.

<table>
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<th>Coordination No., N</th>
<th>U-O1</th>
<th>U-O11</th>
<th>U-N1</th>
<th>U-P2</th>
<th>U-U</th>
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<tr>
<td>Shell Distance, D(Å)</td>
<td>1.79(1)</td>
<td>2.31(1)</td>
<td>2.87(1)</td>
<td>3.72(1)</td>
<td>3.69(15)</td>
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<td>mean square deviation, (\sigma^2)</td>
<td>0.0023(1)</td>
<td>0.0015(1)</td>
<td>0.0015(1)</td>
<td>0.007</td>
<td>0.0033(1)</td>
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Table 3. XPS survey scans of the HDPA mat samples after uptake reaction indicating the atomic composition in the near surface

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<tr>
<th></th>
<th>C 1s</th>
<th>N 1s</th>
<th>O 1s</th>
<th>P 2p</th>
<th>U 4f</th>
<th>Na 1s</th>
<th>Ca 2p</th>
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<tr>
<td>HDPA control</td>
<td>80.6</td>
<td>8.4</td>
<td>9.7</td>
<td>1.3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td></td>
<td>± 0.98</td>
<td>± 2.4</td>
<td>± 3.7</td>
<td>± 0.34</td>
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<td>HDPA+U</td>
<td>79.5</td>
<td>12.7</td>
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<td>0.4</td>
<td>0.2</td>
<td>0.7</td>
<td>n.d.</td>
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<tr>
<td></td>
<td>± 1.1</td>
<td>± 0.37</td>
<td>± 1.3</td>
<td>± 0.05</td>
<td>± 0.04</td>
<td>± 0.09</td>
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<tr>
<td>HDPA+U+Ca</td>
<td>78.8</td>
<td>12.6</td>
<td>7.5</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>± 1.0</td>
<td>± 0.6</td>
<td>± 1.2</td>
<td>± 0.06</td>
<td>± 0.03</td>
<td>± 0.05</td>
<td>± 0.04</td>
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<tr>
<td>HDPA+U+CO3</td>
<td>79.9</td>
<td>14.4</td>
<td>4.4</td>
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<td>0.1</td>
<td>0.7</td>
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<td></td>
<td>± 0.3</td>
<td>± 0.81</td>
<td>± 0.5</td>
<td>± 0.01</td>
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<tr>
<td>HDPA+U+Ca+CO3</td>
<td>77.2</td>
<td>18.8</td>
<td>3.9</td>
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**Figure 11.** High Resolution U 4f photo peak for reacted samples (red) and fittings of U 4f 7/2 components (inset) for reacted HDPA mats from U uptake experiments.
Chapter 5

5. Electrochemically active MnO$_x$-C composites for Removal of Phenolic Micropollutants

Nabil Shaikh, Roxanne Awais, Abdul-Mehdi Ali, Fernando H. Garzon, Brian P. Chaplin, and José M. Cerrato

Abstract:
We investigated the oxidation of acetaminophen with electrochemically active Manganese Oxide – Carbon composite media (MnO$_x$/C composites). In this work we make use of the catalytic properties of manganese oxides, which are naturally abundant, and the high surface area and conductive properties of carbon materials. The development of effective technologies for treating emerging contaminants is a necessary quest. Solid characterization of the synthesized media using XPS and SEM/EDS indicates that mixed valence states of Mn(III)/Mn(IV) are present in MnO$_x$/C composites. Cyclic voltammetry on MnO$_x$/C composites yielded the highest capacitance for MnO$_x$ on particulate activated carbon (37 F/g), followed by MnO$_x$ on Vulcan (26.6 F/g), while lowest capacitance was observed for MnO$_x$ on carbon nanofiber (4.4 F/g). A positive correlation was observed between surface area of composite to its’ capacitive performance. Electrochemical analyses indicate that improved oxidation of acetaminophen was obtained on MnO$_x$/C composite as it showed a higher current density (1.4 mA/cm$^2$) compared to carbon alone (0.8 mA/cm$^2$). The improved electrochemical performance of MnO$_x$/C composites towards phenolic degradation observed in this study indicates that these materials offer promising opportunities for phenolic micropollutant treatment and sensor applications.
5.1. Introduction:

Removal of emerging organic contaminants is a major challenge for water treatment and reuse. Acetaminophen is an analgesic pharmaceutical used in over the counter pain medications and example of endocrine disrupting phenolic micropollutants that are widely observed in natural and engineered water systems.\textsuperscript{3,4,12,13} Acetaminophen is reported in literature to be electroactive towards oxidation to N-acetyl-p-benzoquinone imine using a variety of carbon composites electrodes modified with organic functional groups such as carbon nanotubes, glassy carbon and graphene.\textsuperscript{82–85} Recent studies have shown improved acetaminophen electrochemical oxidation using metal oxide such as TiO\textsubscript{2}, CoO, CuO, MgO – carbon composites for electrochemical sensor applications across a wide pH range.\textsuperscript{86–89} However, limited information is available for acetaminophen electro-oxidation using low cost and environmental friendly MnO\textsubscript{x} carbon composites for water treatment applications.\textsuperscript{90} Previous research demonstrate promising results in the application of MnO\textsubscript{x}(s) in columns and bed filters for removal of phenolic micropollutants via abiotic mechanisms.\textsuperscript{11,30,72,73,104,105} After the initial rapid organic removal, the long-term kinetics is decreased due to saturation of surface sites by reaction products.\textsuperscript{75,94,137,138} Additionally, the reaction between MnO\textsubscript{x}(s) and organic contaminants fits an electron transferred limited model and is inhibited by increasing surficial Mn\textsuperscript{2+} concentrations.\textsuperscript{94,110,115,139,140} Thus, the MnO\textsubscript{x}(s)-organic interaction can be improved by increasing the surface sites and electron transfer resulting in better overall performance of MnO\textsubscript{x} media in the removal of organic micropollutant.
The poor electrical conductivity of pure manganese oxides can be improved by doping with conductive material such as carbon.\textsuperscript{91,92} Carbon based support materials such as carbon nano-fibers (Cnf), powdered activated carbon (PAC) and carbon black (Vulcan) are physically-chemically stable and electrochemically active materials, which provide a support for the MnO\textsubscript{x} media. These MnO\textsubscript{x} doped carbon are used in electrochemistry as catalyst for batteries and fuel cells due to its increased capacitance, improved stability and catalytic activity \textsuperscript{36,37,41,93}. From previous studies, the improved electrochemical activity of these composites is due to pseudocapacitive behavior from electron transfer processes (charge separation at the electrode/solution interface) and redox faradaic reactions that occur within the electrode materials. This pseudocapacitance occurs due to proton exchange and/or surface adsorption of electrolyte cations on the MnO\textsubscript{x} surface.\textsuperscript{37,40,141} The effective surface area associated the MnO\textsubscript{x} particle size and pore distribution is a crucial factor in determining the pseudocapacitance. Thus, the MnO\textsubscript{x}/C composite should have a good distribution of MnO\textsubscript{x} particles on the surface as well as a high surface area to promote the electron transfer. Although these previous studies applicable in catalysis for batteries and fuel cells show good pseudocapacitance of MnO\textsubscript{x}-C composites, the application in water treatment systems is still limited.

The objective of this study is to investigate the application of electrochemically active MnO\textsubscript{x}/C composites for the removal of acetaminophen, a phenolic micropollutant in source waters. There is limited information about the electrochemical application of MnO\textsubscript{x}/C composites on catalytic performance and feasibility for water treatment applications. The novelty of this study is to determine the feasible application of MnO\textsubscript{x}-C composite for treatment of phenolic micropollutants at circumneutral pH.
5.2. Methods:

5.2.1. Materials.

The carbon supports used in this study were particulate activated carbon (Cabot Corp., MA), Vulcan XC72R (Cabot Corp., MA) and carbon nanofibers (Sigma Aldrich, MO) due to their high conductivity and purity. All other chemicals used in this study were of ACS grade or higher purity.

5.2.2. Hydrothermal synthesis of MnOx/C composites:

Carbon support material (100 mg each of particulate activated carbon PAC, Vulcan XC72R, carbon nanofibers CnF) were pretreated overnight with 5% HNO3 at 100°C to remove impurities. The acid-treated carbon was centrifuged and rinsed with DI water until the solution conductivity became equal to that of DI water. The carbon was stirred in 50 ml solution containing 0.2 g potassium permanganate (KMnO4) with a magnetic stirrer for 30 minutes and equilibrated for 1 hour, followed by heating the permanganate sorbed carbon for 16 hours in an 80°C water bath. Presence of brown precipitates on the carbon was observed indicating formation of MnOx coating. The particles were collected from the mixture and washed with DI water followed by heating to 105°C for 24 hours. The zeta-potential of the carbon support was determined using a Malvern zetasizer nano instrument.

5.2.3. Batch experiments.

The batch experimental set-up consists of MnOx(s) media and MnOx/C composite in batch experiments. Batch experiment were performed to evaluate reaction between 5 mg MnOx composite or media with 100 uM Acetaminophen in a 50 ml centrifuge tube using ultrapure water at pH 7.0 (buffered with 5 mM HEPES, 1 mM NaCl added) for 24 hrs. These conditions are environmentally relevant along with promoting fast enough kinetics to appreciably complete the
reaction in the experimental time frame. Aqueous samples were collected at times $t=0$ min., 0.5 min., 5 min., 10 min., 30 min., 60 min., 3 hr., 6 hr., 18 hr., 24 hr. and filtered through a 0.45 μM syringe filter for Mn (ICPMS) and Acetaminophen (HPLC) analyses. Solid media samples will be collected from the reactor at the end of the experiment for solid analysis. Residual acetaminophen concentration obtained from HPLC analysis on the liquid aliquots provided the organic removal for MnO$_x$/C composite and MnO$_x$ media. Characterization of the media was conducted using electrochemistry and x-ray photoelectron spectroscopy to study the surface of MnO$_x$.

5.2.4. Spectroscopy.

The top 5 nm (near surface) of reacted and control material was analyzed using survey and high resolution XPS scans for the spectroscopic features of Mn, C, O. This provides insights on the binding chemistry of organic groups with Mn. The changes in oxidation state of Mn was calculated from Mn 3s and Mn 3p narrow scans.

5.2.5. Aqueous chemistry analysis.

The aqueous samples taken from the batch experiments or the cyclic voltammetry cells were analyzed using a high-performance liquid chromatography (HPLC) coupled with UV detector for the concentrations of acetaminophen. The aqueous samples for soluble Mn were filtered using a 0.22 μm syringe filter and acidified with HNO$_3$ and measured on a PerkinElmer NexION 300D (Dynamic Reaction Cell) inductively coupled plasma mass spectrometer (ICP-MS).

5.2.6. Electrochemical analysis: Cyclic voltammetry

The electrochemical performance of the composite was conducted using a three-electrode glass cell connected to an electrochemical workstation with a saturated Ag/AgCl reference electrode, a
graphite counter-electrode and a 0.1 M borate electrolyte solution at pH 7 under ambient conditions. The cyclic voltammetry is taken in the potential window -0.7 to 0.5 and -0.7 to 1.0 V vs Ag/AgCl at 10-100 mV/s scan rate. All the experiments were carried out at room temperature. The working electrode was prepared by making an ink slurry using 5 mg of the media into 1 ml 4:1 IPA:DI solution containing 0.5 wt% of Nafion. This slurry was sonicated using a microtip sonicator to get a fine ink. About 29.9 μl of this ink was deposited onto a glassy carbon rotating disk electrode (Pine Instruments) with outer diameter of 5 mm which was used as the working electrode. The effective mass loading on the electrode was calculated to be 0.1485 mg of media. For CV experiments for organic oxidation, 100 ml of 0.5 mM Acetaminophen in 0.1 M buffer and 50 mM NaSO₄ at pH 7 was used as the electrolyte. Linear sweep voltammetry experiments were carried out with 100 mV/s scan rate in the buffer solution with N₂ sparging.

The specific capacitance $C_{sp}$ (F/g) was calculated as follows:

$$C_{sp} = \frac{\int I \cdot V \delta V}{2 \cdot v \cdot m \cdot \Delta V}$$

Where $I$ is the measured current (Amperes), $V$ is the measured potential (Volts), $v$ is the scan-rate (V/s), $m$ is the mass of the electrode materials (g), $\Delta V$ is the potential window in the cyclic voltammogram.

The capacitance for MnOₓ/C composites normalized to the MnOₓ loading is defined as:

$$C_{Mn} = \frac{C_{sp}}{wt_{MnO\_x:C}}$$

Where $wt_{MnO\_x:C}$ is the weight ratio of MnOₓ to Carbon support.
5.3. Results and Discussion

5.3.1. Removal of acetaminophen with MnO$_x$/C Composites in batch reactors

The results of the batch experiments indicate that the highest removal of acetaminophen was obtained after reaction with PAC based MnO$_x$ composites. The reactors with carbon only (ie. PAC, Vulcan and CnF) showed lower acetaminophen removal compared to MnO$_x$-PAC composite. The lowest acetaminophen removal was observed in CnF reactors (19% removal) followed by Vulcan (36% removal) after 14 hours of reaction. MnO$_x$-PAC had the highest acetaminophen removal (83% removal) compared to the PAC carbon support (57%). Control experiments conducted in the presence of acetaminophen and absence of solid media showed negligible acetaminophen removal. In addition, the HPLC data showed an increased presence of unknown organic byproduct of acetaminophen oxidation in MnO$_x$/C reactors, while reactors that contained only carbon did not show the presence of this byproduct.

The highest removal of acetaminophen was obtained with MnO$_x$-PAC because of the catalytic activity of MnO$_x$ combined with the high surface area and neutral charge of PAC at pH 7. Other studies have indicated that PAC has neutral charge at pH 7, which facilitates the interaction with negatively charge phenoxy functional group in acetaminophen at circumneutral pH.$^{32,142}$ The point of zero charge for Vulcan has been identified at pH 7, which explain the favorable removal with Vulcan in this study.$^{31,32,143}$ However due to the considerably high surface area of PAC (800 m$^2$/g) vs. Vulcan (200 m$^2$/g), the PAC show greater acetaminophen removal compared to Vulcan. The point of zero charge for CnF was found to be at pH 4.5 using a zeta-potential probe. Thus, the MnO$_x$-CnF has a negative surface charge at pH 7.0 of the batch experiment causing electrostatic repulsion with the negatively charged phenoxy functional group and resulting in the lower removal. Increases in the total concentration of Mn in solution were observed for the duration of
the batch experiments conducted for this study, confirming the reductive dissolution of MnO_x(s) occurs in all of these materials caused by the oxidative removal of acetaminophen (Figure C24). The lowest release of Mn was observed on MnO_x-PAC, indicating that the higher surface area of PAC facilitates adsorption of Mn in this media compared to the others. Additional analyses were conducted to characterize unreacted and reacted solids.

5.3.2. Solid Characterization of Unreacted and Reacted Materials

Analyses of XPS spectra indicate that an increase in reduced Mn was observed on the MnO_x-PAC samples reacted with Acetaminophen. The surface concentration of Mn 2p% decreased as the reaction with acetaminophen continued over 24 hours (Table 5). The MnO_x-PAC showed a decrease of surficial Mn over time, starting at 8.6% Mn 2p before the reaction with acetaminophen to 4.3% in 24-hour reacted samples. Similar decrease in Mn 2p% in the near surface for pure MnO_x (Syn-MnO_x) was observed with control Syn-MnO_x having 11% Mn 2p and 24 hours reacted Syn-MnO_x showing 6.2% Mn 2p. Additionally, the survey scans show an increase in C 1s % for all the reacted samples, indicating build-up of acetaminophen and oxidation by-products on the surface. The MnO_x-PAC showed an increase in surficial C 1s from 46.9% in control samples to 71.3 % in 24-hour reacted MnO_x-PAC. An increase in C 1s % for Syn-MnO_x was observed from 43.9% in control Syn-MnO_x to 60.4% C% in 24-hour reacted Syn-MnO_x. These results are similar to previous studies of phenolic groups with MnO_x resulting in accumulation of organic products on the surface of the media.22,30,94

The average oxidation state of Mn is shown in Table 6 and calculated by comparing these Mn 3s splitting values to the reference Mn(IV), Mn(III) and Mn(II) oxides as done in previous studies.30,94,106 The Mn oxidation state of the control unreacted MnO_x-PAC was calculated to be
3.0. The oxidation state decreased slightly to 2.9 during the reaction with Acetaminophen but remained similar to the oxidation state of the control MnO$_x$-PAC. The pure Syn-MnO$_x$ had multiplet split of 4.9 eV which represents an Mn oxidation state of 3.4. These values are comparable to literature values of pure delta-MnO$_x$ which includes mixed Mn(IV) and Mn(III) oxides.\textsuperscript{19,94,144} On reaction of Syn-MnO$_x$ with acetaminophen, the Mn 3s mutlitplet splitting increased to 5.3 eV which corresponds to a Mn oxidation state of 3.1. Additional experiments were conducted to evaluate the electrochemical activity of these materials reacting with acetaminophen.

5.3.3. Electrochemical Experiments with MnO$_x$/C composites

Cyclic voltammetry (CV) of the different carbon electrodes conducted at pH 7.0 show high capacitance due to double layer capacitance as shown in Figure 14a. The cyclic voltammograms of PAC electrode exhibit a typical rectangular shape for ideal capacitor behavior of carbon electrodes. The capacitance in conductive carbon is due to electrochemical double layer, which have been shown to be dependent on surface area of the electrode.\textsuperscript{35,91,145} The specific capacitance ($C_{sp}$) of PAC electrodes was calculated to be 17.7 F/g using a potential window of 0.5 to -0.7 V. The specific surface areas were obtained by N$_2$ adsorption (BET method) and illustrated in Table 4. A linear correlation ($R^2 = 0.996$) was observed for specific capacitance with the surface areas of the carbon electrode (Figure 14b). A double layer capacitance per unit surface area can be obtained from the linear fit in this study, $C_{dl} = 1.95$ μF/cm$^2$, which is in the same order of magnitude but lower than the literature values of $C_{dl}$ for carbon 7.5 μF/cm$^2$.\textsuperscript{145–147} This decrease of double layer capacitance of the powdered electrodes is because the BET surface area represents the maximum external area accessible for gas sorption and usually overestimates the actual area.
available for ionic interactions. Additionally, the low ionic strength of the electrolyte could contribute to the lower double layer capacitance value.

Comparison of CV voltammograms of MnO$_x$/C composites and PAC control electrodes conducted at pH 7.0 in 0.05 Na$_2$SO$_4$ (illustrated in Figure 14a) shows improved capacitance for MnO$_x$-PAC due to a combination of double layer capacitance and faradaic reactions. The shape of the MnO$_x$-PAC CV shows presence of a broad oxidative peaks starting at 0.5 V and 0.05 V vs. saturated Ag/AgCl. The presence of these redox waves for the MnO$_x$PAC is similar to the literature for amorphous MnO$_x$ (birnessites).\textsuperscript{148–151} The increase in area under CV for MnO$_x$PAC compared to PAC suggests that faradic processes occur during the charge-voltage scans. Previous studies have shown that the MnO$_x$ pseudocapacitance is due to the Mn redox transformation as well as the transitions of interfacial oxycation species such as proton and cation exchange.\textsuperscript{37,141,152} Converting the peaks observed in MnO$_x$PAC samples to standard hydrogen electrode potential results in 0.7 V and 0.25 V, which can be compared to the standard potentials of the redox transitions of Mn between different valence states, such as, Mn(IV)/Mn(III) and Mn(III)/Mn(II) based on the following equations from the Pourbaix diagram at pH 7.0:\textsuperscript{153}

\begin{align*}
Mn_2O_3 + H_2O \rightarrow 2 MnO_2 + 2 H^+ + 2 e^-; E_0 = 0.6 V \\
2 Mn_3O_4 + H_2O \rightarrow 3 Mn_2O_3 + 2 H^+ + 2 e^-; E_0 = 0.275 V
\end{align*}

The MnO$_x$ pseudo capacitance observed in the MnO$_x$PAC CV is also contributed by charge storage in the surface due to association of cations (M$^+$) from the electrolyte such as protons (H$^+$) and Na$^+$ as reported in other studies.\textsuperscript{37,154–156} Since the $\delta$-MnO$_x$ used in this study was poorly crystalline and surface deposited, a predominant adsorption mechanism and limited intercalation of H$^+$ and M$^+$ is expected on MnO$_x$PAC.\textsuperscript{149,157}
Where $M^+ = H^+$ or $Na^+$

The specific capacitance ($C_{sp}$) calculated from the CV plots for MnO$_x$-C composites and carbon supports at different scan rates (5, 10, 50 and 100 mV/s) is illustrated in Figure 14c and Figure C26 shows an increase in capacitance for MnO$_x$-C composite when compared to bare carbon supports. This also confirms the presence of faradaic component of capacitance along with double layer. $C_{sp}$ values for MnO$_x$PAC was highest at 40 F/g when compared to Csp of PAC only = 24.2 F/g. Extrapolating the specific capacitance to zero scan-rate yields a faradaic (redox/charge transfer reactions) and double layer capacitance of 47.6 F/g for MnO$_x$PAC while specific capacitance due to double layer was 33.2 F/g for PAC. Subtracting these both values gives the specific capacitance due to faradaic processes only as 14.4 F/g. Similar values for faradaic only capacitance was observed for MnO$_x$Vulcan (13.5 F/g) and MnO$_x$CnF (13.2 F/g) indicating similar faradaic transformation occurring at the MnO$_x$/C electrode surface. Increasing the scan-rate resulted in decrease in specific capacitance for all the MnO$_x$/C composites, indicating that only outer surface of MnO$_x$ takes part in the reaction. This occurs due to diffusion limitation of cations into the interior pores of MnO$_x$ at higher scan-rates. The Mn normalized capacitance ($C_{Mn}$) was calculated as $C_{sp}$ divided by MnO$_x$ loading. The highest $C_{Mn}$ was observed for MnO$_x$-PAC (141 F/g) > MnO$_x$Vulcan (103 F/g) > MnO$_x$CnF (60.4 F/g), comparable to the capacitance values for powdered MnO$_x$/C pseudo-capacitors in literature (50 to 200 F/g).$^{148,149,156,157}$(156)

5.3.4. Electrochemical Analysis of Acetaminophen oxidation on MnO$_x$/C composites

Cyclic voltammograms (CV) performed in the presence of 1 mM Acetaminophen at pH 7.0 using MnO$_x$-PAC and PAC electrodes indicate higher organic oxidation occurring on MnO$_x$-PAC (Figure 15a). The presence of the peak at 0.8 V vs Ag/AgCl on both electrodes indicates that
MnO$_x$PAC and PAC are electrochemically active towards oxidation of acetaminophen as seen in other studies using carbon electrodes.$^{84,85}$ A higher peak current density ($i_p$) was observed for MnO$_x$PAC (1.4 mA/cm$^2$) compared to PAC (0.8 mA/cm$^2$), which indicates higher reaction rate which is likely indicative of enhanced acetaminophen oxidation on MnO$_x$PAC. Previous literature suggests that Acetaminophen oxidizes to N-acetyl-p-quinone-imine, and the presence of cathodic peak at 0.26 V shows the reduction of N-acetyl-p-quinone-imine back to acetaminophen.$^{83,90}$ An anodic to cathodic current peak ratio of 0.35 and increase in potential of the oxidation peak ($E_P$) with increasing scan rates (Figure C27a) suggests that the electrochemical reaction is irreversible. Additionally, the peak current density ($i_p$) of acetaminophen oxidation decreased with increasing CV cycles and the decrease in Acetaminophen concentrations in the electrolyte. This confirms the quasi-irreversible oxidation of acetaminophen on MnOx-PAC electrode.

Cyclic voltammograms on MnO$_x$-PAC and PAC using 10 mM Acetaminophen at pH 7.0 were performed to assess the charge transfer and electrochemical reaction kinetics (Figure 15b). The acetaminophen oxidation had a higher current density with MnO$_x$-PAC (2.9 mA/cm$^2$) when compared to PAC (2.2 mA/cm$^2$). An increase in acetaminophen oxidation peak current was observed with respect to increasing scan rates (Figure C27b) for both MnOx-PAC and PAC only, which indicates that the oxidation of acetaminophen on the surface of the electrode was limited by the diffusion through the boundary layer.

5.4. Mechanistic Insights

Increasing the scan-rate of cyclic voltammogram resulted in decrease in specific capacitance for all the MnO$_x$/C composites, indicating that only the surface of MnO$_x$ takes part in the reaction. This occurs due to diffusion limitation into the interior pores of MnO$_x$ at higher scan-rates.$^{156}$ The
higher capacitance of MnO\textsubscript{x}/C composites are shown to be a combination of double layer capacitance and faradaic reactions between Mn(IV) and Mn(III).\textsuperscript{149} The higher Acetaminophen oxidation current in MnO\textsubscript{x}/C composites as compared to the PAC electrodes is likely due to a catalytic enhancement of the redox reaction mediated by Mn(IV) electron transfer to adsorbed Acetaminophen.

5.5. Conclusion

The MnO\textsubscript{x}/C composite showed improved electrochemical oxidation activity when compared to high surface area carbon and pure MnO\textsubscript{x}(s) media tested. The increase in peak current for acetaminophen oxidation and higher acetaminophen removal with MnO\textsubscript{x}/C composite indicates enhanced electrochemical oxidation of acetaminophen on the MnO\textsubscript{x}/C composites. Mechanistic insights from the cyclic voltammetry indicate that high surface area, amorphous MnO\textsubscript{x} on highly porous carbon supports, can enhance the electrochemical reactions towards oxidation of phenolic micropollutants at environmentally relevant conditions. The cyclic voltammetry also demonstrated an almost continuous change in Mn valency with applied potential; indicative of facile Mn redox behavior. The ability to detect and control the Mn oxidation state on the MnO\textsubscript{x}/C composite surface using electrochemistry is a promising avenue towards developing optimal heterogenous catalysts for organic oxidation. Thus, the findings from this study about using a cost efficient and ubiquitous manganese oxide on carbon composites for acetaminophen oxidation is promising towards development of engineered materials for water treatment applications.
Figure 12. Characterization of MnO$_x$/C composite (showing MnO$_x$ deposition after hydrothermal synthesis) (a) SEM (b) EDS of MnO$_x$/Cnf composite
Figure 13. Acetaminophen removal in batch experiments by MnO$_x$-PAC composites and carbon support CnF, Vulcan and PAC. Reaction conditions were 5 mg MnO$_x$ composite or carbon median 100 uM Acetaminophen at pH 7.0 for 24 hrs.
Figure 14. Electrochemistry results showing cyclic voltammograms in 0.1 M Borate buffer and 0.05 M Na$_2$SO$_4$ for MnOx-PAC composite, and PAC in (a) blank electrolyte (b) relationship between capacitance and surface area (c) CV in electrolyte containing 1 mM Acetaminophen at 50 mV/s (c) relationship between capacitance and scan rates.
Figure 15. Electrochemistry results showing (a) the CV of 1 mM Acetaminophen on MnO$_x$-PAC and (b) CV of 10 mM Acetaminophen on MnO$_x$-PAC.
Table 4. Surface Area of carbon supports and MnO\textsubscript{x}/C using BET N\textsubscript{2} adsorption

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Surface Area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SynMnO\textsubscript{x}</td>
<td>128</td>
</tr>
<tr>
<td>CnF</td>
<td>28.7</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-CnF</td>
<td>57.7</td>
</tr>
<tr>
<td>PAC</td>
<td>809</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-PAC</td>
<td>532</td>
</tr>
<tr>
<td>Vulcan</td>
<td>209</td>
</tr>
<tr>
<td>MnO\textsubscript{x}-Vulcan</td>
<td>157</td>
</tr>
</tbody>
</table>
Table 5. XPS survey scan of reacted samples

<table>
<thead>
<tr>
<th></th>
<th>C 1s %</th>
<th>Mn 2p %</th>
<th>N 1s %</th>
<th>O 1s %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MnO$_2$PAC</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>46.9</td>
<td>8.6</td>
<td>1.1</td>
<td>43.4</td>
</tr>
<tr>
<td>5 min</td>
<td>54.8</td>
<td>7.7</td>
<td>1.3</td>
<td>36.2</td>
</tr>
<tr>
<td>30 min</td>
<td>59.4</td>
<td>7.1</td>
<td>1.1</td>
<td>31.4</td>
</tr>
<tr>
<td>360 min</td>
<td>57.1</td>
<td>6.8</td>
<td>1.3</td>
<td>34.8</td>
</tr>
<tr>
<td>24 hrs</td>
<td>71.3</td>
<td>4.3</td>
<td>0.3</td>
<td>24.1</td>
</tr>
<tr>
<td><strong>SynMnO$_x$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 min</td>
<td>43.9</td>
<td>11.0</td>
<td>1.1</td>
<td>43.9</td>
</tr>
<tr>
<td>5 min</td>
<td>50.7</td>
<td>8.7</td>
<td>1.4</td>
<td>39.2</td>
</tr>
<tr>
<td>30 min</td>
<td>53.0</td>
<td>5.5</td>
<td>1.7</td>
<td>39.7</td>
</tr>
<tr>
<td>24 hrs</td>
<td>60.4</td>
<td>6.2</td>
<td>n.d.</td>
<td>33.4</td>
</tr>
</tbody>
</table>
Table 6. XPS high resolution Mn 3s multiplet splitting of MnO$_x$/C and MnO$_x$ batch experiments during the reaction with acetaminophen.

<table>
<thead>
<tr>
<th></th>
<th>MnO$_x$PAC</th>
<th></th>
<th>SynMnO$_x$</th>
<th></th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn 3s split</td>
<td>Mn oxidation state</td>
<td>Mn 3s split</td>
<td>Mn oxidation state</td>
<td>Mn 3s split</td>
</tr>
<tr>
<td>0 min</td>
<td>5.36</td>
<td>3.0</td>
<td>4.63</td>
<td>3.7</td>
<td>4.38</td>
</tr>
<tr>
<td>5 min</td>
<td>5.49</td>
<td>2.8</td>
<td>4.96</td>
<td>3.4</td>
<td>4.9</td>
</tr>
<tr>
<td>30 min</td>
<td>5.52</td>
<td>2.8</td>
<td>5.25</td>
<td>3.1</td>
<td>5.33</td>
</tr>
<tr>
<td>360 min</td>
<td>5.57</td>
<td>2.8</td>
<td></td>
<td></td>
<td>5.69</td>
</tr>
<tr>
<td>24 hrs</td>
<td>5.37</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

References:
- MnO$_2$: 4.38, 4.0
- Mn$_3$O$_4$: 4.9, 3.5
- Mn$_2$O$_3$: 5.33, 3.0
- MnO: 5.69, 2.0
Chapter 6

6. Conclusions and Implications

6.1. Overall Conclusions

The results from the experiments performed in this PhD dissertation contribute to a better understanding of organic-inorganic interactions affecting surface reactions. This dissertation provides essential insights on the effect of surface and structure of solid media on the reaction with aqueous contaminants by using advanced spectroscopy, microscopy and analytical chemistry tools.

Chapter 3 of this dissertation investigates the removal of BPA using synthesized (Syn-MnO₅) and commercial (Com-MnO₅) MnOₓ(s) media using the differences in their surficial properties as the basis of comparison. Surface characterization and kinetic modelling analyses indicate that the surface chemistry had a strong influence towards the BPA reaction. The lower effective BPA removal (71%) can be attributed to the presence of impurities (Al, Fe, and Si) and lower surface area of Com-MnO₅ compared to pure Syn-MnO₅ (99.9% BPA removal). Combination of BPA desorption studies and reacted solid analysis data suggested reduced Mn and adsorbed organic compounds on the MnOₓ(s) surface sites contributed to the decrease in long term BPA removal rates when compared to rapid initial oxidation rates. Results from the kinetic modeling suggest that BPA removal using Syn-MnO₅ is electron transfer limited while BPA reaction with Com-MnO₅ fit the surface complex formation limited model. As most studies utilize pure lab synthesized MnOₓ(s) for removal of emerging organic micropollutants such as BPA, the results of this research suggest that differences exist in the reaction mechanism between synthesized and commercial MnOₓ(s) media.
Results from Chapter 4 indicate that the U uptake in phosphonate functionalized electrospun polymers is inhibited by the presence of Ca and CO$_3$ in environmentally relevant conditions. Surface analysis using EXAFS, XPS and extraction experiments suggests that the mechanism of U uptake is inner-sphere complexation. The surface associated U-phosphonate species was identified as a mononuclear monodentate surface complexes with UO$_2$O$_6$ hexagonal bipyramidal on all the reacted mats. Similar U-surface binding characteristics was observed on all the reacted mats despite differences in aqueous U speciation. Thus, the surficial interaction of aqueous U species strongly influences the U uptake on the solid electrospun polymer, but similar surface associated U species are present for all the reaction conditions. The high stability of inner-sphere complexation and consistent surface binding mechanism for U-phosphonates is promising for the application of the phosphonate functionalized electrospun polymers towards U sensing or water treatment applications.

In chapter 5, electrochemically active MnO$_x$/C composites were synthesized for acetaminophen oxidation. The electrochemical behavior was investigated at environmental relevant conditions using cyclic voltammetry and aqueous experiments. Improved charge transfer in the MnO$_x$/C composite was observed due to increased capacitance from combination of faradaic processes of MnOx surface and double layer capacitance of the carbon support. The increase in peak current density for acetaminophen oxidation and higher acetaminophen removal with MnO$_x$/C composite when compared to undoped Carbon or pure MnOx indicates facile oxidation of acetaminophen on the MnO$_x$/C composites. Mechanistic insights from the cyclic voltammetry suggest that synergistic incorporation of MnO$_x$ on highly porous carbon resulted in higher oxidation of acetaminophen due to faster charge transfer.
6.2. Implications and future directions

This Ph.D. research contributes to the body of knowledge by improving the understanding of processes at the solid – liquid interface which affect the organic-inorganic reactions, contaminant removal and reactive media performance. The scientific information obtained from this dissertation, such as the identification of the contaminant associated with the solid surface, mechanism of removal and rate limiting step, is crucial towards proposing appropriate detection and remediation strategies for contaminated sites especially in rural communities with non-centralized potable water treatment system.

Results from Chapter 3 are relevant for the application of commercially available MnOx in removal of phenolic micropollutants in water treatment systems. The physicochemical differences between synthetic-MnOx and commercial-MnOx affect the observed variations in the interfacial interaction of these solids with BPA. Further investigations are necessary to elucidate the influence of mineral impurities and long-term reactivity of MnOx(s) media with environmental relevant organic concentrations to understand the fate and transport of these micropollutants and develop effective water treatment processes.

The identification of U surface complexes in Chapter 4 improves the understanding of U-phosphonate binding towards establishing the necessary framework for functionalized electrospun polymers to be applied as in-situ U sensors in environmental waters. Further studies are required to understand the influence of other competing metal oxides and co-occurring species such as organic matter on uranyl -phosphonate surface complexations.

Implications from the Chapter 5 are promising towards development of enhanced electro-catalysts using cost efficient and ubiquitous manganese oxide on carbon composites for electrochemical reactions such as oxidation of phenolic micropollutants at environmentally
relevant conditions. Additionally, the ability to detect and control the Mn oxidation state on the MnO$_x$/C composite surface using electrochemistry is a promising avenue towards developing optimal heterogenous catalysts for organic oxidation.

Further work is required with consideration of exact water chemistry of contaminated sites. This can be achieved by characterizing the real sites’ samples for co-occurring ions, oxides and organic matter. In addition to aqueous analysis, the solid media must be evaluated for surficial changes while in presence of competing compounds and complexants from real water systems. The spectroscopy and electrochemistry techniques used in this dissertation offers an important basis for these further studies of solid-liquid interactions. Thus, the knowledge gained from this dissertation is important towards understanding the organic-inorganic surficial interaction affecting metal reactivity with implications towards water treatment and sensor applications.
Appendix A

Supplementary Information for Chapter 3: Reaction of Bisphenol A with Synthetic and Commercial MnO\(_x\): Spectroscopic and Kinetic Study

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5 Department of Earth and Planetary Sciences, MSC03 2040, University of New Mexico, Albuquerque, New Mexico 87131, USA
**Table A7.** Summary of physical and chemical characteristics of MnO$_x$(s) media used in this study.

<table>
<thead>
<tr>
<th></th>
<th>Com-MnO$_x$</th>
<th>Syn-MnO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Specific surface area (m$^2$/g)</strong></td>
<td>13.6</td>
<td>128.3</td>
</tr>
<tr>
<td><strong>Elemental composition (%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>71.2</td>
<td>99.9 $^a$</td>
</tr>
<tr>
<td>Aluminum</td>
<td>9.65</td>
<td>-</td>
</tr>
<tr>
<td>Iron</td>
<td>8.97</td>
<td>-</td>
</tr>
<tr>
<td>Silicon</td>
<td>6.88</td>
<td>-</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.425</td>
<td>-</td>
</tr>
<tr>
<td>Barium</td>
<td>0.367</td>
<td>-</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.302</td>
<td>-</td>
</tr>
</tbody>
</table>

Specific surface area data from Multipoint – N$_2$ BET; Elemental composition data from X-ray Fluorescence (XRF); $^a$ data from SEM/EDS.
Table A8. Mn 3s multiplet splitting results for a) Reference Mn oxides and b) control and reacted samples. Curve 1 and curve 2 corresponds to the position/binding energy of $5^5$S and $7^7$S for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curve 1: Mn $5^5$S (eV)</th>
<th>Curve 2: Mn $7^7$S (eV)</th>
<th>Multiplet Splitting (eV)</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) References</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO; Mn(II)</td>
<td>89.10</td>
<td>83.40</td>
<td>5.69</td>
<td>2</td>
</tr>
<tr>
<td>Mn$_2$O$_3$; Mn(III)</td>
<td>88.52</td>
<td>83.20</td>
<td>5.33</td>
<td>3</td>
</tr>
<tr>
<td>Li Mn(III,IV)O</td>
<td>88.94</td>
<td>84.05</td>
<td>4.90</td>
<td>3.5</td>
</tr>
<tr>
<td>MnO$_2$; Mn(IV)</td>
<td>88.89</td>
<td>84.52</td>
<td>4.38</td>
<td>4</td>
</tr>
<tr>
<td>b) Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syn-MnO$_x$ Control</td>
<td>89.40</td>
<td>84.77</td>
<td>4.63</td>
<td>3.7</td>
</tr>
<tr>
<td>Syn-MnO$_x$ Reacted</td>
<td>89.27</td>
<td>84.45</td>
<td>4.82</td>
<td>3.5</td>
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<tr>
<td>Com-MnO$_x$ Control</td>
<td>87.04</td>
<td>82.57</td>
<td>4.47</td>
<td>3.9</td>
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<tr>
<td>Com-MnO$_x$ Reacted</td>
<td>87.93</td>
<td>83.25</td>
<td>4.68</td>
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Table A9. Percentage composition of oxygen species obtained from fitting high resolution XPS O 1s spectra. Uncertainty shown is standard deviation for triplicate data.

<table>
<thead>
<tr>
<th>BE-&gt;</th>
<th>529.6</th>
<th>531.2</th>
<th>532.5</th>
<th>533.7</th>
<th>535.0</th>
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<tbody>
<tr>
<td></td>
<td>MnOₓ</td>
<td>O=N-C/ C=O</td>
<td>-C-OH</td>
<td>C-O-C / COOH</td>
<td>C-O-O-C</td>
</tr>
<tr>
<td>Syn-MnOₓ Control</td>
<td>59.4 ± 3.8</td>
<td>19.4 ± 1.3</td>
<td>13.3 ± 1.2</td>
<td>7.9 ± 1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>Syn-MnOₓ Reacted</td>
<td>33.0 ± 1.4</td>
<td>23.3 ± 0.5</td>
<td>20.7 ± 0.1</td>
<td>17.7 ± 0.7</td>
<td>5.3 ± 0.6</td>
</tr>
<tr>
<td>Com-MnOₓ Control</td>
<td>17.2 ± 1.5</td>
<td>19.8 ± 0.2</td>
<td>28.4 ± 1.7</td>
<td>22.1 ± 1.3</td>
<td>12.5 ± 1.3</td>
</tr>
<tr>
<td>Com-MnOₓ Reacted</td>
<td>13.7 ± 0.4</td>
<td>14.0 ± 6.1</td>
<td>20.6 ± 4.1</td>
<td>30.0 ± 2.6</td>
<td>21.6 ± 8.0</td>
</tr>
</tbody>
</table>
Table A10. Percentage composition of carbon species obtained from fitting high resolution XPS C 1s spectra. Uncertainty shown is standard deviation for triplicate data.

<table>
<thead>
<tr>
<th>Binding Energy (eV) -</th>
<th>284.7</th>
<th>285.6</th>
<th>287.2</th>
<th>288.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Syn-MnO₅ Control</td>
<td>C-C/C=O</td>
<td>C*-C-Ox</td>
<td>C-OH</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>65.2 ± 3.3</td>
<td>4.4 ± 1.1</td>
<td>21.2 ± 3.1</td>
<td>9.2 ± 1.4</td>
</tr>
<tr>
<td>Syn-MnO₅ Reacted</td>
<td>63.4 ± 2.2</td>
<td>0.4 ± 0.3</td>
<td>26.6 ± 0.8</td>
<td>9.7 ± 1.6</td>
</tr>
<tr>
<td>Com-MnO₅ Control</td>
<td>34.7 ± 6.1</td>
<td>3.2 ± 0.3</td>
<td>33.0 ± 4.0</td>
<td>29.1 ± 9.7</td>
</tr>
<tr>
<td>Com-MnO₅ Reacted</td>
<td>26.4 ± 8.4</td>
<td>1.2 ± 0.04</td>
<td>40.9 ± 5.7</td>
<td>31.5 ± 2.6</td>
</tr>
</tbody>
</table>
Figure A16. Batch reactors (200mL) with corresponding reaction conditions used to for study of BPA removal with MnO$_x$(s).
Figure A17. Amount of BPA removed solely by adsorption onto (a) Syn-MnO$_x$ and (b) Com-MnO$_x$. The maximum adsorbed amount was calculated by extrapolating the data to time=0.
Figure A18. Fitting of O 1s XPS high resolution spectra for replicate samples of (a) Syn-MnO\textsubscript{x} Control (b) Syn-MnO\textsubscript{x} Reacted (c) Com-MnO\textsubscript{x} Control and (d) Com-MnO\textsubscript{x} Reacted. The sample XPS spectra are shown as the black dashed lines; the solid green lines are the overall contribution due to fitting of different individual oxygen bonds.
Figure A19. Fitting of C 1s XPS high resolution spectra for replicate samples of (a) Syn-MnO$_x$ Control (b) Syn-MnO$_x$ Reacted (c) Com-MnO$_x$ Control and (d) Com-MnO$_x$ Reacted. The sample XPS spectra are shown as the dashed black lines; the green solid lines are the overall contribution due to fitting of different individual carbon bonds.
Appendix B

Supplementary Information for Chapter 4: U(VI) Binding onto Phosphonate Functionalized Electrospun Polymers
Figure B20. Scanning electron micrographs showing the nanofibers for (a) HDPA+U (b) HDPA+U+Ca and (c) HDPA+U+CO3 reacted mats. (d) The histogram of nanofiber dimensions for HDPA-control analyzed by ImageJ on the SEM images.
**Figure B21.** ATR-FTIR spectra of the HDPA-PAN electrospun mats showing the main vibrational modes.
Figure B22. Surface Enhanced Raman Spectra (SERS) using carboxylated gold nanostars to enhance the U signal at 838 cm$^{-1}$ on HDPA mats.
Figure B23. U(VI) aqueous speciation from chemical equilibrium modelling using Visual Minteq to simulate the different reactors used in this study. The reaction conditions were 10 μM UO$_2^{2+}$, 10 μM NO$_3^{-}$ with additional (a) 5 mM Ca$^{2+}$ (b) 5mM HCO$_3^{-}$ and (c) 5 mM Ca$^{2+}$ + HCO$_3^{-}$.
Appendix C

Supplementary Information for Chapter 5: Electrochemically active MnO\textsubscript{x}-C composites for Removal of Phenolic Micropollutants
Figure C24. Manganese release into solution in batch experiments by MnO\(_x\)/C composite
Figure C25. (a) Cyclic voltammetry of all the carbon and MnO$_x$/C composites used in this study (b) Capacitance of the different media calculated from the cyclic voltammetry plots.
Figure C26. Relationship between capacitance and scan rates for MnO$_x$/C composites and carbon supports.
Figure C27. (a) Cyclic voltammogram of oxidation of 0.5 mM Acetaminophen on MnOx-PAC composite (b) Correlation between peak current from oxidation of acetaminophen vs. scan rate for MnOx/PAC and PAC
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