SynThesis, Characterization, And Functional Evaluation Of Nanocomposites For Water Purification

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SYNTHESIS, CHARACTERIZATION, AND FUNCTIONAL EVALUATION 
OF NANOCOMPOSITES FOR WATER PURIFICATION

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Dedication

To my parents for always pushing and supporting me.

To my sister for always believing in me.

To my brother for showing me that achieving your goals is possible.

To the rest of my family

To my friends for always being there.

To Dr. Noveron for his mentorship and advice and who never gave up on me and pushed me towards the end.

To the professors who helped me along the way, especially Dr. Gardea-Torresdey for his support and reinforcement.

Finally, and most importantly to Veronica for the love that has gotten me through this process and my chiquinina Kaitlin for being my major motivation.
SYNTHESIS, CHARACTERIZATION, AND FUNCTIONAL EVALUATION OF NANOCOMPOSITES FOR WATER PURIFICATION

by

JULIO EDUARDO PADILLA, B.S. in Chemistry

DISSERTATION

Presented to the Faculty of the Graduate School of The University of Texas at El Paso in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

Department of Chemistry

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Abstract

The United Nations estimate that around 780 million people do not have access to clean and safe water and around 2.5 billion people do not have proper water sanitation. As a result, around 6–8 million people die each year due to water related diseases, such as cholera and dysentery, and disasters. As population increases the water problem will become more difficult to solve. Furthermore, climate change threatens to intensify water scarcity. The design of functional materials at the nanoscale offer unique solutions in molecular sorbents and catalytic systems that can develop into cost-effective solutions in water treatment by reducing the cost of the materials used and/or the energy consumption of the process. In this dissertation, the design, synthesis, characterization, and evaluation of function of nanocomposites is presented for (1) the efficient electrochemical generation of reactive oxygen species (ROS) for water treatment and sanitation using a novel composite of benzoyl-functionalized cotton cellulose and multiwalled carbon nanotubes (FC-MWCNT), and (2) a water permeable hydrogel with hyperactive metallic copper nanoparticles (NPs).

The new FC-MWCNT nanocomposite, which utilizes functionalized cotton cellulose as a high-surface area support for pristine multi-walled carbon nanotubes, was characterized via scanning electron microscopy, infrared spectroscopy, thermographic analysis, Brunauer-Emmett-Teller surface area analysis, and cyclic voltammetry, exhibits high surface area (40 m²/g) and efficient electrocatalytic properties toward hydrogen peroxide. Furthermore, they were successfully applied toward the electrochemical degradation of methyl orange using only a -1.0 V potential, with optimal conditions at pH 3, 2.7 mM KCl, 0.219 M NaCl, in a treatment time of 4 minutes.

The Cu-NPs nanocomposite, characterized by transmission electron microscopy, electron paramagnetic spectroscopy, energy-dispersive X-ray spectroscopy, dynamic light scattering, and inductively-coupled plasma-optical emission spectroscopy, were capable of chemoadsorbing arsenate, with a capacity of 5.3 g of As per gram of nanocomposite, and mineralizing it in large
quantities out of water with little to no Cu leakage. By first coordinating Cu (II) ions to polymers capable of photopolymerizing into hydrogels, then reducing the ions to Cu (0), we were able to produce well dispersed, highly active Cu NPs that are capable of chemoabsorbing up to 90% of Arsenic from water in a wide range of pH levels.

The development of functional nanocomposite materials offer new, more efficient methods for the purification of water. FC-MWCNT were synthesized and were capable of electrochemically degrading methyl orange. Furthermore, highly active Cu NPs dispersed and sequestered throughout water-permeable hydrogels were also synthesized and successfully removed 90% of As at a wide pH range.
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Chapter 1: Introduction

The United Nations estimate that around 780 million people do not have access to clean and safe water and around 2.5 billion people do not have proper water sanitation. As a result, around 6–8 million people die each year due to water related diseases and disasters [1]. As population increases the water problem will become more difficult to solve. Furthermore, climate change threatens to intensify water scarcity.

Anthropogenic water pollution caused by industrial, domestic and environmental influences is a major global problem. It is estimated that 300–500 million tons of heavy metals, solvents, and other waste are released into the world's water supplies each year by industrial effluents [2]. Geogenic derived water contamination is also a major concern in countries such as Bangladesh, India, and Nepal. In these countries, arsenic contamination is a serious issue due to the weathering of rocks that naturally contain arsenic [3-7]. Additionally, as global populations continue to grow so does the demand on our water supplies which will undoubtedly lead to increased pollution.

The use of nanotechnology has been increasingly investigated over the last ten years as a possible replacement for traditional treatment methods in order to deliver clean water at a lower cost while meeting increasingly stricter water quality standards [8]. Although there has been discord over the exact definitions of ‘nano-scale’ and ‘nano-material’, the Joint Research Centre (JCR) of the European Commission published a report highlighting the international range of definitions in 2010 [9]. Nanoscale has been defined as 200 nm by some groups, while other organizations used 100 nm. In October 2011, the European Commission adopted the following definition of ‘nano-material’ for regulatory purposes [10];

“A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions are in the size range 1 nm – 100 nm.”
It is well known that nano-materials exhibit different physical, chemical and biological characteristics when compared to their larger, micro- and macro-scale counterparts (<100 nm) [9, 11-14]. Not only do nano-materials have a larger surface area to volume ratio, which consequently leads to a higher density of surface reaction sites per unit mass, but they also display a higher reactivity for surface mediated processes due to the greater surface free-energy. Nano-materials potentially represent a more efficient alternative to current materials used for water treatment.  

However, there exists a possibility of accidental release of nano-materials such as nanoparticles (NPs) and there is relatively little known about the long-term ecotoxicological effects of freely dispersed NPs in the environment [15]. Since remediation methods need to have non-toxic components providing long term and stable removal mechanisms, it is challenging to establish whether this technology, as it currently exists, can be safely applied. There exists a great need for more fundamental research into nano-toxicology and NP behavior in environmental systems.  

It is important that while removing one type of contaminant we do not introduce another. To avoid the introduction of NPs to the environment it would be beneficial to develop a remediation method that utilizes the reactivity of NPs while avoiding the release of free NPs into the environment. One possible method is to develop a ‘nano-composite’, a product defined as, “A multiphase material where at least one of the constituent phases has one dimension less than 100 nm [16].”

**Nanocomposites**

Recent research has led to the development of a multitude of different variations of nanocomposite, where usually the NPs are combined with a micro- or macro-scale support material. In such complexes the nano-reactivity is retained and complemented by the properties of the accompanying material. A type of composite under investigation is static nano-composites for use in fixed bed reactors, filter columns, permeable reactive barriers and domestic filters. These micro-
to macro-scale structures avoid the problems of the free NPs and represent a potential solution by delivering nano-reactivity within a controlled zone and without uncontrolled release of NPs as they are efficiently anchored onto the support structure. Table 1.1 lists the three types of static nano-composites; membranes/sheets, beads and three dimensional porous structures along with their advantages and disadvantages [17].

Table 1.1: A summary of the three general types of static nano-composites and their advantages and disadvantages.

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>· Builds on current membrane technology for water treatment</td>
<td>· High water pressures can cause membrane to rupture, releasing NPs and contaminants into water system.</td>
</tr>
<tr>
<td></td>
<td>· Keeps conventional size exclusion properties.</td>
<td>· Cannot be recycled or reused</td>
</tr>
<tr>
<td>Beads</td>
<td>· Can be easily incorporated into existing infrastructure (e.g. column filters).</td>
<td>· Reactive material within the core of the bead structure does not come into contact with water and contaminants.</td>
</tr>
<tr>
<td></td>
<td>· Water flux can be tailored by altering bead size and packing density.</td>
<td>· Water must flow through channels between beads which generates a high back-flow resistance.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>· Cannot be cheaply recycled or reused without expensive processing</td>
</tr>
<tr>
<td>Porous 3D structures</td>
<td>· Avoids limitations of membranes and beads.</td>
<td>· Relatively little research has gone into developing such materials.</td>
</tr>
</tbody>
</table>
Membrane filtration traditionally utilizes size-exclusion based filters that physically prevent harmful microbes or particles from passing through. However, recently they have been improved by incorporating reactive functional groups into the pores and, most recently, NPs. Due to the membranes relatively large pore sizes (50–200 nm) and open structures integrating NPs into porous micro-filtration membranes has attracted attention for remediation applications [18]. These properties are important because they allow the immobilized NPs contained within the membrane to be freely accessible for reaction with the aqueous contaminants.

Bulk nano-composites also come in the form of micro- or macro-scale beads or particulates. Beads may be employed in static treatment systems like filter columns as well as permeable reactive barriers. The key advantage of these spherical nano-composites is that they can

\begin{itemize}
  \item Size and shape can be tailored to existing infrastructure and flow rate requirements
  \item Good capacity for recycling and reusing the substrate material
\end{itemize}
be incorporated into existing technology. Multiple studies have demonstrated the effectiveness of introducing iron into traditional sand filter column systems [19-23]. By substituting the sand and bulk iron with nano-composite beads, reactivity could be further improved due to the increase in active surface area.

The incorporation of NPs into 3D porous, continuous, bulk structures, in theory, limits unreactive volumes and the large structure can be applied to previously established infrastructure such as column filters and permeable reactive barriers. However, when compared to the large amount of membrane and bead nano-composites there is relatively little literature covering this topic, some which include polymers [24,25], graphene [26], carbon [27], and chitosan [28].

**Electrochemical advanced oxidation processes**

Industrial waste usually contains a mixture of organic and inorganic compounds which makes it particularly difficult to apply a universal strategy of reclamation that mainly depends on the nature and concentration of pollutants. Biological oxidation is the cheapest process for the treatment of effluents polluted with organic compounds, but the presence of toxic or biorefractory molecules hinders this approach [29]. The traditional incineration method, if the treatment conditions are not controlled poses problems of emission, and above all, it can be conveniently applied only for concentrated solutions. Chemical oxidation using chlorine, ozone, or hydrogen peroxide is currently used for the treatment of biorefractory contaminants to decompose them into harmless or biodegradable products. However, in some reactions, the intermediate products persist in the solution which may be of similar or even higher toxicity than the original compounds. In these cases, the pollutants can be removed using a special class of oxidation technique known as advanced oxidation processes (AOPs). AOPs can be generally defined as aqueous phase oxidation methods based on the production of highly reactive species (primarily but not exclusively) in the mechanisms leading to the destruction of the target pollutant [30].
The hydroxyl radical (•OH) is a potent oxidant which is able to non-selectively degrade most organic and organometallic contaminants until their complete mineralization into CO₂, water, and inorganic ions. A large number of non-photochemical and photochemical AOP methods have been developed. The AOPs have been effectively applied mainly for the treatment of wastewaters, but they are also used in many fields including groundwater treatment, soil remediation, municipal wastewater sludge conditioning, as well as odor and taste removal from drinking water.

In recent years, new AOPs based on the electrochemical technology (EAOPs) have been developed [31-35]. EAOPs have several advantages for the remediation of pollution problems because the electron is a clean reagent. They also possess other advantages which comprise of high energy efficiency, flexibility to automation, easy handling because of the simple equipment required, safety because they operate under mild conditions (room temperature and pressure), and adaptability because they can be applied to effluents with chemical oxygen demand (COD) in the range of 0.01 to 100 g/L. Figure 1.2 shows the applicability based on the organic load of different water treatment technologies, as well as that EAOPs exhibit the widest range compared to other systems [30].
EAOPs include anodic oxidation (AO), where heterogeneous hydroxyl radicals (•OH) are generated at the anode surface, as well as electro-Fenton (EF), photoelectro-Fenton (PEF), and sonochemistry (SE), in which homogeneous •OH are produced in the bulk solution [29]. There have been a large number of publications on EAOPs due to very good results obtained in laboratory-scale tests, but their real-world application for the treatment of organic pollutants has been deficient. Recent investigations that have enhanced the electrocatalytic activity and stability of electrode materials, causing EAOPs to reach an advanced stage of development and, recently, some pilot-scale or full-scale plants have been effectively applied commercially for the disinfection and purification of wastewater polluted with organic compounds.
Research Aims

The aim of the first part of this research was to produce a low-cost, high surface area nanocomposite composed of cheap biomass (cotton) and carbon nanotubes CNT, which possess outstanding electrical properties, for the electrochemical treatment of industrial wastewater which is based on the production of \( \cdot \text{OH} \) and other oxidants, such as chlorine, using only water, salt, and low energy.

Encapsulated Metal Nanoparticles

Development of organic–inorganic nanocomposites, often achieved by incorporating inorganic particles onto synthetic polymers by adding NPs into polymer matrices, is intended to produce composite materials with improved mechanical and other properties. Inorganic nanoparticles and organic polymers represent a new class of materials called nanocomposites that exhibit improved performance when compared with their microparticle counterparts [36].

Polymer matrices reinforced with inorganic nanoparticles combine the functionalities of polymer matrices, which include low weight and easy formability, with the unique features of the inorganic nanoparticles. The nanocomposites created by combination of these types of materials can lead to improvements in several properties, such as optical, mechanical, electrical, magnetic, rheological, and fire retardancy properties [37, 38]. However, the nanoparticles have a strong tendency to undergo agglomeration followed by insufficient dispersal in the polymer matrix, degrading the optical and mechanical properties of the nanocomposites [39, 40]. To improve the dispersion stability of nanoparticles in aqueous media or polymer matrices, it is essential that the particle surface modification involving polymer surfactant molecules or other modifiers generates a strong repulsion between NPs or that the polymer itself can act as a buffer zone between the NPs preventing agglomeration.

The polymerization processes, which may include radical, anionic and cationic polymerization methods, involves propagation of the grafted polymers from the surface of the
particle. Surface modification of nanosized alumina particles was carried out by grafting polystyrene and polyacrylamide (PAAM) on the particles [41]. Wang et al. [42] reported the synthesis of poly(methyl methacrylate)-grafted TiO$_2$ nanoparticles by a photocatalytic polymerization process.

Nanogels are internally cross-linked particles of sub-micrometer size made of hydrophilic polymers [43] and are considered to be a distinct type of macromolecule, compared to linear and branched polymers or macroscopic gels [44]. Such structures, along with their bigger analogues—microgels—have been tested for various practical applications, starting from fillers in a coating industry to “smart” drug delivery systems [45]. Nanogels from hydrophilic polymer matrices are crosslinked by several methods. One method is physical crosslinking, such as hydrogen bonds, crystallized domains, hydrophobic interactions and temperature-induced sol-gel transition. These physically crosslinked gels can reversibly degrade into the corresponding precursors upon external stimuli. Another method involves chemical crosslinking in the presence of various crosslinkers. However, the chemical method had a few problems, including toxicity and an elimination of catalysts after a reaction [46]. In this study, UV radiation technology was used for the gel preparation, as this method is capable of sterilization and crosslinking simultaneously. The radiation-induced nanogels can be synthesized using the following two methods: inter-molecular and intra-molecular crosslinking of a linear-chain polymer by radiation [47, 48]. The radiation-induced synthesis of nanogels is initiated by irradiation of a dilute polymer solution. Reactive radical intermediates are formed by this process in the polymer chains. These can then recombine via inter- or intra-molecular crosslinking [49]. As a result, gels are produced from intra-molecular recombination of the radicals.

**Research Aims**

The aim of this project was to synthesize these nanocomposite, permeable materials that are synthesized by complexing metal ions within photopolymerized solvogels and then reducing the ions to yield gel encapsulated nanoparticles (GENs). The potential for GENs is great due to
the combination of the desirable physical and chemical properties of the encapsulated nanoparticles with the surface area and sequestration properties of the gels.

**Research Summary**

First, chapter two discusses the synthesis of benzoyl-functionalized cotton cellulose via esterification of the hydroxyl groups is discussed followed by its complexation with multi-walled carbon nanotubes forming a high-surface area nanocomposite. Then, characterization of the nanocomposite via electron microscopy, infrared spectroscopy, thermographic analysis, Brunauer-Emmett-Teller surface area analysis, and cyclic voltammetry verifying functionalization, structure, and electrochemical properties is discussed. Chapter three then explores the application of the nanocomposite as the active electrode for the electrochemical degradation of organic pollutants, an electrochemical advanced oxidation process.

In chapter four, the synthesis of a nanocomposite of copper nanoparticles encapsulated in a, radically polymerized tetra(ethylene glycol) diacrylate/acrylic acid, hydrogel is discussed. The transmission electron microscopy, X-ray diffraction, electron paramagnetic resonance spectroscopy, energy-dispersive X-ray spectroscopy, dynamic light scattering, and characterization of the nanocomposite gel is also discussed. Finally, the inductively coupled plasma-optical emission spectroscopy data from bulk chemoabsorption of arsenic experiments performed is presented.
Chapter 2: Synthesis and Characterization of Functionalized Cotton-supported Pristine Multi-walled Carbon Nanotubes

INTRODUCTION

Carbon nanotubes (CNTs) have garnered much attention since their discovery by Iijima in 1991 [1], along with single walled carbon nanotubes (SWCNTs) in 1993 [2] due to their unique structural, mechanical, and electronic properties. Some of these properties include high chemical and thermal stability, high elasticity, and high tensile strength, along with some tubes displaying metallic conductivity [1]. Because of their small size and conductivity they have been proposed as molecular wires in molecular electronics [3] and electrodes [4,5]. For example, Britto et al. reported CNT’s electrochemical properties using a paste of multiwall carbon nanotubes (MWCNT) in bromoform and packing it into a glass tube in order to investigate the oxidation of dopamine [6] and showed the near ideal reversible two electron redox process for dopamine which had previously showed irreversible electrochemistry. Compared to graphite electrodes, the nanotube array electrode oxidized dopamine at a low potential and at a much faster rate demonstrating the unique features of CNTs could be extended to include electrocatalysis. Since this study, CNTs have been shown to be superior to other electrode materials [7-10].

Although modified CNTs can be easily dispersed in organic solvents, they tend to aggregate irreversibly in a short period of time because of Van der Waals interactions between the side walls. In order to avoid agglomeration, several approaches have been developed such as using surfactants, ionic liquids, chemical functionalization, and polymer wrapping [11,12]. Polymer wrapping was employed using commercially purchased cotton functionalized with an aromatic group in order to bind MWCNTs via \(\pi-\pi\) interactions. Cotton makes for an ideal support due to its ease of functionalization as well as its high-surface area available for MWCNT wrapping. Herein, we report that benzoyl-functionalized cotton cellulose fibers bind CNT via \(\pi-\pi\)-stacking interactions to generate a high-surface area electrode. Although several successful CNT composites have been reported, employing both covalent interactions such as chitosan grafted CNT composites, and non-covalent interactions such as blending, layer-by-layer self-assembly,
surface-deposition and crosslinking sol-gel, and electrochemical deposition, on the surface of nanotubes, most of these techniques modify the surface of the CNTs, thereby changing the targeted electrical properties of the CNTs. Wu et al. synthesized a chitosan-grafted MWCNT composite by covalently grafting chitosan onto the surfaces of MWCNT. They reported excellent electrocatalytic ability of the composite modified electrode towards hydrogen peroxide and suggested its application to the development of oxidase-based amperometric biosensors [13]. Following their experimental procedure, FC-MWCNT was fitted onto an FTO electrode which then revealed, using cyclic voltammetry, 10x more catalytic activity compared to chitosan grafted MWCNT electrode.

This chapter reports that benzoyl-functionalized cotton cellulose fibers interact with CNT via \( \pi-\pi \)-stacking interactions to generate a high-surface area electrode. The nanocomposite was characterized via electron microscopy, infrared spectroscopy, thermographic analysis, Brunauer-Emmett-Teller surface area analysis, and cyclic voltammetry.

**MATERIALS**

The chemicals were purchased and all used as received without further purification. The MWCNT were purchased from Sigma-Aldrich and have a length of 0.1-10 µm, an outer diameter of 10-15 nm, and an inner diameter of 2-6 nm. All other reagents were commercially available and of analytical grade. Electrochemical measurements were performed in phosphate buffer (0.1 M, pH 7.4) which was employed as supporting electrolyte.

**FUNCTIONALIZATION OF COTTON WITH BENZOYL CHLORIDE**

In a roundbottom flask, 1.00 g of cotton (5.56 mmol) was placed in 200 mL of dimethyl formamide. While stirring, ten equivalents of trimethylamine (5.628 g, 55.6 mmol) were added followed by the slow, dropwise addition of ten equivalents of benzoyl chloride (7.819 g, 55.6 mmol) to the reaction mixture and set to reflux for 48 hrs. After 48 hours, the mixture was allowed to cool down then was filtered via vacuum filtration and washed 3 times with 100 mL of water.
then, 3 times with 20 mL of ether. The reaction is depicted in scheme 1. The dried product was quantitative and was collected for complexation with MWCNTs.

Scheme 2.1. Benzylation of hydroxyl groups in cellulose contained in cotton.

**SYNTHESIS OF FUNCTIONALIZED COTTON/MWCNTS COMPOSITE**

In order to test the dependence of the loading ratio of MWCNTs to the functionalized cotton, four different CNT loadings were used: 5, 25, 50 mg of MWCNTs were added to 25 mg of functionalized cotton. The respective amounts of CNTs were added to 15 mL solution of 10% TritonX in a 20 mL scintillation vial and sonicated in an 85°C water bath for 20 minutes. Then 25 mg of functionalized cotton was added to each vial and sonicated in the hot bath for an additional 20 minutes. After sonication, the dispersion was left stirring overnight. Then, the dispersion was vacuum filtered and washed with DI water until no surfactant was detected in the filtrate, the composite was then washed with 20 mL of ether and allowed to dry in the funnel. The dry composite was then ground in a mortar with a pestle along with 25 mg of KBr to facilitate the grinding. After the composite was ground to a fine powder, 25 mL of water was added and subsequently vacuum filtered and washed again with water and ether in order to remove the KBr and allowed to dry. The final composites were then collected for characterization and electrode preparation.
Preparation of FC-MCWNTElectrodes

In order to construct a FC-MWCNT modified electrode, 10 mg of each of the FC-MWCNT composites were dispersed in 1 mL of dichloromethane, deposited onto a silver adhesive-coated, fluoride doped tin oxide glass, and annealed at 150°C under vacuum for 18 hrs.

Instruments

The S-3400N Type II scanning electron microscope was manufactured by Hitachi High-Technologies Corp., (www.hitachi-hta.com), Pleasanton, CA. TA instruments Q50 analyzer was used for thermogravimetric analyses at a heating range of 10°C per minute under a nitrogen purge gas flow of 40 mL per minute. Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used for nitrogen adsorption isotherms. Samples were weighed and heated at 150°C and evacuated at 10mmTorr for 12 hours. After evacuation, nitrogen isotherms were obtained volumetrically at 77 K. The obtained data was fitted into the Brunauer-Emmett-Teller (BET) equation to determine the surface area. Electrochemical analysis was performed using a CHI760D Potentiostat with Pt mesh auxiliary electrode and Ag/Ag+ (AgCl) reference electrode.

Results and Discussion

This study aimed at binding homogeneously dispersed MWCNT on the surface of high surface area cotton polymer resulting in a conductive, high-surface area composite. Since MWCNTs could not be bound to crude cotton due to the lack of attractive forces between the two. Cotton was first functionalized with a benzoyl group via an esterification reaction with benzoyl chloride providing cotton with sites to bind MWCNT via π-π-stacking.

Fourier Transform Infrared Spectroscopy

The FTIR spectra of crude cotton, along with functionalized cotton (F-Cotton), and functionalized cotton-multiwalled carbon nanotubes (FC-MWCNT) is shown in Figure 1.1. The unfunctionalized cotton spectra, as expected, showed absorbance at around 3300 and 2900 cm⁻¹ which correspond to O-H and C-H stretching frequencies, respectively [14]. The same absorbance appeared for both the F-Cotton and FC-MWCNT which indicated that not all of the –OH groups
of the cellulose were functionalized. However, after functionalization, a new peak at around 1700 cm\(^{-1}\) appeared for F-Cotton corresponding to the C=O stretch of an ester, which was also present, as expected, in FC-MWCNT [15].
Scanning Electron Microscopy

In order to elucidate the effect of different MWCNT loadings on the F-Cotton, a 1:5 (5:25 mg), 1:1 (25:25 mg), and 1:2 (25:50 mg) F-Cotton to MWCNT ratios by weight were prepared. As illustrated in Fig. 2.2, SEM revealed MWCNTs completely covering the surface of the F-Cotton in all three ratios. In contrast, the control cotton, which was left unfunctionalized, was unable to bind the CNTs. This indicates that the benzyl groups allow the fibers to bind the CNTs via π-π-stacking resulting in an interconnected blanket of dispersed MWCNT tightly bound on the surface of the cotton fibers.

Figure 2.2: SEM images of as is (top left), and functionalized cotton (top right) to MWCNT 1:1; and FC:MWCNT ratios of 5:1 (bottom left), and 1:2 (bottom right).
However, the 5:1 loading has a significantly less amount of MWCNTs complexed with the functionalized cotton compared to the 1:1 and 1:2 loadings. SEM also confirmed that as the MWCNT loadings were increased, the FC coverage by the MWCNT increased. In order to determine the % MWCNT coverage, thermogravimetric analysis was employed.

**Thermogravimetric Analysis**

Figure 2.3 shows the thermographic analysis of both the F-Cotton and the FC-MWCNT. The results indicate an onset temperature of 300 °C indicative of the decomposition of cellulose in both samples, as expected. The F-Cotton lost about 80% of its composition between 300 and 390 °C and another 5% between 390 and 550 °C. The FC-MWCNT only lost about 60% of its weight between 300 and 355 °C and another 5% between 355 and 550 °C.

![Thermogravimetric Analysis graph](image)

Figure 2.3: Thermographic analysis of FC-MWCNT (red), and F-Cotton (blue) ran from RT to 550°C under N₂ atmosphere 20°C min⁻¹
The difference in the weight lost by the two samples can be attributed to the 20% by weight MWCNT composition of the FC-MWCNT. Although the sample was initially produced by adding a 1:1 ratio (25 mg) of MWCNT to F-Cotton, TGA results revealed that only 40% (~10 mg) of the added MWCNT was actually bound to the F-Cotton.

**Brunauer–Emmett–Teller Analysis**

In order to investigate the surface area of the composite material, BET analysis was carried out. The surface area measurement of carbon nanotubes is most commonly based upon N$_2$ gas adsorption. The BET (Brunauer–Emmett–Teller) model was developed in 1938, and it is applied to isothermal N$_2$ adsorption measured at 77 K [16]. Figure 2.4 shows the isotherms obtained from the N$_2$ adsorption experiments. As shown in Table 1 the F-Cotton has a BET surface area of 0.2674 m$^2$/g, while the addition of MWCNT on the surface of the F-Cotton increased the surface area to 40.5287 m$^2$/g. The BJH adsorption cumulative volumes of the pores were 0.002244 and 0.106731 cm$^3$/g for the F-Cotton and FC-MWCNT respectively.

![Figure 2.4: BET Isotherms of F-Cotton (left) and FC-MWCNT (right). Samples were evacuated at 100°C for 12 Hrs. N$_2$ Isotherm obtained at 77 K.](image-url)
Table 2.1: BET surface area analysis results

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>BJH Adsorption cumulative volume of pores (cm²/g)</th>
<th>BJH Adsorption average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-Cotton</td>
<td>0.2674</td>
<td>0.002244</td>
<td>83.150</td>
</tr>
<tr>
<td>FC-MWCNT</td>
<td>40.5287</td>
<td>0.106731</td>
<td>69.585</td>
</tr>
</tbody>
</table>

**Electrochemical Analysis**

For the first set of electrochemical measurements, the composites with varying loadings of MWCNT increasing from 5.0 mg to 50.0 mg were tested all while maintaining the concentration of H₂O₂ constant throughout the experiments. Figure 2.5 shows that a multiple electron reduction was observed at -0.424 V and a multi-electron oxidation was observed at 0.241 V for the 5.0 mg electrode. When using the 25.0 mg, a reduction at -0.671 V and an oxidation at 0.303 V were observed. Finally, for the 50.0 mg electrode Epc = -0.898 V and Epa = 0.564 V. A constant increase in current intensity was observed as the ratio of the carbon nanotubes to functionalized cotton was increased.
Figure 2.5: Cyclic Voltammograms of FC-MWCNT with weight ratios (FC:MWCNT mg) 5:1 (blue), 1:1 (orange), and 1:2 (red) electrodes in phosphate buffer (pH 7) with 10 mM H₂O₂.

During the second set of measurements the 25.0 mg loading of carbon nanotubes was used, while the concentration of H₂O₂ was gradually increased 0.1 M at a time, from 0.1 M to 0.5 M. Figure 2.6 reveals that an oxidation was observed at 0.887 V, while a reduction appeared at -1.176 V for the first measurement. For the 0.2 M concentration, the oxidation was observed at 0.979 V and -1.187 V for the reduction. For the final measurement of 0.3 M, the oxidation and the reduction appeared at 0.997 V and -1.202 V, respectively. When trying to further increase the concentration
of H₂O₂, the hydrogen evolved caused interference with the measurement. The current intensity increased from the first run to the second one, but there was minimal change from the second run to the third.

Figure 2.6: Cyclic Voltammograms of 1:1 (mg:mg) FC:MWCNT electrode with 0.1 M (blue), 0.2 M (orange), and 0.3 M (red) H₂O₂ concentration in phosphate buffer (pH 7).
CONCLUSIONS

A novel cotton-CNT composite is reported by phenyl functionalized cotton fibers and MWCNT. FTIR spectroscopy, indicated that cotton fibers were functionalized with phenylester groups with 20% coverage by weight. SEM revealed a web-like coating of the cotton fibers with the MWCNT which resulted in a highly conductive, high surface area nanocomposite. The FC-MWCNT was deposited on a FTO plate electrode and, using cyclic voltammetry, exhibited excellent electrical conductivity properties and it was shown to have excellent electrocatalytic ability towards H₂O₂.
Introduction

The textile and printing industry are known to release large volumes of dyes-contained wastewater. Azo dyes are among the most important materials since it constitutes about 50–70% of the world dye production [1] and [2]. These dye effluents are characterized by intense color, high organic content as well as stable chemical structures due to the existence of azo groups. Furthermore, they are toxic and recalcitrant to biodegradation; therefore, they are regarded as a serious risks for environmental pollution [3] and [4].

Advanced oxidation processes (AOPs) have been proposed as an efficient alternative for the treatment of wastewater containing toxic or refractory organic pollutants. Several processes such as Fenton oxidation, ozonation, wet air oxidation, and electrochemical oxidation have been investigated [5], [6] and [7]. Among these AOPs, electrochemical oxidation has been a promising area due to its high efficiency and environmental compatibility [8], [9] and [10].

Materials that function as anodes play a significant role on the electrochemical degradation of organic pollutants. The requirements for an ideal anode material include reasonable efficiency, cost-effectiveness, and stability even in extreme conditions. Numerous anodes have been tested and evaluated for dye wastewater treatment, including ACF [11], Pt [12] and [13], boron-doped diamond (BDD) [14], [15], [16], [17] and [18], PbO₂ [19], and mixed metal oxide (MMO) (e.g., RuO₂, TiO₂, IrO₂) [20]. Therefore, since the FC-MWCNT showed promising electrocatalytic activity, its application as an anode for the electrochemical degradation of methyl orange was investigated.

Solution pH is a key factor for wastewater treatment. There are many reports on the influence of solution pH on anodic oxidation, but the results are diverse and even contradictory due to different experimental conditions such as organic structures and electrode materials [15],
The color of MO solution is observed in red below pH 3 and in yellow above pH 4.5. Generally, a quinoid structure is the main chemical structure at low pH values while the azo structure predominates at high pH values. Therefore, different electrocatalytic degradation performances are anticipated due to the dependence of MO structure with solution pH.

This chapter describes that benzoyl-functionalized cotton cellulose fibers that interact with CNT via π-π-stacking interactions to generate a high-surface area electrodes efficiently produce reactive oxygen species (ROS). Terephthalic acid was used as an indicator of the electrochemical generation of ROS. Methyl orange was degraded using ROS and the pH and electrolyte concentration effect was investigated.

**Materials**

The chemicals were purchased and all used as received without further purification. The MWCNT were purchased from Sigma-Aldrich and have a length of 0.1-10 µm, an outer diameter of 10-15 nm, and an inner diameter of 2-6 nm. All other reagents were commercially available and of analytical grade. Bulk electrolysis measurements were performed in phosphate buffer (0.1 M, pH 7.4) which was employed as supporting electrolyte. NaCl was added in electrolyte dependence measurements and the pH was adjusted using HCl or NaOH for the pH dependence measurements.

**Preparation of the FC-MWCNT Electrode**

In order to construct a FC-MWCNT modified electrode, 10 mg of the 1:1 by weight ratio FC-MWCNT composite were dispersed in 1 mL of dichloromethane, deposited onto a silver adhesive-coated, fluoride doped tin oxide glass, and annealed at 150° C under vacuum for 18 hrs.

**Instruments**

Electrochemical bulk electrolysis was performed using a CHI760D Potentiostat with Pt mesh auxiliary electrode and Ag/Ag+ (AgCl) reference electrode. UV/Visible spectroscopy was performed using an Agilent Cary 50 Conc UV-Visible Spectrophotometer using a quartz cuvette of path length 10 mm.
**Bulk Electrolysis of Methyl Orange**

Firstly, the predicted capability of the FC-MWCNT electrode to efficiently degrade MO was tested on a 25 mg/L, pH 7.4, 0.1 M phosphate buffered MO solution. A bulk electrolysis experiment was performed with a -1.0 V potential applied to the solution. The results of the time-dependent kinetics were tracked via UV-Vis spectrometry and are shown in figure 3.1.

Dye concentration was determined using UV-Vis spectrophotometry at the maximum visible wavelength between 450 to 500 nm depending on pH. The degradation percentage was determined by the change of absorbance using the following formula,

\[
\% \text{ Degradation} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\]

where \(A_0\) and \(A_t\) is the absorbance of MO at the initial and the given time, respectively.

Aliquots were taken every 15 minutes and the MO concentration was measured. The UV-Vis spectra showed absorbance at 260 and 450 nm. The results show an immediate decrease in absorbance in both peaks which indicates the degradation of MO by electrolysis with a 96% degradation, following the decrease of the 450 nm peak, occurring after 90 minutes. This confirmed the application of the FC-WWCNT as an efficient electrochemical electrode capable of degrading MO.
Figure 3.1: UV-Vis spectroscopy kinetics of the electrochemical degradation of MO. Conditions: -1.0 V applied potential, 25.0 mg/L MO, 0.1 M Phosphate buffer.
pH Effect on Methyl Orange Degradation

The color of MO solution is observed as red below pH 3 and as yellow above pH 4.5. Generally, a quinoid structure is the main chemical structure at low pH values while the azo structure predominates at high pH values. Therefore, different electrocatalytic degradation performances are anticipated due to the dependence of MO structure, depicted in fig. 3.2, with solution pH.

![Yellow form of methyl orange](image1)

![Red form of methyl orange](image2)

Figure 3.2: Structures of MO with changing pH

The pH effect on the electrochemical degradation of MO is shown in Fig. 1.9. A 25.0 mg/L MO solution with an adjusted pH of 3.0 was subjected to a -1.0 V applied potential which led to the >99% degradation of MO within 90 minutes. In contrast, a neutral solution (pH 7.4) and a basic solution (pH 11), at the same potential, were only decolorized up to 96% in 90 min and 35% in 105 min, respectively.
Figure 3.3: Effect of pH 11 (blue), pH 7.4 (red), and pH 3 (yellow) on MO degradation kinetics. Conditions: -1.0 V applied potential, 25.0 mg/L MO, 0.1 M Phosphate buffer.

The solution was degassed by bubbling N₂ gas for 45 min and the experiment was repeated in order to test for the dependence of O₂. There was no significant degradation observed which indicated that the oxidation depended on the presence of dissolved oxygen. In order to test for the production of reactive oxygen species, a hydroxyl radical probe was employed. The FC-MWCNT composite, electrocatalytically generated hydroxyl radicals (OH) were monitored by the photoluminescence (PL) technique using terephthalic acid (TA) as a probing molecule. TA reacts with hydroxyl radicals resulting in a highly fluorescent product of 2-hydroxyterephthalic acid that has an intense fluorescence emission band centered at 426 nm with an excitation wavelength of 315 nm. Moreover, it is well established that the fluorescence intensity of 2-hydroxyterephthalic...
acid is directly proportional to the amount of OH radicals produced at the interface of water and the electrode [22].

![Graph of PL Intensity vs Time](image)

**Figure 3.4**: Kinetics of the hydroxyl radical production by the FC-MWCNT electrode measured by the PL study on 2-hydroxyterephthalic acid. Conditions: pH 7.4, 0.1 M phosphate buffer, 0.02 mM TA.

The production of hydroxyl radicals coupled with the dependence of oxygen in the degradation experiments led to the conclusion that the mechanism for reactive oxygen species formation follows that of previously proposed mechanism for the photocatalytic pathway shown in scheme 2 [23]. First, the applied negative potential applied to FC-MWCNT promotes the reduction of molecular oxygen producing superoxide which, in turn, reacts with two protons to produce hydrogen peroxide which then creates a highly reactive hydroxyl radical confirmed with
the PL experiment shown in Fig. 3.4 which explains the increased efficiency in degradation with the increase in H\(^+\) concentration (i.e. pH decrease).

\[
O_2^{2-} + 2H^+ + e^- \rightarrow H_2O_2 \tag{1}
\]

\[
H_2O_2 + H^+ + e^- \rightarrow \cdot OH + H_2O \tag{2}
\]

Scheme 3.1. Reaction mechanism for ROS production.

It has been reported that the supporting electrolyte concentration has an important effect on the degradation of MO in various systems. Therefore, in the present work, the degradation of MO was investigated in three systems: phosphate buffer (PB) (2.7 M KCl, 0.134 M NaCl), NaCl 1 (PB + 0.0428 M NaCl), and NaCl 2 (PB + 0.856 M NaCl). As can be seen in Fig. 3.5, the addition of 0.0428 M NaCl to the phosphate buffer salt concentration only slightly increased the % degradation from 98 to 99% but it shortened the degradation time from 60 to 30 minutes. When the addition of NaCl to PB was doubled to 0.0856 M, the degradation reached 100% within 4 minutes.

This indicated that increasing NaCl concentration can enhance degradation efficiency and shorten reaction time, possibly by the indirect oxidation of MO by active chlorine species such as chlorite/hypochlorite generated by the reactions shown in scheme 3.2.

Anode reaction: \(2Cl^- \rightarrow Cl_2 + 2e^-\)

Cathode reaction: \(2H_2O + 2e^- \rightarrow H_2 + 2OH^-\)

Bulk solution reaction: \(Cl_2 + H_2O \rightarrow HOCl + HCl\) \hspace{1cm} \(HOCl \rightarrow H^+ + OCl^-\)

Scheme 3.2. Reaction mechanism for the production of active chlorine species.
Figure 3.5: Effect of supporting electrolyte, NaCl, concentration, phosphate buffer (2.7 M KCl, 0.134 M NaCl) (blue), NaCl1 (PB + 0.0428 M NaCl) (orange), and NaCl2 (PB + 0.856 M NaCl) (red), on MO degradation.
CONCLUSION

The formation of hydroxyl radicals which depends on the formation of hydrogen peroxide showed a direct correlation to the presence of oxygen in the solution as well as a strong dependence on proton concentration given by the pH studies results. Furthermore, increasing the NaCl salt concentration had a profound effect by increasing the efficiency of the MO degradation which resulted from the production of active chlorine species and possibly from the increased conductivity of the solution. The FC-MWCNT electrode showed the ability produce reactive oxygen species, confirmed with fluorescence spectroscopy, capable of electrochemically degrading methyl orange solutions by 100% with increased efficiency in low pH, high salt concentration solutions with only a small applied potential of -1 V.
Chapter 4: Synthesis and Characterization of Gel-encapsulated Active Copper Nanoparticles for Arsenate Removal

INTRODUCTION

An emerging area of nanoscience and nanotechnology is the application of nanoscale materials and structures. Nanomaterials can offer results to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatment [1,2]. An assortment of metal and metal oxide nanoparticles (NPs) have distinctive properties as sorbents, catalysts, sensors, reducing agents, and bactericides [3-10]. Due to their high surface to volume ratio, they have very fast kinetics and heightened sorption capacity. However, their application to real-life systems is often hampered due to their tendency to aggregate, high pressure drop in flow-through systems, lack of specificity for reactions in complex systems, and weak mechanical strength. In order to lessen some of these disadvantages, nanogels have been employed to disperse and encapsulate the nanoparticles creating a novel nanocomposite.

Nanogels are internally cross-linked particles of sub-micrometer size made of hydrophilic polymers [11] and are considered to be a distinctive type of macromolecule, compared to linear and branched polymers or macroscopic gels [12]. Such structures, along with microgels, have been tested for several practical applications [13]. Nanogels from hydrophilic polymer matrices are crosslinked by several methods including, physical crosslinking, such as hydrogen bonds, crystallized domains, hydrophobic interactions and temperature-induced sol-gel transition. These physically crosslinked gels can reversibly degrade into their precursors. Another method involves chemical crosslinking in the presence of various crosslinkers. However, the chemical method had a few problems, including toxicity and an elimination of catalysts after a reaction [14]. In this study, UV radiation technology was used for gel preparation, as this method is capable of sterilization and crosslinking simultaneously. The radiation-induced nanogels can be synthesized using the following two methods: inter-molecular and intra-molecular crosslinking of a linear-
chain polymer by radiation [15, 16]. The radiation-induced synthesis of nanogels is initiated by irradiation of a dilute polymer solution. Reactive radical intermediates are formed by this process in the polymer chains. These can then recombine via inter- or intra-molecular crosslinking [17]. As a result, gels are produced from intra-molecular recombination of the radicals.

This chapter reports the synthesis and characterization of gel-encapsulated nanoparticles (GENs). Briefly, these nanocomposite, permeable materials are synthesized by complexing metal ions within photopolymerized solvogels and then reducing the ions to yield GENs. The potential for GENs is great due to the combination of the desirable physical and chemical properties of the encapsulated nanoparticles with the surface area, permeability and sequestration properties of the gels. Recently, nanogels with diameters in the range of tens to hundreds of nanometers, have attracted attention because of their importance in fundamental studies and practical applications. Emulsifying the gels in water followed by sonication reduces the gels’ size to the nanoscale producing nanogel-encapsulated nanoparticles (nGENs). The size of the nGENs can be controlled by varying the metal-to-polymer ratio as well as the photopolymerization exposure time. Furthermore, the application as an arsenic absorbent was investigated along with its effectiveness in a variety of pH levels.

**MATERIALS**

The tetra(ethylene glycol) diacrylate, acrylic acid, copper acetate monohydrate, and photoinitiator, 2,2’-Azobis(2-methylpropionitrile were purchased from Sigma Aldrich and all used as received without further purification.

**INSTRUMENTS**

The X-band (~9.5 GHz) EPR spectrums was obtained using a BrukerEMXplus spectrometer with an ER073 magnet. Transmission electron microscopy (TEM) experiments were performed using a Hitachi H-7650 transmission electron microscope with an acceleration voltage of 80 kV. Carbon coated copper grids with 200 mesh (Electron Microscopy Science) were used for TEM imaging. Arsenic and Copper concentrations were determined by inductively coupled
plasma-optical emission spectroscopy (ICP-OES) (Optima 4300 DV, PerkinElmer). Dynamic light scattering (DLS) was carried out by using Zetasizer Nano ZS90 with quartz cuvette of 10 mm path length. Energy dispersive X-ray (EDX) analysis was carried out on a Hitachi S-3400N Type II scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer with accelerating voltage of 15 kV.

**SYNTHESIS OF COPPER HYDROGEL**

The first step in the synthesis of the hydrogel was to synthesize a gel with the right consistency so that it can be water permeable yet robust enough to not leach copper into the solution. The consistency depended on the amount of polymerization the material underwent which could be controlled by the ratios of copper acetate to tetra(ethylene glycol) diacrylate (TEGDA) and acrylic acid (AA) as well as the method of polymerization. First, the ratios were varied using polymerization induced by heat. Ratios 1 and 2, listed in Table 4.1 were each dissolved in methanol along with 10% by weight AIBN photoinitiator and refluxed overnight.

<table>
<thead>
<tr>
<th>Gel #</th>
<th>Amount of CuOAc (g)</th>
<th>Amount of TEGDA (g)</th>
<th>Amount of Acrylic acid (g)</th>
<th>Mole Ratio:</th>
<th>Consistency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (Δ)</td>
<td>0.3017</td>
<td>2.00</td>
<td>1.00</td>
<td>1:2:8</td>
<td>honey</td>
</tr>
<tr>
<td>2 (Δ)</td>
<td>0.0868</td>
<td>2.00</td>
<td>0.2508</td>
<td>1:7:7</td>
<td>plastic</td>
</tr>
<tr>
<td>3 (UV)</td>
<td>0.0890</td>
<td>2.00</td>
<td>0.2572</td>
<td>1:7:7</td>
<td>jello</td>
</tr>
</tbody>
</table>

The resulting material was dried via rotary evaporation which resulted in Gel 1 having a honey-like consistency that was water soluble and Gel 2 having a rigid, plastic consistency which seemed to not be water permeable. Next, the ratio for Gel 2 was used for photopolymerization
instead of using heat which resulted in a jello-like material which did not dissolve and absorbed water giving the material the desired properties of a hydrogel shown in figure 4.1.

![Figure 4.1: Polymerization of Cu, acrylic acid, and tetra(ethylene glycol) diacrylate.](image)

Photopolymerization was subsequently used in further synthesis. The ratios were further optimized until TEM showed the desired properties which resulted in the 1:10:2 ratio of Cu to TEGDA to AA, respectively.

**Cu (II) Hydrogel (1)**

**Synthesis**

In a 250-mL quartz, round-bottom flask, Cu(Ac)$_2$ · H$_2$O (0.199, 1 mmol), Tetra(ethylene glycol) diacrylate (3.02 g, 10 mmol), acrylic acid (0.140 g, 2 mmol), and photoinitiator, 2,2′-Azobis(2-methylpropionitrile) (0.103 g, 0.627 mmol) dissolved in 50 mL of methanol. The blue solution was irradiated with UV light for 18 hrs. The solvent is then removed via rotary evaporation and the resulting gel is emulsified by adding water and sonicating. The qualitative yield of 1 was 100%.
EPR Characterization

Figure 4.2 shows the EPR spectra of the Cu gel revealed two lines at ~1500 and ~3300 G with g values of 4.42 and 2.14, respectively. The spectra indicates a centrally tetra-coordinated Cu (II) complex [18].

![EPR spectra of Cu (II) gel](image)

Figure 4.2: EPR spectra of Cu (II) gel.

TEM Characterization

Figure 4.3 shows a TEM image which revealed discrete, interconnected polymers of sizes ranging from 50 nm up to 3 microns. The sizes of the discrete structures we believe varied due to uneven exposure to UV light during photopolymerization.
**REDUCTION OF Cu HYDROGEL (2).**

In a 250-mL round-bottom flask, under N₂ atmosphere, containing solution 1, NaBH₄ (0.250 g, 6.61 mmol) was added to reduce Cu (II) to highly reactive Cu (0), the black solution was stirred overnight at room temperature then dried under vacuum. Figure 4.4 shows a visual representation of the Cu reduction process within the gels.
EPR Characterization

Figure 4.5 shows the EPR spectra for the reduced Cu gel. The spectra showed signals at the same position as the Cu (II) gel although the intensities were reversed and the signal with the \( g \) value = 4.42 was stronger than the signal with \( g \) value = 2.14. There were also differences in that the 2.14 signal contained hyperfine signals.

![EPR spectra of reduced Cu gel](image)
TEM Characterization

Figure 4.6 shows that the Cu ions coordinated throughout the gel network were successfully reduced, with sodium borohydride, to Cu NPs varying in size from 5 to 10 nm.

![Figure 4.6: TEM image of NPs dispersed in gel.](image)

The morphology of the emulsified gels were observed with TEM (Figure 4.7). The images in figure 1 shows the gels are globular in shape, with sizes ranging from 20-50 nm. The images after reduction revealed that the NPs produced are 5-10 nm in size and copper NPs are dispersed throughout the gel, which is in agreement with DLS results which also showed a decrease in size when the gels were reduced with NaBH₄.
**Figure 4.7:** TEM images of Cu gels (a) and (b) and their NaBH$_4$ reduced counterparts (c) and (d).

**CHEMOABSORPTION OF ARSENIC BY REDUCED CuNP HYDROGEL (3).**

A degassed emulsion of Cu gel (1) (0.100 g) in water was reduced with NaBH$_4$ (0.020 g, 0.52 mmol). Then, to the reduced gel emulsion, a 20 mL solution containing 5.89 g/L of Arsenic was added and left stirring overnight. The resulting solution was centrifuged at 2500 rpm for 30 min. The supernatant was analyzed with ICP-OES to determine the amount of As absorbed. The experiment was repeated with varying pH to determine the effect and the results are shown in table 4.2. ICP analysis revealed a ~90% absorption for all of the experiments which indicated that pH
had no effect on absorption. Furthermore, pH 6 and 7 showed no Cu leaching while pH 5, 8, and 9 showed a small amount of Cu, 8.0, 3.98, and 4.22 mg/L respectively, was released into solution.

Table 4.2. pH dependence on Arsenic uptake and Copper leaching.

<table>
<thead>
<tr>
<th>pH</th>
<th>Initial [As] (mg/L)</th>
<th>Final [As] (mg/L)</th>
<th>% As Absorbed</th>
<th>[Cu] leached (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5,890</td>
<td>593</td>
<td>89.9</td>
<td>8.00</td>
</tr>
<tr>
<td>6</td>
<td>5,890</td>
<td>638</td>
<td>89.2</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>5,890</td>
<td>588</td>
<td>90.0</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>5,890</td>
<td>551</td>
<td>90.7</td>
<td>3.98</td>
</tr>
<tr>
<td>9</td>
<td>5,890</td>
<td>538</td>
<td>90.9</td>
<td>4.22</td>
</tr>
</tbody>
</table>

EDX analysis of Arsenic absorption experiments

The solid gel before and after As exposure was analyzed with EDX in order to confirm that the As was absorbed by the material. Figure 4.8 shows the EDX analysis of the gel before exposure which shows, as expected, carbon, copper and oxygen peaks. After exposure to the As solution, figure 4.9 shows a new peak for As which confirms that the material successfully absorbed As and removed it from solution.
Figure 4.8: EDX of Cu gel before As exposure.
Figure 4.9: EDX of reduced Cu gel exposed to As.
Figure 4.10 shows the TEM images of all three stages of the Cu absorption of As experiments. The Cu (II) gel begins as a cohesive network of nano- to micro-sized material which is then reduced and turns into a network of Cu NPs distributed throughout the gel support. After As exposure, the network breaks apart into discrete Cu-arsenate complex as the NPs presumably chemoabsorb and oxidize the Cu (0).

Figure 4.10: TEM images of Cu(II) gel before reduction (top) after reduction with NaBH₄ (middle) and after exposure to arsenic (bottom).
CONCLUSION

A hydrogel was synthesized containing Cu (II) ions coordinated to polymers who were polymerized utilizing radical photopolymerization. After photopolymerization the Cu ions were successfully reduced to Cu nanoparticles who were dispersed throughout the hydrogel. The nanocomposite was exposed to As and was capable of chemoabsorbing 90% of the heavy metal independent of the solution pH.
References

Chapter 1


Chapter 2


Chapter 3


Chapter 4


Vita

Julio Eduardo Padilla earned his Bachelor of Science degree in Chemistry with a minor in Physics from The University of Texas at El Paso in 2008. In 2009, he joined the Chemistry PhD program at The University of Texas at El Paso and has been under the supervision of Dr. Juan Noveron since 2012.

Dr. Padilla is a Louis Stokes Alliance for Minority Participation-Bridge to the Doctorate fellow for the 2009-2011 cohort. In the course of his PhD studies, he has worked as a research associate and teaching assistant at the Department of Chemistry. He has been a student member of the American Chemical Society and the Society for the Advancement of Chicanos and Native Americans in Science (SACNAS). In 2012, he interned at the United States Department of Agriculture-Agricultural Research Services in Lubbock, Texas, where he worked in a soil microbiology lab studying the composition of wind-eroded dust and its effects on agricultural systems under the supervision of Dr. Veronica Acosta-Martinez.

After graduation, he will pursue a career in industry. Dr. Padilla presented his research in numerous national conferences. He presented a poster at the USDA/NIFA Hispanic Serving Institution Project Directors Conference in Washington, D.C. in 2012 titled: *Biomass Conversion*. In 2013, he presented a poster at the Center for Education and Training in Agricultural and Related Sciences Symposium which took place in Mayaguez, Puerto Rico. In 2014, at the SACNAS National Conference in Los Angeles, CA, he presented a poster titled: *Metal-Mediated Anchoring of [6,6]-Phenyl-C61-Butyrate to Gold Nanoparticles*. Also in 2014, his poster presentation titled, *Surface Functionalization of Cotton Cellulose and its Applications for the Adsorption of Aromatic Pollutants*, placed second at the Agri-Science: Education for the 21st Century conference in Miami,
FL. He has authored and co-authored three publications published in peer-reviewed journals. He has another manuscript under review and two others under preparation.

Dr. Padilla’s dissertation, *Synthesis, Characterization, and Functional Evaluation of Nanocomposites for Water Purification*, was supervised by Dr. Juan C. Noveron.

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This dissertation was typed by Julio E. Padilla.