NOVEL HETEROGENEOUS FENTON OXIDATION USING MAGNETIC IRON OXIDE-DECORATED CARBON NANOTUBE TO REMOVE ENDOCRINE DISRUPTING COMPOUNDS IN WASTEWATER AND WATER

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAI‘I AT MĀNOA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN MOLECULAR BIOSCIENCES AND BIOENGINEERING

DECEMBER 2014

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Keywords: Fenton Oxidation, Carbon Nanotube, Wastewater, BPA
Acknowledgments

It has been said that producing a thesis is like giving birth. I can hardly say this has been an easy labor, and I would not of been able to complete it without the assistance of my coworkers and friends. My labmates Jihyun “Rooney” Kim and Stuart Watson were essential for keeping my sanity through the process and acted as critical sounding boards for developing my half-baked ideas. I would also like to thank Patrick Gasda for use of the Raman lasers. My use of magnetic separation was greatly facilitated by Jonathan Moroney through supplying me with several rare earth hard drive magnets. Finally I would like thank my parents for their support throughout my education.
Abstract

Endocrine disrupting compounds are becoming a growing concern in our modern world. Bisphenol A, a known estrogen mimic, is produced on a massive scale exposing it to humans and the environment on a daily basis. Recent studies since 1995 have shown that bisphenol A has negative effects even at ultra-low concentrations. Unfortunately, bisphenol A is biologically recalcitrant and passes through most traditional waste water treatment methods. In order to develop an effective and efficient treatment method, a combined approach is proposed. Iron amended carbon nanotubes can act as a heterogeneous Fenton catalyst and as an adsorbent of the contaminant. This project synthesized and characterized a magnetite decorated carbon nanotube catalyst. Additionally the adsorption kinetics and thermodynamics were investigated in both batch adsorption and column adsorption reactors.
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Chapter 1 Description of Thesis

1. Prologue
UN resolution 64/292 “Recognizes the right to safe and clean drinking water and sanitation as a human right that is essential for the full enjoyment of life and all human rights.” Endocrine disrupting compounds are manmade contaminants affecting water sources around the world. These compounds have recently been brought to the spotlight for their effects on human and environmental health. While these compounds are often only found in trace quantities their impacts can compile of the course of a person’s lifetime. By developing water treatment methods which can efficiently and effectively remove these contaminants from water, the overall health of a municipality and the surrounding environment can be protected. This thesis describes a method for treating one such endocrine disrupting compound, bisphenol A.

1.1 Description of Chapters
Chapter 2 is the literature survey, investigating the effects of bisphenol A and endocrine disruptors on the environment. The Survey then investigates the current state of bisphenol A treatment methods, comparing physical, chemical, and biological methods. Finally the literature survey describes the various Fenton oxidation methods, including potential catalysts and carbon supports.

Chapter 3 is the proof of concept showing the feasibility of magnetite amended carbon nanotubes as a method for bisphenol A treatment. For ease of measurement this section uses a concentration of bisphenol A higher than that found in the natural environment. The goal of this section was to quickly and effectively degrade bisphenol A with a minimal dose of hydrogen peroxide for Fenton Oxidation.

Chapter 4 describes the adsorption of bisphenol A through kinetic, thermodynamic, and isocratic data. This information is then applied to a carbon nanotube and sand fixed bed column.

Chapter 5 Investigates the use of non-traditional Fenton catalysts and conditions for the oxidation bisphenol A.
Chapter 7 discusses future work for the use of magnetite coated carbon nanotubes as a treatment option for bisphenol A. These are theories with no current experimental data.

1.2 Overall Aims of Research

The aim of this study was to develop a heterogeneous Fenton reagent for the treatment of bisphenol A in water sources. Previous studies Fenton oxidation focused on very high doses of hydrogen peroxide.

The specific aims of this project follow three phase. 1) Develop and characterize a Fe$_3$O$_4$-multiwalled carbon nanotube Fenton catalyst, and optimize the parameters for the oxidation of bisphenol A. 2) Investigate and fully describe the adsorption kinetics and thermodynamic properties of bisphenol A onto multiwalled carbon nanotube based catalysts. 3) Investigate and describe the operating conditions for a carbon nanotube fixed bed column.

1.3 Impact of This Thesis

BPA contamination has been observed in water sources around the world. This means that every day humans are constantly exposed to the endocrine disrupting effect for their entire life. While the day to day dose may be insignificant alone there are still signs that the cumulative effects of BPA exposure has deleterious effects on humans especially children.
Chapter 2 Literature Survey

2.1 Endocrine-Disrupting Compounds
The endocrine system is the communication network of the cells. Hormones produced in one part of the body can have dramatic effects on several throughout the entire body. Some hormones, such as adrenaline and insulin, are fast acting, generating cellular responses nearly instantly. Other hormones act over months and years, regulating processes such as sexual and physical development. Estrogen is an example of one of these slow-acting hormones. Although commonly referred to as the female sex hormone, estrogens play a key role during development at all stages of life for both males and females. The body is constantly regulating the amount of estrogen produced, and changes in the concentrations can cause major alterations in reproduction and development. Through the use of natural and synthetic hormones humans have been able to better control the endocrine system, alleviating developmental disease and even controlling the reproductive cycle in women. However, advancements in synthetic chemistry have led to an increase in xenobiotic hormones entering into and remaining in the environment.

Endocrine-disrupting compounds (EDC) are chemicals that interfere with the cellular hormone signaling pathways. Since the late 1990’s these compounds have become a growing concern. EDCs come from a variety of compounds such as pharmaceuticals, pesticides, personal care products, and plastics, among other sources [1]. Table 2.1 describes bisphenol A and other xenobiotic EDCs. These compounds show effects even at nano-molar concentrations, making them particularly difficult contaminants to treat with traditional wastewater treatment methods. Additionally, determining the dose effects of EDC is difficult. Part of the problem is that the dose effect is not always linear. Measuring reproductive effects can be time- and resource-consuming, requiring multiple generations of test animals.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Trade Name</th>
<th>Use</th>
<th>$K_{ow}$</th>
<th>pKa</th>
<th>Toxicity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estradiol</td>
<td>Climeratm, Menostartm</td>
<td>Hormone Supplement</td>
<td>3.7</td>
<td>10.5</td>
<td>NOEC= 100-387 ppb</td>
<td>[2]</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>BPA</td>
<td>Plastic Monomer</td>
<td>3.3</td>
<td>9.6-10.2</td>
<td>24 h $EC_{50}$ (Daphnia magna) = 24 ppm</td>
<td>[3]</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>Phthaltic acid</td>
<td>Plastic Monomer</td>
<td>0.73</td>
<td>2.94, 5.49</td>
<td>$EC_{50}$ (Vibrio Fischeri) = 6.61 ppm</td>
<td>[4]</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>SMX</td>
<td>Antibiotic</td>
<td>0.89</td>
<td>6.16</td>
<td>$EC_{50}$ (D. magna) 48 h = 189 ppm</td>
<td>[5]</td>
</tr>
<tr>
<td>Butylparaben</td>
<td>Butylparaben</td>
<td>Cosmetic Preservative</td>
<td>3.57</td>
<td>8.5</td>
<td>$EC_{50}$ (D. magna) 48 h = 1.9 ppm</td>
<td>[6]</td>
</tr>
</tbody>
</table>
2.2 Bisphenol A

Bisphenol A (BPA) has been studied since the 1930’s as an estrogen mimic. In 1936 Dodds and Lawson investigated the potential of BPA as a synthetic estrogen supplement [7]. As a pharmaceutical BPA underperformed compared to natural estrogens, and previous studies using yeasts have shown that BPA is 50,000 times weaker than estradiol when eliciting a cellular response [8]. Although ineffective as a pharmaceutical, BPA was later used as a monomer for manufacturing polycarbonate plastics. In the 1950’s the use of BPA as a plastic material began to take off. Today over 8 billion pounds of BPA are produced annually, making it one of the world’s most widely manufactured chemicals.

2.3 Sources of Bisphenol A Contamination

To determine the threat that BPA poses to humans and the environment it is essential first to understand the extent to which BPA contaminates the environment. BPA itself is produced on a massive scale, and it is ubiquitous in our modern life. The huge scale of BPA production leads to widespread environmental prevalence.

Figure 2.1 depicts the pathway of BPA in water systems. After production, BPA-containing products are used in households, industry, and agriculture. Wastewater and sewage from these sources then enter water-treatment facilities. BPA that has been adsorbed, but not treated, to activated sludge may return to agriculture processes when the biosolids are used as fertilizer. Effluent from wastewater treatment plants may also be used as irrigation for agriculture, thereby exposing more food crops to BPA. Effluent and agricultural runoff can then enter surface and ground waters, contaminating them with BPA; when these waters become used for drinking water, the BPA remains.

The compound itself is quickly degraded in the environment by UV light and aerobic bacteria. River surface water generally has a BPA concentration ranging from only a few ppt to as much as 21 ppb [9, 10]. However, the hydrophobic nature of the compound enables it to be compartmentalized in sediment and anaerobic environments. In these situations BPA becomes significantly more stable. BPA contents in soil samples from river and estuary sources range
from 21 ppt to 56 ppm, more than twice the highest amounts detected in river waters [11-13]. Landfill leachate can further concentrate BPA to the ppm level. A maximum concentration of BPA of 17,200 was found in the leachate of a Japanese hazardous-waste landfill [10]. Wastewater treatment can remove BPA to single-digit ppt levels, but the BPA is primarily adsorbed to the sludge and biosolids are not degraded. Over time the BPA levels in the solids rise to as high as 32,000 ppm in sewage sludge.

**Figure 2.1.** Visual representation of bisphenol A contamination in the water system.

### 2.4 Effects of Bisphenol A on the Environment

BPA is quickly degraded/metabolized in aerobic environments, and in stream and river environments the concentration of BPA will decrease farther downstream from the contamination source. Toshinari et al. investigated BPA and its metabolites in a Japanese river. They observed a decrease in the concentration of BPA further downstream, but an increase in BPA metabolites [14]. One of the primary metabolites detected in the Toshinari study is carboxylated BPA (BPA-COOH), a primary metabolite of the MV1 strain of bacteria [15]. If, however, BPA enters an anaerobic environment, such as wastewater sludge or lake sediment, it is less biodegradable and much more stable [13, 16]. BPA can then leach from these sediments, leading to prolonged contamination in the environment.
2.5 Effects of Bisphenol A on Living Organisms

Invertebrates are commonly used for toxicology studies because of their ease of raising and short lifecycle. The U.S. EPA uses water fleas (most often Daphnia magna) as model organisms to determine acute and chronic toxicity. Other invertebrates such as mollusks, crustaceans, and nematodes have been studied [10-12, 17, 18]. Often changes in developmental and reproductive abnormalities have been observed. BPA concentrations and exposure time are critical to determine the toxicity. For example, a crustacean (Acarita tonsa) exhibits developmental inhibition when exposed to 100 ppb BPA for 2 weeks, but it is developmentally stimulated by lower concentrations (12.5 ppb) for longer periods (3 weeks). Even lower concentrations can still alter invertebrate development, however; a concentration of 80 ppt BPA was sufficient to delay midge (Chironodae) larva from emerging [10].

Fish are also susceptible to BPA contamination because they live entirely immersed in water and are constantly exposed to contaminants. Concentrations as low as 1 ppb can inhibit male hormones and alter gonad structure. Other hormonal effects include the induction of Vtg, a juvenile hormone responsible for development. Zebra fish (Danio rerio) embryos begin to show feminization of the brain at doses as low as 228 ppb; when the dose reaches 1000 mg/kg body mass, the sex ratio is skewed toward females [10]. Several species of fish are economically important, and if BPA contamination can have adverse effects on fish populations, the effects can extend well beyond environmental impacts.

Amphibians exposed to BPA undergo significant changes in response to doses as low as 2.28 ppb, which can adversely affect their development and reproduction. Even at 22.8 ppb a female-biased sex ratio begins to become apparent after 12 weeks of exposure. Other research has shown that the same concentrations for 2 years can lead to sex reversal. Reptiles likewise are susceptible to sex reversals at low exposures of BPA. A study with broad-snouted caiman (Caiman latirostris) found that at egg concentrations of 1.4 ppm (90 µ/egg) male seminiferous tubules appear abnormal. Higher concentrations (140 ppm 9 mg/egg) lead to 100% sex reversal, even when eggs are incubated at male body temperatures [10].

Determining the toxicity of an EDC can be extremely difficult using current toxicological definitions. Often EDC response is not a linear response curve, so low and high doses might be more damaging than moderate doses [19]. This factor can lead to artificially high no observed
effect concentration (NOEC) values that incorrectly reflect the nature of the compound. Furthermore the damage of the EDC may occur at specific points in an organism’s development. If a study does not investigate the full development of an organism, only partial toxicity may be reported. The toxicology of a compound may also be partial if the interactions with other compounds are not investigated. Only on rare occasions is only one xenogeneic contaminant found in water sources [20]. The interactions between multiple EDCs are unknown, and they may be additive or synergetic, greatly increasing the impact of a contaminant. Finally there is much variation of the endocrine systems among phyla. Invertebrates will have substantially different responses to estrogenic compounds compared to the reactions in birds, which differ from the responses of amphibians and mammals.

When interacting with nuclear estrogen receptors BPA is several orders of magnitude less responsive than estradiol [8, 21]. However non-nuclear estrogen receptors are more sensitive to BPA. Walsh et al. reported similar responses when MCF-7 human breast cancer cell lines were treated with 0.1 nM BPA or estradiol. Although too weak to cause a nuclear response, an influx of intracellular calcium ions indicated a rapid response of non-nuclear estrogen receptors [22]. These non-nuclear estrogen receptors can activate rapid kinase cascades through the mitogen-activated protein kinase (MAPK) pathways. Zsarnovszky et al. investigated the effects of ultralow injections ($10^{-12}$ - $10^{-11}$ M) of BPA and estradiol on the rapid response of non-nuclear estrogen receptors. At ultra-low injections BPA and estradiol had a similar response. When BPA was injected with estradiol there was approximately a 50% lower kinase response than the response resulting from a pure injection of BPA alone. This indicates that although BPA is estrogenic, it can also act as an estrogen inhibitor. Zsarnovszky et al. also showed that BPA has a non-linear dose response at ultra-low concentrations, with a sharp increase in response at $10^{-10}$ M doses. However, high doses of BPA were significantly less efficacious [23].

The human liver will respond to BPA in the body by two different methods, glucuronidation and sulfation. Glucuronidation takes place in the liver via the enzyme glucuronosyltransferase (UGT). Sulfation is carried out by sulfotransferases in the liver, adding a sulfo group to the BPA. These metabolites are both present in humans exposed to BPA, but the glucuronidation metabolites are observed at significantly higher concentrations [24]. The presence of BPA and BPA metabolites in umbilical cords indicates that BPA can cross the placental barrier during
fetal development, making BPA a particular concern for women during pregnancy [25]. Fetuses and infants lack the UGT enzymes in their liver, changing the primary BPA metabolism to the sulfation pathway [26]. Recently an increased concern has arisen about the effects of BPA on humans. The effects of BPA on children is of particular concern because infants do not have the liver enzymes to remove BPA from the body [27-29]. Some correlation exists between maternal BPA exposure and developmental problems in infants [30-33], and these issues may manifest later in life. Higher maternal BPA concentrations have been linked to aggression in boys and anxiety or depression in girls. BPA concentrations in urine as low as 0.4 µg/L have been strongly associated with cases of obesity; BPA has been associated with several sexual development issues in men and [30]. Li et al. (2009) observed an increase in self-reported sexual dysfunction in men with high occupational exposure to BPA [34]. As a more quantitative measure Meeker et al (2011) demonstrated a strong correlation between urinary BPA concentrations and a decline in sperm quality [35]. In women, high serum BPA concentrations have been associated with an increased risk of premature delivery [36] and miscarriage [37, 38].

2.6 Effects of BPA on Society
The growing evidence linking BPA to human health issues has evoked responses from many government agencies. European health ministries were some of the first to adopt restrictions on BPA use in their home territories. Private companies such as Nalgene began to follow suit and willingly discontinued production of polycarbonate food and drink containers [39]. As an indication of widespread public concern about BPA, Google searches for BPA peaked during this time (Figure 2.2). In the spring of 2012 public pressure called for the U.S. Food and Drug Administration (FDA) to ban the use of BPA in food and drink packaging. In April 2012 the FDA refused to institute regulations on the use of BPA, stating that “...as a matter of science and regulatory policy, the best course of action at this time is to continue our review and study of emerging data on BPA.” [40]. Eventually in October 2012, the FDA responded to community pressure and implemented a ban on BPA in infant formula bottles.
Figure 2.2. Google search trends for the term “BPA” from 2004 to the present (6/10/2014). Values are relative to the peak search traffic.

2.7 State of Research

Bisphenol A has been and continues to be widely studied as an ideal contaminant. Advances in research have been in three major methods of treatment: physical, biological, and chemical. Each treatment method has advantages and disadvantages that must be taken into consideration when developing an optimal treatment policy.

Secondary biological treatment uses bacteria either suspended in solution or attached to a solid surface to degrade contaminants in the wastewater stream. Wastewater treatment plants use a variety of methods to encourage biological growth, and thus contaminant consumption. During secondary treatment BPA can be physically removed by adsorbing to biological solids, or it can be consumed and incorporated into living material. Volatilization during aeration is minimal due to BPA’s low Henry’s constant. In one of the few BPA mass balance studies Stasinakis et al. determined an average of 72% +/- 10% of BPA in the influent to be transformed or lost, while 15% +/- 4% remained in the sludge and 13% remained in the effluent [41]. Porthitou and Voutsas investigated BPA partitioning during different segments of municipal and industrial wastewater treatment plants, and they concluded that during aeration most of the BPA is in the particulate phase, but during secondary settling and in the final effluent most BPA is dissolved in the
solution [42]. Any BPA remaining in the leftover sludge potentially can be returned to the environment. Traditional anaerobic digestion of activated sludge is generally ineffective at removing BPA [16].

Various wastewater treatment methods have different degrees of removal of BPA (table 2.2). Traditional methods such as using activated sludge are somewhat effective at removing BPA if the solids retention time (SRT) is long enough. Other methods such as trickle biofilters are ineffective at removing BPA because they do not have a long enough retention time to give bacteria adequate time to degrade the contaminant.

**Table 2.2.** BPA removal efficiency by selected wastewater treatment plants around the world.

<table>
<thead>
<tr>
<th>Location</th>
<th>Reactor type</th>
<th>BPA influent (ng/L)</th>
<th>BPA effluent (ng/L)</th>
<th>SRT (days)</th>
<th>Removal efficiency (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greece</td>
<td>AS and BNR</td>
<td>730</td>
<td>150</td>
<td>NR</td>
<td>79</td>
<td>[41]</td>
</tr>
<tr>
<td>Canada</td>
<td>AS and BNR</td>
<td>186</td>
<td>33</td>
<td>NR</td>
<td>82</td>
<td>[43]</td>
</tr>
<tr>
<td>Canada</td>
<td>AS and BNR</td>
<td>590</td>
<td>0</td>
<td>NR</td>
<td>100</td>
<td>[43]</td>
</tr>
<tr>
<td>Japan</td>
<td>AS and BNR</td>
<td>1140</td>
<td>40</td>
<td>NR</td>
<td>97</td>
<td>[44]</td>
</tr>
<tr>
<td>Austria</td>
<td>AS</td>
<td>1710</td>
<td>1530</td>
<td>2</td>
<td>11</td>
<td>[45]</td>
</tr>
<tr>
<td>Austria</td>
<td>AS</td>
<td>1255</td>
<td>723</td>
<td>19</td>
<td>42</td>
<td>[45]</td>
</tr>
<tr>
<td>Austria</td>
<td>AS</td>
<td>720</td>
<td>125</td>
<td>48</td>
<td>82</td>
<td>[45]</td>
</tr>
<tr>
<td>Canada</td>
<td>TF</td>
<td>284</td>
<td>203</td>
<td>NR</td>
<td>28</td>
<td>[43]</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>TF</td>
<td>451</td>
<td>141</td>
<td>NR</td>
<td>68</td>
<td>[46]</td>
</tr>
<tr>
<td>Austria</td>
<td>AS/MBR</td>
<td>2376</td>
<td>16</td>
<td>82</td>
<td>99</td>
<td>[45]</td>
</tr>
<tr>
<td>Austria</td>
<td>MBR</td>
<td>2154</td>
<td>158</td>
<td>55</td>
<td>92</td>
<td>[47]</td>
</tr>
<tr>
<td>California</td>
<td>MBR</td>
<td>597</td>
<td>47</td>
<td>15</td>
<td>92</td>
<td>[48]</td>
</tr>
</tbody>
</table>

AS = Activated Sludge, BNR = Biological Nutrient Removal, TF = Trickle biofilter, MBR = Membrane Bioreactor. NR = Not reported.
Continuous-flow stirred tank reactors (CSTR) are the most common form of wastewater treatment in the industrialized world. These reactors use biological cultures to degrade contaminants. Continuous mixing aerates the tanks and ensures homogeneous concentrations of cells, contaminant, and oxygen across the total volume of the reactor. Mixed liquor suspended solids (MLSS) are formed from bacteria cells and other nonsoluble organic matter. When these solids are settled in a clarifier they form a viscous sludge. Recycling the sludge can increase cell concentrations in the reactor, improving degradation rates.

Solids retention time (SRT) is a mechanical factor that can have a pronounced effect on BPA and EDC removal. Increasing the SRT can greatly increase the removal efficiency of an activated sludge treatment system. The removal of BPA from AS-treated wastewater has shown a significant increase when the SRT is at least 5 days, and shows near total effluent removal when the SRT is at least 20 days [45]. Most of the effluent removal efficiency is due to the adsorption of BPA to suspended solids. Unless the pH of waste water is very alkaline (>pH 10) BPA has strong adsorption to activated and inactivate sludge [49]. In a study of 5 waste water treatment plants across 2 seasons the median effluent BPA removal was 99.5%, but when the amount of BPA adsorbed to sludge was a factor, he total removal rate dropped to 70% [50]. Though only represented in a few cases, AS systems with biological nutrient removal modifications increased BPA removal. Even with the BNR additions to treatment most estrogenic compounds are adsorbed to the sludge and can leach out during dewatering processes [43, 44].

Membrane bioreactors (MBR) make use of activated sludge and aeration like CSTR, but they use a membrane filtration system to separate MLSS from treated wastewater. This method greatly increases SRT while maintaining a compact footprint. At laboratory scale Chen et al. observed that MBRs had higher BPA capacity and a higher BPA removal rate. The long hydraulic retention time (HRT) had little effect on the BPA removal efficiency [51]. MBR systems are hindered by biofouling, the buildup of biological material on the membrane. To control biofouling the MBR must be either regularly backwashed or scrubbed.

### 2.7.1 Biological Treatment of Bisphenol A

There are two major pathways for BPA degradation by bacteria. The metabolic route first identified, in the bacteria strain MV1, utilizes hydroxylases to add an OH group to the central CH₃ groups of BPA. The other main pathway uses monooxygenase to split the central backbone
creating hydroquinone and 4-(2-Hydroxypropan-2-yl) phenol. The monooxygenase pathway is generally used by \textit{Sphingnimonus} strain TTNP\textsubscript{3}. Both pathways can feed into energy cycles in the bacteria cells, but many BPA degrading bacteria exhibit no growth when BPA is the only carbon source. Other degradation pathways are currently being studied on strains of \textit{pseudomonas} which produce extracellular laccase. Some strains of ammonia oxidizing bacteria have been shown to be able to degrade BPA through nitrification processes.

One of the first strains of bacteria isolated for the removal of BPA was bacterial strain MV1, isolated from manufacturing waste water sludge by Lobos et al. in 1992 [52]. Strain MV1 was isolated from sludge taken at a plastics manufacturing waste water treatment plant. The sludge was placed in PAS medium containing 2 mg/mL BPA. Samples of the medium were then used to inoculate agar with BPA crystals dispersed throughout the gel. The high concentrations of BPA selected for a strain resistant to the toxic effects of BPA, and the lack of an alternative carbon source ensured that MV1 metabolized BPA. MV1 was identified to be from the \textit{Sphingnimonus} genus [53]. The only metabolite of MV1 to show increased estrogenic activity was 4-hydroxyacetophenone (4-HAP) [24]. The enzymes required for the degradation of BPA are not abundant in MV1 cells, and when grown on media containing alternative carbon sources the rate of BPA degradation decreases. MV1 is also inhibited by the build-up of the metabolite 4-HAP [52]. While able to degrade BPA under ideal laboratory conditions MV1’s ability to degrade BPA is inhibited by competing carbon sources in wastewater. Additionally, long-term buildup of the metabolite 4-HAP would lead to an overall increase of the estrogenic activity of the contaminated water.

Strains of bacteria isolated from activated sludge or solid waste leachate often exhibit some degree of BPA acclimation. Very few strains of BPA degrading bacteria show high removal rates (>50%) of the contaminant. Some strains like B-16 identified by Zhang et al. are sensitive to the cytotoxic effects of BPA, and the removal efficiency decreases as the initial BPA concentrations increase [54]. Strains like JF-1 isolated by Fischer et al. hindered by slow growth rates and removal rates. BPA degradation could be increased by the addition of phenol as a bio stimulant. The increase in degradation only occurred after the phenol was metabolized. Even with phenol biostimulation JF-1’s removal of 3 ppm BPA was less than 50% [55].
Recently Sun et al. used *N. europaea*, an ammonia oxidizing bacteria, to treat BPA contaminated water. Though BPA was not directly metabolized nitrous groups were added, forming nitro and dinitro bisphenol A. These metabolites were screened using a yeast estrogenic screening assay and determined to be significantly less estrogenic than BPA. The nitrification process required high concentrations of ammonium and may only be effective for certain waste water treatment schemes [56].

BPA degrading bacteria can also be found outside of waste treatment processes. Several soil and river bacteria have been found to have at least slight BPA degrading capabilities. These bacteria are primarily in the *Psdeudomous* and *Sphinnimonous* geneses. Matsumara et al. isolated 26 BPA metabolizing strains of soil bacteria in 2009. When exposed to 300 ppm BPA solution the removal efficiency of the bacteria ranged from 8-60% after 48 hours of incubation. Kang and Kodo isolated 11 strains of bacteria from three river systems in Japan. After 10 days of incubation the removal of 1 ppm BPA ranged from 0-91%. The two most effective strains were identified as being *Psdeudomous sp.* and *P. putida*, with 90 and 91% removal of BPA from river water after 10 days [57]. BPA degradation rates are positively influenced by both cell counts and temperature [58].

Degrading BPA via individual bacteria strains becomes a catch-22; in order to achieve high degradation rates high cell concentrations are required. High cell concentrations can only be achieved by using non-BPA carbon sources. When non BPA carbon sources are available BPA degradation is significantly reduced. Furthermore BPA degradation rates can be greatly influenced by many factors. Some can be easily controlled by operating procedures such as biomass concentrations, but others like metal ion concentrations are more dependent on environmental conditions.

### 2.7.2 Physical Treatment of Bisphenol A

Biological treatments of BPA are hampered by the requirements of high retention times and inefficiency at ultra-low concentrations. Physical treatments are faster than biological treatments and can often be implemented with a smaller footprint. The use of filters and adsorbents keeps their efficiency even with low and ultra-low concentrations. An inherent drawback of physical treatments is that they do not degrade the contaminant, which must be dealt with later.
Regeneration techniques can be energy intensive and can greatly increase the cost of such treatments.

2.7.3 **Nanofiltration/Reverse Osmosis**

Nanofiltration (NF) uses materials with nanoscale pores to physically separate contaminants from wastewater streams. Different materials have varying abilities to separate BPA. A fully aromatic polyamide layer has a higher removal efficiency (>95%) than does a semiaromatic polyamide active layer (80%) [59]. Similar to using pH to allow BPA to adsorb to zeolite, controlling the ability for nanofilters to remove BPA can be improved by increasing the pH. Polyethersulfone filters achieved 90% removal efficiency at a pH greater than 8, but the effectiveness quickly dropped in acidic solutions [60].

As does NF, reverse osmosis (RO) uses pressure to force water to cross a semi-permeable membrane against the osmotic gradient. A study of various exclusion membranes has shown that RO has very high removal of BPA, at 50 mg/L [59]. Both RO and NF fail to destroy BPA, and a stock of concentrated BPA must be dealt with after treatment. Biofouling can also significantly reduce the lifetime of NF and RO membranes, increasing maintenance costs and reducing overall efficiency.

**Table 2.3. Filtration and reverse osmosis methods for BPA treatment**

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>Concentration of treated BPA*</th>
<th>Removal efficiency (%)</th>
<th>Notes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanofiltration</td>
<td>5 ppm</td>
<td>90, from pH 8 wastewater</td>
<td>Polyethersulphone nanofiltration membrane, modified to have a negative charge</td>
<td>[61]</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>10 ppb</td>
<td>47</td>
<td>BPA removal efficiency was initially high, about 89%, but dropped after sufficient solution was filtered</td>
<td>[62]</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>50 ppm</td>
<td>98</td>
<td>AD Reverse Osmosis membrane from GE Osmonics</td>
<td>[60]</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>100-600 ppb</td>
<td>92</td>
<td>Polyethersulphone ultrafiltration membrane with molecular weight cutoff ranging from 2000 to 10000</td>
<td>[59]</td>
</tr>
</tbody>
</table>

*Measured in parts per million (ppm) or parts per billion (ppt)
2.7.4 Adsorption of BPA onto Activated Carbon, Carbon Nanotubes, Biochar, and Zeolite

Adsorption is a passive process in which a chemical contaminant interacts with the surface of an adsorbent. The process removes the contaminant from the aqueous phase and locks it in the solid phase. All adsorbents eventually foul and must be regenerated in some manner. Thermal regeneration is common, but it is difficult to perform on site and often requires massive energy input.

Adsorption can be driven by a variety of chemical interactions between the adsorbent and the adsorbate. Some of these forces can be generally weak, e.g., Van der Waals or π-π interactions. Interactions such as hydrostatic forces and hydrogen bonding can form significantly stronger bonding between the adsorbent and adsorbate. BPA has a high pKa (~10.9) and has a high K_{ow} (~3.9) at pH 7, indicating that it is relatively non polar except in environments having strongly alkaline pH.
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbent type</th>
<th>BPA concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Adsorption time (days or hours)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Notes</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powdered biochar (75 µm sieve)</td>
<td>Powdered activated carbon</td>
<td>2-11</td>
<td>NR</td>
<td>3.5</td>
<td>7</td>
<td>39.5</td>
<td>Activated in a pure Nitrogen atmosphere</td>
<td>[63]</td>
</tr>
<tr>
<td>Powdered biochar (75 µm sieve)</td>
<td>Powdered activated carbon</td>
<td>2-11</td>
<td>NR</td>
<td>3.5</td>
<td>7</td>
<td>19.4</td>
<td>Activated in a 97% Nitrogen 7% Oxygen atmosphere</td>
<td>[63]</td>
</tr>
<tr>
<td>PAC (Calgon WPH)</td>
<td>Powdered activated carbon</td>
<td>2-11</td>
<td>NR</td>
<td>3.5</td>
<td>7</td>
<td>33.8</td>
<td></td>
<td>[63]</td>
</tr>
<tr>
<td>Powdered biochar (75 µm sieve)</td>
<td>Powdered activated carbon</td>
<td>2-11</td>
<td>NR</td>
<td>10.5</td>
<td>7</td>
<td>33.3</td>
<td>Activated in a pure Nitrogen atmosphere</td>
<td>[63]</td>
</tr>
<tr>
<td>Calgon BPL activated carbon 200 Mesh</td>
<td>Granular activated carbon</td>
<td>60-100</td>
<td>25</td>
<td>7</td>
<td>2 h</td>
<td>253.8</td>
<td>Bituminous-coal-based activated carbon</td>
<td>[64]</td>
</tr>
<tr>
<td>Calgon PCB activated carbon 200 Mesh</td>
<td>Granular activated carbon</td>
<td>60-100</td>
<td>25</td>
<td>7</td>
<td>2 h</td>
<td>208.1</td>
<td>Coconut-based biochar</td>
<td>[64]</td>
</tr>
<tr>
<td>Westvaco A1100 0.4-0.8 mm</td>
<td>Granular activated carbon</td>
<td>60</td>
<td>25</td>
<td>7</td>
<td>50 h</td>
<td>382.12</td>
<td></td>
<td>[65]</td>
</tr>
<tr>
<td>Westvaco A1100 (acid treated) 0.4-0.8 mm</td>
<td>Granular activated carbon</td>
<td>60</td>
<td>25</td>
<td>7</td>
<td>50 h</td>
<td>59.17</td>
<td>Acid treated with concentrated nitric acid, and heated to 95°C for 6 h</td>
<td>[65]</td>
</tr>
<tr>
<td>Westvaco A1100 (Thermal Oxidized) 0.4-0.8 mm</td>
<td>Granular activated carbon</td>
<td>60</td>
<td>25</td>
<td>7</td>
<td>50 h</td>
<td>432.34</td>
<td>Thermally Oxidized in a nitrogen atmosphere at 800°C for 3 h</td>
<td>[65]</td>
</tr>
<tr>
<td>Graphene</td>
<td>Carbon Nanomaterial</td>
<td>2-50</td>
<td>29</td>
<td>6</td>
<td>5 h</td>
<td>181.6</td>
<td></td>
<td>[66]</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>Adsorbent type</td>
<td>BPA concentration (ppm)</td>
<td>Temperature (°C)</td>
<td>pH</td>
<td>Adsorption time (days or hours)</td>
<td>Adsorption capacity (mg/g)</td>
<td>Notes</td>
<td>Source</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------------------</td>
<td>-------------------------</td>
<td>------------------</td>
<td>----</td>
<td>-------------------------------</td>
<td>---------------------------</td>
<td>--------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>MWCNT OD 30-50</td>
<td>Carbon Nanomaterial</td>
<td>0.1-40</td>
<td>25</td>
<td>NR</td>
<td>7 d</td>
<td>100.0</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>(Sigma Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWCNT</td>
<td>Carbon Nanomaterial</td>
<td>0.1-40</td>
<td>25</td>
<td>NR</td>
<td>7 d</td>
<td>912.0</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>(Sigma Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fullerene</td>
<td>Carbon Nanomaterial</td>
<td>0.1-40</td>
<td>25</td>
<td>NR</td>
<td>7 d</td>
<td>2.3</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>(Sigma Aldrich)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWCNT</td>
<td>Carbon Nanomaterial</td>
<td>0.23</td>
<td>NR</td>
<td>7</td>
<td>4h</td>
<td>16.05</td>
<td>Brackish Water</td>
<td>[68]</td>
</tr>
<tr>
<td>Surfactant-Modified</td>
<td>Mineral</td>
<td>0.5-100</td>
<td>25</td>
<td>10.4</td>
<td>24 h</td>
<td>114.9</td>
<td></td>
<td>[69]</td>
</tr>
<tr>
<td>Zeolite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrophobic Zeolite</td>
<td>Mineral</td>
<td>10-90</td>
<td>25</td>
<td>7</td>
<td>2 h</td>
<td>111.1</td>
<td></td>
<td>[70]</td>
</tr>
<tr>
<td>Polyethersulfone</td>
<td>Mineral</td>
<td>23-55</td>
<td>25</td>
<td>NR</td>
<td>8 h</td>
<td>32.05</td>
<td></td>
<td>[71]</td>
</tr>
<tr>
<td>(PES)–organophilic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>montmorillonite (OMMT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hybrid particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Fe(III)/Cr(III)</td>
<td>Mineral</td>
<td>10-50</td>
<td>Room Temp</td>
<td>NR</td>
<td>NR</td>
<td>31.96</td>
<td></td>
<td>[72]</td>
</tr>
<tr>
<td>Imprinted polymers</td>
<td>Polymer</td>
<td>20-400</td>
<td>25</td>
<td>3</td>
<td>12 h</td>
<td>112.4</td>
<td>Kaolinite core coated in a layer of Fe₃O₄, and a layer of polymer</td>
<td>[73]</td>
</tr>
</tbody>
</table>
Carbon-based materials are widely used as adsorbents. Carbon can be altered to be either polar or non-polar, which allows for various contaminants to be adsorbed. Adsorbents can be manufactured from natural sources, in the case of biochar, or petroleum sources to make activated carbon. Carbon Nanotubes (CNT) are a relatively new adsorbent, based on tubes of graphene on the nanoscale.

### 2.7.5 Zeolite and Mineral Based Adsorbents

Zeolite has been widely used for the adsorption of organic contaminants from wastewater [69, 70, 74-80]. Most mineral adsorbents such as titanium dioxide or activated bleaching earth are hydrophilic and have low BPA adsorption capacities [64]. Hydrophobic zeolite, however, has BPA adsorption capacities similar to those found with activated carbon. Unlike activated carbon, zeolite is more resilient to thermal decomposition during regeneration [69, 70]. Attaching a surfactant to the zeolite surface greatly enhances BPA adsorption, but only at alkaline pH. These pH levels are not normally seen in most wastewaters and would require pre- and post- treatment adjustments [69]. BPA binds best to zeolite when it has been deprotonated, becoming an organic ion.

### 2.7.6 Biochar

Because it is made mostly from agricultural wastes, biochar is a very economical adsorbent. Its natural origin also means that it has a variety of functional groups on the surface. For polar contaminants this can greatly improve adsorption. BPA as a mostly non-polar compound can often be repelled by polar functional groups. Even slight alterations to the production of the biochar can lead to greatly altered surface chemistry and surface area [81-83]. Because of these changes in chemistry several sources of and manufacturing methods for biochar need to be changed to define the optimum chemistry for BPA removal.

Biochar has been studied for the physical treatment of BPA in wastewater environments. However, most biochar has polar surface chemistry. BPA is non polar, and partially hydrophobic at acidic and even neutral pH, at high pH (>11) the hydrogens disassociate from the OH groups,
giving BPA a negative charge. As seen in Jung et al. the adsorption of BPA is relatively low, except in basic pH [63].

2.7.7 Activated Carbon
Activated carbon (AC) is similar to biochar, but it is derived from carbon materials such as coal or oil. Activated carbon can be used in both a granular form (GAC) and a powdered form (PAC). Both types have been widely used in wastewater treatment as a method for adsorbing organic contaminants. AC’s adsorption potential is derived from the large number of mesopores throughout the body of the material. This greatly increases the functional surface area, providing many sites for adsorption [65, 84, 85].

2.7.8 Graphene
Graphene is a 2-dimensional sheet of carbon, which has shown potential for waste water treatment [66, 86, 87]. The multiple C=C bonds allow for effective π-π interactions with contaminants [66]. Graphene has been shown to be more effective than CNTs as an adsorbent of BPA (table 2.4), it still has less capacity than activated carbons. Computer modeling of the adsorption of BPA to the surface of graphene estimates the energy of adsorption to be -34.1 kcal/mol, greater than that of single walled CNTs, estimated at -22.5 kcal/mol [88].

2.7.9 Carbon Nanotubes
Carbon nanotubes are a new technology offering many possible applications in wastewater treatment. Though produced using many different methods, basically they are all composed of sheets of graphene forming three-dimensional cylinders. Two primary types are single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Both offer the high adsorption potential of organic contaminants, due to their very large surface area to mass ratio. The graphene surfaced can be modified with a variety of functional groups, thus changing the surface chemistry of the nanotubes [89-93]. Treatment of CNTs with strong acids can create negatively charged functional groups on the surface of the CNTs and cut the capped ends, increasing surface area. To achieve this level of modification the CNTs must be suspended in a 3:1 mixture of concentrated H₂SO₄ and HNO₃, then refluxed at high temperature [94]. Acid modification generally creates –OH and –COOH functional groups on the surface of CNTs. Other modification methods can create several functional groups –NH₂, -COOR, and –NR, to
name a few. Different functional groups have different effects on CNT dispersion in water, and several can have other compounds amended to them through secondary treatments [95].

The adsorption of aromatic compounds with benzene rings, like BPA, is mainly a result of $\pi-\pi$ interactions. The molecular structure of graphene has many $\pi$ electron sites for these compounds to bind to [96]. BPA though, also has a three dimensional “butterfly” shape, with the two phenol moieties folding in toward each other. The butterfly shape allows BPA to form a wedge, thus better fitting into the space between CNTs. Additionally BPA has access to binding sites not normally available to other planar molecules, like estradiol. Figure 2.3 shows the three-dimensional structure of BPA compared to estradiol [91]. Pan and Xing describe the binding of BPA in both the presence and the absence of estradiol. BPA was still able to be adsorbed to carbon nanomaterials previously saturated with estradiol. Their research indicated both competitive and complementary adsorption of BPA and estradiol [67].

![Figure 2.3. Three-dimensional structure of BPA (A) and Estradiol (B) as rendered with Accelrys Draw 4.1 SP1.](image)

Several studies have used SWCNT and MWCNT to observe the adsorption of EDCs and other contaminants for wastewater treatments [49, 68, 86, 91, 92, 97-101]. Though effective at removing contaminants from wastewater streams, CNTs, like other adsorbents, must be
regenerated or replaced once they have become saturated. Fewer studies have looked at combining regeneration processes with the adsorbent [100, 102-104].

2.7.10 Chemical Treatment of Bisphenol A
Chemical treatments, unlike physical treatments, actually degrade contaminants to the point that they become harmless compounds. Chemical treatments of tainted ground water have been used in the past for remediation. Reduction and oxidation are two chemical reactions commonly used for the treatment of contaminants. Advanced oxidative processes (AOP) are becoming of greater interest for the field of water treatment. Utilizing a variety of methods including ozonation, ultraviolet light, electrolysis, and Fenton oxidation, these processes all rely on the production of hydroxyl radicals to oxidize electron-rich contaminants.

2.7.11 Ozonation
Ozone ($O_3$) can be used to oxidize a wide range contaminants, including BPA. In terms of oxidative potential $O_3$ is surpassed only by hydroxyl radicals. Ozone can be generated on site, but it requires significant energy input. Oxidation by ozone is initiated via two pathways: first aqueous ozone reacts directly with the target contaminant; aqueous ozone also reacts with hydroxide ions ($OH^-$) to form hydroxyl radicles ($\bullet OH$) through a chain of radical-radical and radical-solute reactions [105, 106]. The radical production process less effective at lower pH as fewer hydroxide ions are available to decompose the ozone. Ozone gas is also toxic and is considered an air pollutant. Kusvran et al. found that high concentrations of BPA (100 ppm) can be nearly completely removed with an ozone treatment at pH=3 in under 30 minutes [107]. Using lower concentrations of BPA (10 ppm) Garoma et al. found that ozone remained effective even up to pH 7. Their ideal ozone/BPA ratio to fully degrade the BPA ranged from 7.0 to 9.5 mol/mol [105].

2.7.12 Fenton Oxidation
The Fenton reaction was originally discovered in the late 1800’s. It utilizes the generation of hydroxyl radicals by reacting hydrogen peroxide and ferrous iron. The radicals generated quickly react with electron-rich compounds like the phenol rings in BPA. Fenton and Fenton-based reactions have been successfully shown to degrade a wide variety of compounds, using environmentally safe compounds [108-122]. The reaction itself is most efficient around pH=3. When ferrous ions are suspended in aqueous solution, known as homogeneous Fenton oxidation,
the reaction is controlled by the formation of insoluble iron hydroxides. Because these hydroxides precipitate less and less iron is available to catalyze hydrogen peroxide and radicals, production is slowed. Eventually an insoluble iron sludge forms and must be disposed of [123].

The basic reactions for Fenton oxidation are reported as follows:

\[
\begin{align*}
\text{Fe(II) + H}_2\text{O}_2 & \rightarrow \text{Fe(III)} + \cdot\text{OH} + \text{OH}^- \quad (1) \\
\text{k} & = 63 \text{ M}^{-1}\text{s}^{-1} \\
\text{Fe(III) + H}_2\text{O}_2 & \rightarrow \text{Fe(II)} + \text{HO}_2\cdot + \text{H}^+ \quad (2) \\
\text{k} & = 0.01 \text{ M}^{-1}\text{s}^{-1} \\
\cdot\text{OH} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2\cdot + \text{H}_2\text{O} \quad (3) \\
\text{k} & = 2.7\times10^7 \text{ M}^{-1}\text{s}^{-1} \\
\cdot\text{OH} + \text{Fe(II)} & \rightarrow \text{Fe(III)} + \text{OH}^- \quad (4) \\
\text{k} & = 3.2\times10^8 \text{ M}^{-1}\text{s}^{-1} \\
\text{Fe(III) + HO}_2\cdot & \rightarrow \text{Fe(II)} + \text{H}_2\text{O}^+ \quad (5) \\
\text{k} & = 3.1\times10^5 \text{ M}^{-1}\text{s}^{-1} \\
\text{Fe(II) + HO}_2\cdot + \text{H}^+ & \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2 \quad (6) \\
\text{k} & = 1.1\times10^6 \text{ M}^{-1}\text{s}^{-1} \\
\text{HO}_2\cdot + \text{HO}_2\cdot & \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O} \quad (7) \\
\text{k} & = 8.3\times10^5 \text{ M}^{-1}\text{s}^{-1}
\end{align*}
\]

Reactions 1-7 have been widely studied, and they address the iron cycling (Reactions 1, 2, 5, and 6) and the regeneration of hydrogen peroxide (Reactions 6 and 7) [124-126]. The formation of •OH radicals, the primary contaminant oxidant, is generated only during reaction 1. The Fe(III) generated in reaction 1 is slowly regenerated by reaction 2. HO_2• radicals are more efficient at regenerating Fe(II) (Reaction 5). The Fenton reaction cycle is terminated by reactions 3 and 4, where hydroxyl radicals are scavenged by excess hydrogen peroxide or Fe(II). As reactive Fe(II) is consumed Fenton reactions will exhibit a two-phase process. The first phase is the rapid
consumption of H₂O₂ and conversion of Fe(II) to Fe(III). The second phase is when the conversion of Fe(III) to Fe(II) becomes the rate limiting step.

The addition of aromatic hydrocarbons greatly changes the equilibrium of the reaction. When hydroxyl radicals react with aromatic ring structures, a carbon-centered radical forms. This radical cycles through the resonance structures of the aromatic compounds, stabilizing the complex. When O₂ is present in the solution, further reactions will generate HO₂•, which is a major radical in the formation of H₂O₂ (Reactions 6 and 7). The reactions that generate the HO₂• have a very high rate constant (10⁹ M⁻¹ S⁻¹) [125]. The regeneration of H₂O₂ via HO₂• is also very fast compared to the consumption of H₂O₂ through hydroxyl radical formation. This means that under acidic and oxygenated conditions hydrogen peroxide can be generated almost as quickly as it can be consumed. Eventually the concentration of O₂ or organic contaminants will become a limiting factor in the production of HO₂•, and the rate of peroxide regeneration will slow to below that of consumption.

The carbon radicals can also undergo condensation reactions with other carbon-based radicals, forming ester bonds between two partly oxidized contaminants. As the reaction progresses these condensation byproducts are eventually oxidized into smaller compounds [126].

2.7.13 Heterogeneous Fenton Oxidation

A heterogeneous Fenton system can be created by keeping the iron in the solid phase, either as a colloid or utilizing a solid support. Heterogeneous Fenton oxidation does not produce iron sludge, and the manufactured catalysts can be reused multiple times. Even at higher pH the catalyst remains active, but higher doses of H₂O₂ are required to enable the reaction [122, 127]. Heterogeneous catalysts can also act as an adsorbent of the contaminant, localizing it near the site of radical formation. With this localization even low and ultra-low levels of BPA can be treated without radical scavenging.

Multiple compounds can be used to support iron oxides/hydroxides. Generally carbon-based adsorbents such as biochar, GAC, and CNTs are effective at adsorbing contaminants including BPA. Biochar and GAC have mesopores and micropores that can be clogged by excess iron, thus reducing the adsorption capacity. CNTs behave slightly differently, as the amount of iron adsorbed onto the CNTs the exposed carbon surface area is reduced. Eventually all of the active
adsorption sites are replaced by iron and the adsorption capacity becomes negligible. Often carbon-based supports are pretreated with acid. This serves two purposes: first, the carbon supports are cleaned of amorphous carbon, and second, –COOH functional groups are formed. The negatively charged groups attract the positively charged iron ions. As an alternative to carbon supports iron can also be supported by inorganic supports such as clays, iron-rich minerals, and zeolite [119].

The oxidative state of the iron amended to the support plays an important role in the Fenton reaction. Generally ionic iron is more reactive than iron hydroxides, and iron oxides are even less reactive. An advantage of iron oxides is that they are more stable than other species. There is even variation among different iron oxides. Two predominant species, Fe₃O₄ and Fe₂O₃, have been shown to have both Fenton potential and magnetic properties. Fe₃O₄ (magnetite) has the advantage of being composed of both Fe²⁺ and Fe³⁺, the Fe²⁺ is more Fenton active than the Fe³⁺ [128]. Fe₂O₃ can form multiple crystal forms. Hematite α-Fe₂O₃ is the most common crystal, and it effectively catalyzes Fenton reactions for the degradation of contaminants. In contrast, γ-Fe₂O₃ (maghemite) has the same crystal structure as magnetite. It possesses the same Fenton potential as hematite, but it has the magnetic properties of magnetite. The species of FeOOH vary greatly. Goethite has been shown to be active as a Fenton catalyst. Green rust, a Fe (II) (OH)₂, is an active catalyst, but it is less stable in aerobic aqueous environments, eventually oxidizing and forming new species of iron [129].

The physical characteristics of the iron catalysts, such as, size, crystal shape, and crystallinity, affect the surface area of the catalyst. An increase in the exposed surface allows more iron to be available for the hydrogen peroxide. Changes in the crystal shape also alter the exposed surface area. Hermanek et al. found that whereas surface area plays an important role in the catalytic decomposition of H₂O₂, the quality of the surface can cause a profound increase in the reaction rate. By heat treating Fe₂O₃ nanoparticles at 175°C the surface area decreases with prolonged exposure to the high temperatures. While the surface area decreased, the crystallinity of the nanoparticles increased [130].

Fenton-like reactions use non-iron transition metals to produce hydroxyl radicals. Iron oxides like magnetite can easily have different ions take the place of the iron atoms in the crystal structure. Depending on the metal added to the catalyst the Fenton activity can be greatly
enhanced [131-133]. Some metals, on the other hand, greatly decrease the Fenton activity. When using zinc as a doping metal researchers found that FeZnO4 was an effective photo-catalyst at the visible wavelength [134].
Chapter 3 Proof of Concepts

3.1 Introduction

Harmful effects of endocrine disrupting chemicals on human and environments has been of great concern over the past couple of decades [101]. Significant amounts of bisphenol A (BPA), an endocrine disrupting chemical, have been released from the manufacturing process of plastics, epoxy resins, dental material and flame retardants [12-14, 135, 136]. The level of BPA in wastewater treatment facilities ranges from a few ppb up to several ppm [137]. Recent studies have reported estrogenic activity of BPA at concentrations as low as 0.2 pg/mL causing disruption in the endocrine system while leading to infertility, breast and thyroid cancers [21, 138]. Therefore, there is an urgent need for developing effective technology to remove BPA from wastewater and water.

Up to date, several methods such as adsorption, biological treatment and advanced oxidation have been studied for destruction of aqueous BPA [137, 139-141]. Biological treatment would be economical, but requires long time to degrade BPA [52, 57, 142, 143]. Conventional biological treatment has demonstrated poor and fluctuating removal efficiency of BPA because of the high bio-refractory property and very low concentration of BPA [20, 144]. Adsorption is simple and effective, but it requires high operating costs associated with the regeneration of contaminant-spent adsorbents [112, 145].

Compared to adsorption and biodegradation, advanced oxidation processes have shown excellent removal of various contaminants because of the non-selective and strong oxidation capacity of hydroxyl radicals [146]. Advanced oxidation processes include ozone, H$_2$O$_2$, O$_3$/H$_2$O$_2$, H$_2$O$_2$/UV, O$_3$/UV, Fenton or photo-Fenton oxidation, photocatalytic oxidation, electrochemical oxidation and sonochemical oxidation [117, 120, 125, 147-150]. Fenton oxidation, among advanced oxidation technologies, has been widely used for wastewater and soil treatment [151]. Fenton oxidation generates hydroxyl radicals to oxidize a variety of contaminants when H$_2$O$_2$ is reacted with transition metal catalysts including various forms of iron [132, 133]. Fenton oxidation has several advantages such as high oxidation efficiency, mild reaction conditions, environmentally benign materials and simple operation[152]. However, it is efficient only at
acidic pH (pH< 4), production of iron sludge and costs for disposal of iron sludge after Fenton oxidation[151].

For overcoming the shortcomings of homogeneous Fenton oxidation, heterogeneous Fenton oxidation was found to be an efficient and cost-effective method, in which iron catalyst are immobilized onto solid supports (i.e., activated carbon, carbon nanotube, zeolite, clay [97, 104, 108, 110, 111, 153, 154]). Heterogeneous Fenton oxidation can destroy organic contaminants over a broad range of pH, reduce the loss of iron catalyst, and generate little iron sludge [155, 156]. Particularly carbon nanotube-supported iron oxides have been actively studied for heterogeneous oxidation of contaminants such as azo dyes and estrogens due to their large reactive area, good dispersion of iron oxides, and high reaction rate [97, 157]. However, the small size of carbon nanotube-based catalyst makes them difficult to remove or recycle after treatment. The health risks associated with releasing carbon nanotube into the environment are not completely known, and therefore it is necessary for carbon nanotube-based catalyst to be recycled before discharge to the environment [158]. Recently the multi-walled carbon nanotube-supported magnetite (Fe₃O₄-MWCNT) as the heterogeneous catalyst for Fenton oxidation has been synthesized [97, 159]. The Fe₃O₄-MWCNT has demonstrated high oxidation efficiency of the aqueous contaminants (i.e., 17α-methylestosterone and synthetic dyes) and excellent magnetic separation after treatment [97, 160].

Most of Fenton oxidation of BPA in water have been conducted using homogenous Fenton reactions except a few studies utilizing iron based nanoparticles. Huang et al. [161] investigated the sonochemical heterogeneous Fenton of BPA using Fe₃O₄ nanoparticles. Zhang et al. [155] and Wang et al. [156] investigated the Fenton oxidation of BPA using CuFeO₂ and BiFeO₃ nanoparticles. However, to the best of our knowledge, there have been no studies for the heterogeneous Fenton of aqueous BPA using the MWCNT-supported magnetite (Fe₃O₄-MWCNT). So far most studies were mainly focused on the novel synthesis and characterization of the Fe₃O₄-MWCNT catalysts and their potential application for heterogeneous oxidation of contaminants.

Therefore, the objective of this study is to investigate the effects of the reaction conditions (catalyst and H₂O₂ loading, initial pH and reaction temperature) on Fenton oxidation of BPA using the Fe₃O₄-MWCNT catalyst. The reusability and stability of the Fe₃O₄-MWCNT catalyst
for treating aqueous BPA was also examined over the multiple cycles of Fenton oxidation. In addition, the removal of BPA by Fenton oxidation using the Fe₃O₄-MWCNT in this study was compared with those by homogeneous and heterogeneous Fenton oxidation of BPA reported by others.

3.2 Methods
3.2.1 Catalyst Synthesis
Originally a passive adsorption method was used in attempt to amend iron ions to the surface of the MWCNT. MWCNT were suspended in 50 ppm Fe²⁺ solution prepared with FeCl₂. The iron concentration was monitored until it reached equilibrium, over the course of several days. MWCNT were also treated in a 2:1 solution of concentrated sulfuric and nitric acid. The acid treated MWCNT were then treated with the 50 ppm Fe²⁺ solution. After the adsorption of Fe²⁺ concentration reached equilibrium the MWCNTs were separated from the solution and dried at 70°C.

The pH point of zero charge (pHpzc) was calculated by adding 10 mg of MWCNT samples to 20 mL of nanopure H₂O, which was sparged with He gas and set to pH ranging from 3 to 11. The samples were shaken overnight and the pH was then remeasured. The pHpzc was the point where there was no change between the initial pH and the final pH.

To synthesize Hematite (Fe₂O₃)-MWCNT catalysts, a hydrogen peroxide was applied drop wise to a solution of FeSO₄ and MWCNT. The addition of hydrogen peroxide initiated the precipitation of Fe(OH)₂ onto the surface of the MWCNT. The temperature of the reaction was kept at 70°C by controlling the rate of H₂O₂ addition. When the reaction was finished an orange/yellow powder formed mixed with black MWCNT. The resulting powder was then calcined at 400°C for 4 hours, resulting in an ocher red powder. The calcination process further oxidized the Fe(OH)₂ to form Fe₂O₃.

The Fe₃O₄ (magnetite)-MWCNT catalyst was synthesized by the in-situ chemical precipitation/oxidation method modified reported by Hu et al. (2011) [97]. For preparing Fe₃O₄-MWCNT catalyst, the MWCNT slurry (30 mg of the MWCNT in 150 mL DI H₂O) was sonicated with a ultrasonic cell disruptor (Misonix, Farmdale, NY; 22.5 kHz, 30 watt) for 1 minute and then suspended in 450 mL DI H₂O. The solution was sparged with nitrogen gas for 25 minutes and placed in a 95 °C water bath. 10 g ferrous sulfate was then dissolved into the
warmed solution while 9 g NaOH and 4.5 g NaNO₃ were dissolved in 200 mL DI H₂O and placed in a 95 °C water bath. The mixture of the MWCNT and ferrous sulfate was placed under vigorous stirring and a nitrogen flow. This method of magnetite synthesis has been described before, as a combination of deposition of ferrous hydroxides and controlled oxidation forming Fe₃O₄ nanocrystals [162] (Reactions 8-11).

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe (OH)}_2 \tag{8}
\]

\[
3\text{Fe(OH)}_2 + \text{NO}_3^- \rightarrow \text{Fe}_3\text{O}_4 + \text{NO}_2^- + 3\text{H}_2\text{O} \tag{9}
\]

\[
3\text{Fe(OH)}_2 + \text{NO}_2^- \rightarrow \text{Fe}_3\text{O}_4 + \text{NO} + 3\text{H}_2\text{O} \tag{10}
\]

\[
15\text{Fe(OH)}_2 + 2\text{NO} \rightarrow 5\text{Fe}_3\text{O}_4 + 2\text{NH}_3 + 12\text{H}_2\text{O} \tag{11}
\]

After the NaOH/NaNO₃ solution was slowly added to the MWCNT/ferrous sulfate mixture dropwise, the mixed solution was transferred to a 95 °C water bath for 2 h to finish the reaction. The Fe₃O₄-amended MWCNT separated from the solution was washed in DI water and absolute methanol under sonication. The final Fe₃O₄-MWCNT catalyst was dried overnight in a 100 °C oven.

The by replacing some of the initial ferrous iron with transition metals. Zn²⁺ can be incorporated into the Fe₃O₄ crystal lattice and maintain the reverse spinal structure. However because Zn cannot form ³⁺ ions it does not replace the ferric atom in magnetite. For this project on third of the Fe²⁺ in the initial reaction was replaced with Zn²⁺ in the form of ZnCl₂, the NaOH and NaNO₃ were kept at the same ratio to ensure complete deposition and oxidation of the zinc ferrites.

**3.2.2 Electron Microscopy, XRD, and XPS Characterization**

The scanning electron microscopy (SEM) images and X-ray energy dispersive spectroscopy data (EDX) were obtained with Hitachi HT7700 field emission scanning electron microscope (10 kV). Transmission electron microscopy (TEM) images were obtained with Hitachi S-4800 at 100kV. Powder X-ray diffraction (XRD) patterns of the powered sample were performed on a Rigaku MiniFlex II diffractometer with a Cu Kα radiation source.
3.2.3 Fenton Oxidation

Batch style Fenton oxidation was initially investigated with 98% Fe₃O₄-MWCNT and with high (70 ppm) concentrations of BPA. Unless otherwise stated 50 mg of Fe₃O₄-MWCNT were suspended in 100 mL 70 ppm BPA solution which was previously set to pH 3. The Fenton reaction was initiated by injecting H₂O₂ into the flask. Samples were taken at regular intervals, and measured via HPLC after centrifuging. The effect of pH was tested ranging from 3-7, all other reactions were carried out at pH 3. The effect of catalyst loading was investigated by altering the Fe₃O₄-MWCNT dose from 25-100 mg. To investigate both efficient removal of BPA, and total mineralization of the contaminant both low (2-12 mol H₂O₂/mol BPA) and high (36-108 mol H₂O₂/mol BPA) were investigated.

3.2.4 Toxicology Testing

The toxicity of BPA and the reaction intermediates was calculated using the Toxi-Chromo biotoxicity test kit (Environmental Bio-detection Products Inc. Ontario, Canada). This kit measures the ability for Escherichia coli to recover and produce β-galactosidase. In the presence of a toxic compound the bacteria are unable to recover, and no color will develop. Non-toxic compounds result in a dark blue color which can be measured on a spectrophotometer at 615 nm. By measuring the intensity of color development the minimum inhibition concentration (MIC) can be calculated, the MIC is the concentration which causes 20% inhibition.

3.2.5 High Performance Liquid Chromatography

BPA concentration in water was measured on a Waters 2690 separations module with a Waters 996 photo diode array at 235 nm using a Phenomenex Aries Peptide column (3.6 µm XB-C18, 150x4.60 mm). The Aries Peptide columns are solid cores of silica encased in layers of pours silica, then coated with XB-C18 to produce a hydrophobic surface. The solid core style of packing material allows for reduced adsorption/desorption time onto the particles. The Aries Peptide packing material also has a narrower size distribution, allowing for more even packing in the column. The even packing further reduces spreading. The mobile phase was 42% water and 58% HPLC grade methanol applied as an isocratic run with a constant flow rate of 1 ml/min. The runs lasted for ten minutes with a five minute delay between injections to allow for the column to equilibrate. Separate calibration curves were created for varying sample methanol concentrations.
To measure sub ppb concentrations of BPA, a waters 2475 fluorescence detector was used with an excitation wavelength of 285 nm and emission of 325 nm. The same column, flow rate, and solvent conditions were used. A waters 2695 separation module was used, and data was acquired with Empower™ software.

3.3 Results and Discussion

3.3.1 Catalyst Characterization

The SEM images of the H$_2$O$_2$ deposited iron MWCNTs show a clear difference before and after the calcination process. The non calcined Fe-MWCNT showed large flaky deposits of iron hydroxides attached to the surface of the MWCNT (Figure 3.1 A). After calcination (Figure 3.1 B) the flat rod like iron deposits were replaced with small (10-30 nm) beads of iron oxide. Most of the iron was found separate from the MWCNT, and only after significant searching of the TEM grid was a MWCNT associated with the iron particles found. The MWCNT’s surface was pitted and damaged indicating severe oxidation.

Figure 3.1. TEM image of H$_2$O$_2$ deposited iron-MWCNT before (A) and after calcination for four hours at 400°C (B).
The Fe₃O₄-MWCNT showed excellent crystal formation under TEM imaging. There was a regular distribution of octahedral crystals ranging from ~150-200 nm. Though larger than the Fe₂O₃ crystals the Fe₃O₄ crystals were regularly associated with the MWCNTs (Figure 3.2).

![Figure 3.2. TEM image of Fe₃O₄-MWCNT](image)

SEM imaging of the Fe₃O₄-MWCNT catalyst further confirmed the crystal shape and gross topography of the catalyst particles and aggregates (Figure 3.3). EDX analysis confirmed the presence of iron, oxygen, and carbon (Figure 3.4).
Figure 3.3. SEM image of the Fe$_3$O$_4$-MWCNT catalyst.

Figure 3.4. EDX chromatogram indicating the presence of carbon oxygen and iron in the Fe$_3$O$_4$-MWCNT catalyst.

XRD analysis was used to determine the crystal structure of the catalyst. The H$_2$O$_2$ precipitated iron-MWCNT did not have a strong crystal structure and did not correlate with either Fe$_2$O$_3$ or Fe$_3$O$_4$ spectrums in the libraries available (Figure 3.5). However after calcination the 2θ peaks associated with Fe$_2$O$_3$ became very apparent (Figure 3.6). This indicates that the calcination
process further oxidized iron hydroxides to form crystalline Fe$_2$O$_3$ the XRD data also indicates that the Fe$_2$O$_3$ is in the $\alpha$ phase not the $\gamma$ phase, and therefore not magnetic. The Fe$_3$O$_4$-MWCNT had clear peaks and Miller indices associated with Fe$_3$O$_4$ (Figure 3.7), with XRD data alone it is possible that the crystals could be $\gamma$-Fe$_2$O$_3$ measuring the surface chemistry with XPS could further verify the composition of the catalyst.

Figure 3.5. XRD comparison of Non Calcined H$_2$O$_2$ Precipitated iron-MWCNT catalyst (Black Line) and Fe$_2$O$_3$ spectrum from the RUFF.info library (Red line).
Figure 3.6. XRD comparison of Non Calcined H$_2$O$_2$ Precipitated iron-MWCNT catalyst (Black Line) and Fe$_2$O$_3$ spectrum from the RUFF.info library (Red line).

Figure 3.7. XRD spectrum of Fe$_3$O$_4$-MWCNT (black) compared with the RUFF.info libraries of Fe$_3$O$_4$ (green) and Fe$_2$O$_3$ (red).
To confirm the surface chemistry of the Fe₃O₄-MWCNT the catalyst was sent to an offsite lab for XPS analysis. The Fe 2p ½ and the Fe 2p 3/2 were at 724 and 710 eV respectively (Figure 3.8). These peaks indicate the presence of both Fe²⁺ and Fe³⁺ characteristic of magnetite.

![Figure 3.8. XPS analysis of the Fe₃O₄-MWCNT the insert is the detailed scan of the Fe 2p section.](image)

### 3.3.2 Heterogeneous oxidation of BPA by the Fe₃O₄-MWCNT catalyst

There was negligible adsorption of BPA onto the Fe₃O₄-MWCNT over a 24 h adsorption test. This was mainly due to the structure of the Fe₃O₄-MWCNT in which the Fe₃O₄ (∼90% of Fe₃O₄-MWCNT) fully covered the MWCNT.

The charged surface of the Fe₃O₄ also interfered with BPA adsorption on the Fe₃O₄-MWCNT catalyst as other authors have observed hydrophobic interaction (π-π interaction) as the major adsorption mechanism of BPA [65, 68]. Thus, the Fe₃O₄-MWCNT did not act as an adsorbent for BPA. Rather, the major role of MWCNT for the heterogeneous Fenton oxidation of BPA was the excellent support for the Fe₃O₄ while the MWCNT enhanced dispersion of iron oxide onto large surface area of MWCNT. As observed by our investigation and others’ studies, the Fe₃O₄ nanoparticles exhibited significant aggregation which reduced their reactive area and Fenton oxidation rate [161].
Although the Fe₃O₄-MWCNT showed little adsorption of BPA, Fenton oxidation using the Fe₃O₄-MWCNT as a catalyst showed high removal of BPA as seen in Figure 3.9-3.12. Due to the insufficient hydrophobic surface in Fe₃O₄-MWCNT the oxidation of BPA would primarily occur in the bulk aqueous phase. 50-100 mg of the Fe₃O₄-MWCNT catalyst (0.5 g catalyst/L to 1 g catalyst/L) resulted in a rapid and high removal of BPA (66-68% in 2 h; k= 0.58 - 0.61 h⁻¹) whereas 25 mg of the catalyst showed slower removal of BPA (68% in 4 h; k=0.33 h⁻¹) (Figure 3.10). It indicated that increasing loading of the Fe₃O₄-MWCNT catalyst would increase the reactive surface area, the amount of Fe₃O₄ and ·OH production thus enhancing oxidation rate of BPA [127, 130, 161, 163]. The Fenton oxidation of BPA at various catalyst loading (Figure 3.10) also showed significant consumption of the initial H₂O₂ concentration (>90%) and similar decay constant of H₂O₂ (0.038-0.041 h⁻¹).

![Figure 3.9](image_url)

**Figure 3.9.** Effects of catalyst (Fe₃O₄-MWCNT) loading on removal of BPA. Conditions: initial BPA (0.3mM, 0.1 L); initial pH, 3; initial H₂O₂, 0.6 mM; temperature, 20°C. The all measurements were conducted in triplicate.

Fenton oxidation is greatly influenced by the initial pH of the solution. To investigate the effect of pH on the Fenton oxidation of BPA using the Fe₃O₄-MWCNT catalyst, the reaction was
carried out at initial pH of 3-7. The results showed significant removal of BPA at pH 3 (k=0.22 h\(^{-1}\) in 6 h) while surprisingly very slow and little removal of BPA at pH 4, 5 and 7 (0.0001-0.002 h\(^{-1}\) in 48 h; the data not shown). An initial pH of 3 was found to be the optimum pH for the heterogeneous Fenton oxidation of BPA using the Fe\(_3\)O\(_4\)-MWCNT catalyst. This result was similar to the optimum pH for the homogeneous and heterogeneous Fenton oxidation as reported by others [120, 164, 165]. For instance, Hu et al. (2011) showed highest removal of 17α-methyltestosterone at pH 2.5-3.5 and much slower and lower removal at pH 5 and 8 when 17α-methyltestosterone was degraded by heterogeneous Fenton using the Fe\(_3\)O\(_4\)-MWCNT catalyst [97]. Huang et al. also reported decreasing removal of BPA at increasing pH (from 3 to 7) in the heterogeneous Fenton using the Fe\(_3\)O\(_4\) nanoparticles [161].

Determination of the optimum concentration of H\(_2\)O\(_2\) is important to enhance treatment efficiency and minimize operating costs in Fenton oxidation [166, 167]. An increase of [H\(_2\)O\(_2\)]:[BPA] (mol H\(_2\)O\(_2\)/mol BPA) from 2 to 12 enhanced BPA and COD removal efficiency (an indicator for removal of BPA intermediate/products) at 20°C (Figure 3.10). It was found that the [H\(_2\)O\(_2\)]:[BPA] above 4 (4 to 108) showed nearly complete removal of BPA (97%-100%) and significant removal of COD (8%-60%). Besides, the biotoxicity tests using Toxi-Chromotest™ (Environmental Biodetection Products Inc.) revealed minimal inhibition of \(E.\ col\) amongst the final reaction effluents from the Fenton oxidation at the [H\(_2\)O\(_2\)]:[BPA] of 4-12 (data not shown). This clearly showed no biological toxicity of the BPA intermediates and products at these conditions. But, as a control test, 40-100 ppm BPA showed significant biotoxicity effects (inhibition % of 54-100, please see Table 3.1). These results confirmed that the intermediates and products from the Fenton oxidation at the [H\(_2\)O\(_2\)]:[BPA] of 4-12 had negligible toxicity, and could be compatible with further biological treatment. The Fenton oxidation of BPA at various [H\(_2\)O\(_2\)]:[BPA] also exhibited significant consumption of the initial H\(_2\)O\(_2\) concentration (88-100%) except the [H\(_2\)O\(_2\)]:[BPA] of 12 showed only 65% H\(_2\)O\(_2\) consumption over the same time period. However, the H\(_2\)O\(_2\) decay constants increased at increasing molar ratio ([H\(_2\)O\(_2\)]:[BPA]) at the ratio of 2 to 8 (please see the inset in Figure 3.10). Therefore, the [H\(_2\)O\(_2\)]:[BPA] ratio of 4 was found to be the cost-effective condition to achieve high removal of BPA and generate non-toxic intermediates/products.
Table 3.1. Biotoxicity of bisphenol A

<table>
<thead>
<tr>
<th>[BPA] (ppm)</th>
<th>% inhibition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>54</td>
</tr>
<tr>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

* % inhibition based on the color development of diH$_2$O (negative control) and HgCl$_2$ (positive control). HgCl$_2$ positive control indicated inhibition down to 0.2 µg/L.

The [H$_2$O$_2$]:[BPA] ratio of 4 in this study (4 mol H$_2$O$_2$/mol BPA at pH 3, 20°C and the initial BPA of 70 ppm) was comparable to the homogeneous Fenton of BPA carried out by Ioan et al. (2 mole H$_2$O$_2$/mol BPA at pH 4, 25°C and the initial BPA of 23 ppm) and Katsumata et al. (9 mol H$_2$O$_2$/mol BPA, at pH 4, 25°C and the initial BPA of 91 ppm) [113, 168]. It was much lower than that by other heterogeneous Fenton of BPA (54 mol H$_2$O$_2$/mol BPA, Fe$_3$O$_4$ nanoparticle, pH 3, 20°C and the initial BPA of 18.4 ppm, [161]) reported by Huang et al. (2012).

![Graph](image)

**Figure 3.10.** Effect of [H$_2$O$_2$]:[BPA] on removal efficiency of BPA and COD. The inset presents the H$_2$O$_2$ decay constants at various [H$_2$O$_2$]:[BPA]. Conditions: initial BPA (0.3mM, 0.1L); initial pH, 3; catalyst, 50 mg; temperature, 20°C.
The effect of temperature on the BPA removal was investigated using the optimum conditions (pH 3, 4 molar ratio of [H$_2$O$_2$/[BPA], and 50 mg catalyst) at 20-50 °C. Figure 3.11 shows a drastic enhancement of the reaction rate by the factor of 3.5 when the temperature increased from 20 to 50 °C. There was negligible loss of BPA at the elevated temperature due to low Henry’s constant for BPA (4 x 10$^{-6}$ Pa-m$^3$/mol, [169]). The results in Figure 3.11 support that the elevated temperature enhanced the reaction rates in Fenton oxidation for enhancing the removal of BPA in shorter time. Traditional Fenton oxidation is initiated by ferrous iron (Fe$^{2+}$) reacting with H$_2$O$_2$ to form ferric iron and 2•OH radicals (Eq. 2). The ferrous iron is regenerated when Fe$^{3+}$ reacts with H$_2$O$_2$ forming Fe$^{2+}$, a peroxyl radical (•OOH), and a proton (Eq. 3). The reaction in Equation 3 requires higher activation energy than the other reactions. The catalysis of H$_2$O$_2$ often results in an increase in solution temperature [145].

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \\
k_1 &= 51 \text{ M}^{-1} \text{s}^{-1} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot\text{OOH} + \text{H}^+ \\
k_2 &= 0.001-0.01 \text{ M}^{-1} \text{s}^{-1}
\end{align*}
\] (2)

(3)

Increasing the reaction temperature whether through external input or through the exothermic decomposition of H$_2$O$_2$ will increase the reaction rate of Fenton oxidation [145]. As an example, increasing the reaction’s temperature during homogeneous Fenton oxidation of 2,4-dichlorophenoxyacetic acid enhanced the contamination removal reaction rates by a factor of 1.6-2.5 (avg. 2.2) for every 10°C increased [170].
In order to remain economical for wastewater treatment the Fe$_3$O$_4$-MWCNT must be stable throughout multiple oxidation reactions. The five cycles of the Fenton oxidation using the same catalyst resulted in the removal of BPA (89% – 90%) which confirms high stability of the Fe$_3$O$_4$-MWCNT catalyst over the multiple Fenton reactions (Figure 3.12). However, the COD removal by the Fenton oxidation of BPA decreased over the multiple cycles probably due to the accumulation of intermediates and byproducts onto the Fe$_3$O$_4$-MWCNT.
Figure 3.12. Reusability of the catalyst (Fe₃O₄-MWCNT) for Fenton oxidation of BPA. Conditions: initial BPA (0.3mM, 0.1 L); initial pH, 3; catalyst, 50 mg; H₂O₂, 1.2 mM; temperature, 50°C.

3.3.3 Effect of the presence of radical scavengers on Fenton Oxidation

To demonstrate the role of hydroxyl radicals during the reaction, the reaction was carried out in the presence and absence of a radical scavenger. Ethanol was used as a radical scavenger, and added at the beginning of the reaction. Ethanol was added at 0:1, 1:1, and 10:1 (mmol Ethanol:mmol H₂O₂) The scavenging efficiency was estimated by using the following equation [171]:

\[
\text{Scavenging efficiency (\%) = \left(1 - \frac{k_i}{k_0}\right) \times 100}
\]

where \(k_0\) and \(k_i\) are the pseudo first-order rate constants for BPA degradation in the absence and the presence of the scavengers. Table 3.2 presents the \(\cdot\)OH scavenging with ethanol during the Fenton oxidation of BPA.
Table 3.2. Effects of ethanol on scavenging of OH radicals in the Fenton oxidation of bisphenol A. Conditions: initial BPA (0.3mM, 0.1L); initial pH, 3; catalyst, 50 mg; H₂O₂, 1.2 mM; temperature, 20°C.

<table>
<thead>
<tr>
<th>[Ethanol]/[H₂O₂] (mM:mM)</th>
<th>Scavenging efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>64</td>
</tr>
<tr>
<td>10</td>
<td>94</td>
</tr>
</tbody>
</table>

The Fe₃O₄-CNT-driven Fenton oxidation of BPA in the presence of ethanol showed significant scavenging effects (64-94%) at [ethanol]/[H₂O₂] (1:1 to 10:1) compared to the Fenton oxidation of BPA without any ethanol. It clearly demonstrated that the Fenton oxidation of BPA using Fe₃O₄-MWCNT mainly relies on •OH-driven oxidation. It also emphasizes importance of the cycling of Fe³⁺/Fe²⁺ during the Fenton oxidation which influences on the •OH production for the rapid oxidation of contaminants.

Figure 3.13 summarizes the Fenton oxidation pathway proposed by Poerschmann et al. (2010) [126], Luo et al. (2011) and Hua et al. (2014) [172, 173]. Among various intermediates and oxidative products, the aromatic products such as hydroquinone, 4’-hydroxyacetophenone (4-HAP), 4’-isoproenylphenone, and catechol were commonly detected as the major oxidative products. Some ring opened compounds such as oxalic acid, lactic acid, and fumaric acid were detected to a lesser degree which are more common by the Fenton oxidation at high dose of H₂O₂, indicating more complete oxidation [172]. Interesting findings are that hydroquinone and 4-HAP were mainly considered as the primary products from the sub-stoichiometric Fenton oxidation of BPA ([H₂O₂]/[BPA] of 2.2 to 4.4) which are similar conditions used for our study [126]. Although a detailed analysis of intermediates and oxidative products was not the scope of this paper, our HPLC analysis showed that the final solutions treated by the Fenton oxidation of BPA at [H₂O₂]/[BPA] of 2 to 12 kept hydroquinone, catechol and 4-HAP as the persistent oxidative products. While 4-HAP was reduced at [H₂O₂]/[BPA] higher than 4, hydroquinone was clearly increased as [H₂O₂]/[BPA] increased.
3.4. Conclusion

The Fe$_3$O$_4$-MWCNT exhibited an octahedron crystal structure of tiny size Fe$_3$O$_4$ (100-150 nm) which was well-dispersed onto the MWCNT with little agglomeration when it was synthesized using the in-situ Fenton coprecipitation method. The Fe$_3$O$_4$-MWCNTs possess a strong catalytic ability for the oxidation of BPA in the presence of H$_2$O$_2$. The effects of the key operating conditions (pH, loading of catalyst and H$_2$O$_2$ and reaction temperature) on Fenton oxidation of BPA were investigated. The Fenton oxidation showed high removal efficiency of BPA at 0.5-1 g catalyst/L while no further increasing of BPA removal above 0.5 g catalyst/L. High removal of BPA was achieved at an initial pH of 3 while the removal of BPA significantly dropped off as the pH increased above 4. The increase of [H$_2$O$_2$]:[BPA] (mol H$_2$O$_2$/mol BPA) from 4 to 108 at 20°C and 50°C led to similar removal of BPA (97-100%) while significant enhancement of COD removal (32-100%). Furthermore, the final reaction effluents from the Fenton oxidation at the
[\text{H}_2\text{O}_2]:[\text{BPA}]$ of 4-108 showed no biological toxicity of the BPA intermediates and products at these conditions. Thus, the $[\text{H}_2\text{O}_2]:[\text{BPA}]$ ratio of 4 was found to be the cost-effective condition to achieve high removal of BPA which is far from the stoichiometric demand of $\text{H}_2\text{O}_2$. The $[\text{H}_2\text{O}_2]:[\text{BPA}]$ ratio of 4 for oxidation of BPA was much lower than those for the heterogeneous Fenton oxidation of BPA while it was comparable to those for the homogeneous Fenton oxidation of BPA. Increasing temperature from 20°C to 50°C enhanced the oxidation rate of BPA by a factor of 3.5 which clearly indicated enhancement of the reaction rate while reducing the reaction time at increasing temperature. The five cycles of the Fenton oxidation using the same $\text{Fe}_3\text{O}_4$-MWCNT catalyst resulted in the removal of BPA (89% – 90%) which confirms high stability of the $\text{Fe}_3\text{O}_4$-MWCNT catalyst over the multiple Fenton reactions.
Chapter 4 Adsorption of bisphenol A onto Magnetic Iron Oxide-Coated Multi-Walled Carbon Nanotubes.

4.1 Introduction
This paper focuses on a Fe$_3$O$_4$-MWCNT catalyst which allows for the adsorption of BPA, by reducing the amount of Fe$_3$O$_4$ amended to the MWCNT surface. While many papers investigated the isotherm models of BPA adsorption [64, 67, 82, 91], few investigate the kinetic and thermodynamic properties of adsorption onto nano-adsorbents [66]. Additionally these researchers’ models are based on single batch based conditions. CNTs are rarely used in column based studies because of their small size generate high operating pressures. Mixing CNTs with sand has been shown to be effective when designing CNT adsorption columns. The sand particles distribute the CNTs throughout the whole column length, reducing their packing density and the pressure generated [174].

This paper was designed to investigate the detailed adsorption characteristics of BPA onto magnetite amended MWCNT. Adsorption characteristics include; isotherm, kinetics, and thermodynamic properties. The data was then used to determine the mechanism of adsorption and design a Fe$_3$O$_4$-MWCNT and sand adsorption column.

4.2 Methods and Material
4.2.1 Catalyst Synthesis
The Fe3O (magnetite)-MWCNT catalyst was synthesized by using the same procedure as in chapter 3. The amount of Fe$_3$O$_4$-MWCNT amended to the MWCNT was controlled by limiting the initial amount Fe$_2$SO$_4$.

4.2.2 Electron Microscopy, XRD, and XPS
The scanning electron microscopy (SEM) images and X-ray energy dispersive spectroscopy data (EDX) were obtained with Hitachi HT7700 field emission scanning electron microscope (10 kV). Transmission electron microscopy (TEM) images were obtained with Hitachi S-4800 at 100kV. Powder X-ray diffraction (XRD) patterns of the powered sample were performed on a Rigaku MiniFlex II diffractometer with a Cu Kα radiation source.

4.2.3 Adsorption Isotherms
The adsorption capacity of the MWCNTs was calculated using both the Langmuir and the Freundlich isotherm models. Both of these models compare the initial concentration of the
contaminant in the aqueous phase with the concentration of the contaminant in the solid phase, at equilibrium. The Langmuir isotherm describes a single layer of the contaminant adsorbing to the surface of the MWCNT. The Langmuir equation (equation 1) is used to describe this model.

\[
Q_e = \frac{q_m K_L C_e}{(1 + b C_e)}
\]  

(1)

Where \(Q_e\) is the concentration of BPA in the solid phase (mg BPA/g CNT) in the solid phase, \(C_e\) is the concentration of BPA in the liquid phase (mg/L), \(q_m\) is the maximum adsorption capacity (mg BPA/g CNT), and \(b\) is the Langmuir fitting parameter (L/mg).

The Freundlich model likewise describes multiple layers of adsorption onto the surface of the MWCNT.

\[
Q_e = K_f C_e^{1/n}
\]  

(2)

Here \(Q_e\) is the concentration of BPA in the solid phase (mg BPA/g CNT) in the solid phase, \(C_e\) is the concentration of BPA in the liquid phase (mg/L), \(K_f\) is the Freundlich adsorption coefficient ((mg/g)/(mg/L)\(^{1/n}\)), and \(n\) is dimensionless, and related to the surface heterogeneity [68].

To develop the Langmuir and Freundlich models the concentration of BPA at equilibrium ([BPA]\(_e\)) in the aqueous phase (\(C_e\)) was compared to the [BPA] in the solid phase (\(Q_e\)). 25 mg of MWCNT or Fe\(_3\)O\(_4\)-MWCNT were suspended in 20 ml of BPA solution with initial concentrations ranging from 2.5-70 ppm. The difference of the initial BPA concentration (\(C_i\)) and \(C_e\) was used to determine \(Q_e\).

To determine the effect of pH on MWCNT adsorption capacity, 20 mg of adsorbent was suspended in 20 mL of 20 ppm BPA. The solutions were left overnight to ensure equilibrium. Samples were then centrifuged and measured on the spectrophotometer at 276 nm.

4.2.4. Kinetic Modeling

To determine the adsorption kinetics, 50 mg of virgin and Fe\(_3\)O\(_4\) amended MWCNT were suspended in 100 mL 40 ppm BPA. Regular samples were taken every minute, unamended MWCNT were filtered through a glass wool filter and Fe\(_3\)O\(_4\)-MWCNT were separated with a rare earth magnet. The adsorption process was repeated at 20, 40, and \(\)°C.
The pseudo-first order kinetics were calculated with equation 3.

\[ \log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \]  

(EQ 3)

Where \( q_e \) is the amount of adsorbed BPA (mg) at the time of equilibrium. When plotted as a pseudo-first order reaction there was very low correlation at any temperature, indicating that this model was not a good fit for the adsorption of BPA onto MWCNT based adsorbents.

To calculate the fit of pseudo-second order kinetics, equation 2 was fit with the adsorption kinetic data.

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} \]  

(EQ 4)

The pseudo-second order model had a much stronger fit to the data \( R^2 > 0.98 \). Additionally, the calculated \( q_e \) was within 2% of the observed \( q_e \), indicating that the adsorption of BPA onto the surface of the MWCNT based catalyst is a second order model, similar to results published in other studies with nanomaterials.

4.2.5. Thermodynamic Analysis

The thermodynamic parameters such as Gibb’s free energy \( \Delta G^\circ \), change in enthalpy \( \Delta H^\circ \) and entropy \( \Delta S^\circ \) for the adsorption of BPA on the Fe\(_3\)O\(_4\)-MWCNT have been calculated by using the Eq. 5 and 6 [175]:

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \]  

(EQ 5)

\[ \log \left( \frac{q_e}{c_e} \right) = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \]  

(EQ 6)

where \( q_e \) is the amount of BPA adsorbed per unit mass of the Fe\(_3\)O\(_4\)-MWCNT (mg/g), \( c_e \) is BPA concentration at equilibrium (mg/L), \( T \) is temperature in K, and \( R \) is the gas constant (8.314 J/mol-K).

4.2.6. Column Based Adsorption Studies

To study the adsorption of BPA in a column system a glass 1 cm diameter column was prepared. The packing bed consisted of inert 16X20 mesh (0.84 mm-1.19 mm) sand, washed with water and burned at 550 °C, and then mixed with the MWCNT adsorbent and packed to the desired bed height. Tian et al (2009) were able to demonstrate the ability for sand to retain carbon
nanomaterials during filtration [176]. Distilled water was pumped through the system with a peristaltic pump to pack the sand. Figure 4.1 is a schematic of the column based adsorption apparatus. The flow rate was controlled from 1-7 mL/min. 20 ppm BPA concentrations were initially used for ease of measurement on the spectrophotometer. Effulgent samples were then taken at regular intervals to calculate the time for breakthrough (Removal efficiency <95%) and the time of exhaustion (Removal efficiency <5%). The amount of BPA adsorbed was also used to calculate the total BPA loading on the catalyst in mg BPA/g CNT.

![Schematic of sand-MWCNT column adsorption apparatus.](image)

**Figure 4.1.** Schematic of sand-MWCNT column adsorption apparatus.

Three major factors to consider when operating a column adsorption system are; flow rate, inlet concentration, and bed height. These are mechanical factors which can be adjusted when designing an optimal treatment method. For the Fe₃O₄-MWCNT and sand column studies three flow rates were investigated; 1.2, 3, and 7 mL/min. Three inlet concentrations were used; 10, 20, and 30 ppm BPA. Finally two bed lengths were investigated, 20 and 40 cm as one and two columns respectively. In addition to these three major factors, the heterogeneous nature of the Fe₃O₄-MWCNT and sand packing material called for an additional investigation into the effect of adsorbent loading. As more adsorbent is packed between the grains of the sand there is more contact area between the adsorbent and the water. However eventually the adsorbent can be packed so closely that BPA loading sites become occupied by other MWCNT walls, thus
reducing overall efficiency [174]. Three adsorbent loadings were investigated; 100, 150, and 200 mg Fe$_3$O$_4$-MWCNT/18.3 g sand. When testing for these conditions different were used to determine the efficiency of the column. Breakthrough time ($t_b$) is the time until $C/C_0 = 0.10$, while exhaustion time ($t_e$) is the time until $C/C_0 = 0.90$. These times were used to calculate the mass transfer zone (MTZ), which describes the area where BPA is actively being adsorbed to the Fe$_3$O$_4$-MWCNT. The column’s BPA removal efficiency was determined by calculating the mass of BPA adsorbed by the carbon then dividing by the total mass of BPA passed through the column during the run.

4.2 Results and Discussion
4.2.1 Characterization
XRD, XPS, and EDX data was discussed in chapter 3.3.1. However TEM imaging of the lower load catalyst showed more available MWCNT for the adsorption of BPA. The 50% Fe$_3$O$_4$-MWCNT maintained the regular octahedral crystal structure (Figure 4.2). The low 6% Fe$_3$O$_4$-MWCNT were malformed and more rod like in shape. This indicates that the iron hydroxides were not fully oxidized to magnetite.
4.2.2 Isotherm Modeling

Using initial BPA concentrations ranging from 2.5-70 ppm isotherm adsorption models were developed. Using the Ce and Qe data gathered both Freundlich and Langmuir isotherm models were developed for five (0%, 6%, 12.5%, 25%, and 50% Fe$_3$O$_4$) different loadings of magnetite on MWCNTs. The R$^2$ values for both the Langmuir and the Freundlich models was high, indicating that both models of adsorption can be used to model BPA adsorption. However the Langmuir model did have higher (though only slightly) R$^2$ values indicating a slightly better fit. (Table 1). The maximum adsorption capacity ($q_{max}$) was reduced as the amount of magnetite in the catalyst increased. This drop in adsorption capacity is related to the presence of hydrophilic magnetite covering the adsorption sites on the MWCNT.
Table 4.1. Freundlich and Langmuir isotherm model coefficient for adsorption of BPA on MWCNTs.

<table>
<thead>
<tr>
<th>Magnetite %</th>
<th>Freundlich Model</th>
<th>Langmuir Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$ ((mg/g)/(mg/L)^{1/n})</td>
<td>$n$</td>
</tr>
<tr>
<td>Virgin MWCNT</td>
<td>1.367</td>
<td>0.482</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (6%)-MWCNT</td>
<td>1.309</td>
<td>0.766</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (12.5%)-MWCNT</td>
<td>1.225</td>
<td>0.708</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (25%)-MWCNT</td>
<td>1.601</td>
<td>0.601</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (50%)-MWCNT</td>
<td>0.968</td>
<td>0.517</td>
</tr>
</tbody>
</table>

The effect of solution pH was also investigated. BPA has a pKa between 9.6 and 10.2. At higher pHs the hydroxyl groups deprotonate giving BPA a negative charge. This charge increases the hydrophilic nature of the compound, reducing the ability to adsorb to the hydrophobic MWCNT. At pHs below 11 the removal efficiency of BPA remains the same (85-90%) however at pH 11 the removal efficiency drops significantly to 70% (Figure 4.3). Both the unamended MWCNT and the 50% Fe$_3$O$_4$-MWCNT had the same adsorption pattern in relation to the pH.
4.2.3 Effect of Magnetite Loading on H$_2$O$_2$ Consumption Rate

To investigate the effect of altering the magnetite loading on the reaction rate, multiple forms of the Fe$_3$O$_4$-MWCNT catalyst were synthesized with varying loads of magnetite on the MWCNT. The iron loading was controlled by reducing the initial amount of FeSO$_4$ used in the synthesis. The iron content of the manufactured catalyst was calculated by burning off the MWCNT structure in an 800 °C furnace. In the process the magnetite further oxidized to form Fe$_2$O$_3$, which was then massed. Four different iron loadings were synthesized (6%, 12.5%, 25%, and 50% Fe$_3$O$_4$ by mass). Using 50 mg of each catalyst to treat 100 mL of 70 ppm BPA solution, set to pH 3, and initiated with a dose of 4 mmol H$_2$O$_2$:mmol BPA, it was found that the reaction rate of Fe$_3$O$_4$-MWCNT catalysts decreased in relation to the decrease of Fe$_3$O$_4$-MWCNT loading (Figure 5.1). While the reaction rate decreased, the overall removal efficiency of BPA remained the same, indicating that the oxidation capacity of the catalyst remained.
4.2.4 Adsorption Kinetics

The pseudo-first order kinetics were calculated with equation 3. To calculate the fit of pseudo-second order kinetics, equation 4 was fit with the adsorption kinetic data. By plotting \( t/q_t \) against time \( (t) \) the slope and intercept can be used to estimate \( k_2 \) and \( q_e \) respectively [66]. The pseudo-second order model had a much stronger fit to the data (\( R^2 > 0.98 \)). Additionally the calculated \( q_e \) was within 2% of the observed \( q_e \), indicating that the adsorption of BPA onto the surface of the MWCNT based catalyst is a second order model, similar to results published in other studies with nanomaterials, see table 4.2.

While the increase in temperature greatly increased the rate of adsorption, the total amount of BPA adsorbed per gram adsorbent decreased in correlation with the increase in temperature (Figure 4.4). The decrease in adsorption capacity was substantially less than the increase in adsorption rate. Increasing the temperature of adsorption to 60 °C led to a 270% increase in reaction rate, but only a 35% reduction in adsorption capacity.
Figure 4.4. Pseudo-First order (a and b) and Pseudo-Second order (c and d) adsorption kinetics of BPA onto virgin MWCNT (a and c) and 50% Fe₃O₄-MWCNT (b and d) in relation to temperature. [Conditions] initial BPA, 40 ppm, 100 mL; Adsorbent, 50 mg; temperature, 20-60 °C, points were conducted with n=3 pseudo replication.
Table 4.2. Adsorption kinetic parameters for BPA adsorption onto virgin and (50%) Fe₃O₄-MWCNT Conditions: 100 mL of BPA 40 ppm; adsorbent, 50 mg; temperature, 20°C.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Experimental $q_e$ (mg/g)</th>
<th>$q_e$ (mg/g)</th>
<th>$k_1$ (min⁻¹)</th>
<th>$R^2$</th>
<th>$q_e$ (mg/g)</th>
<th>$K_2$ (g/mg min⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>68.62</td>
<td>1.434</td>
<td>0.066</td>
<td>0.742</td>
<td>72.64</td>
<td>0.011</td>
<td>0.998</td>
</tr>
<tr>
<td>(50%) Fe₃O₄-MWCNT</td>
<td>47.67</td>
<td>1.133</td>
<td>0.079</td>
<td>0.938</td>
<td>48.54</td>
<td>0.015</td>
<td>0.997</td>
</tr>
</tbody>
</table>

The pseudo-second order model had a much stronger fit to the data ($R^2>0.98$). Additionally the calculated $q_e$ was within 2% of the observed $q_e$, indicating that the adsorption of BPA onto the surface of the MWCNT based catalyst is a second order model, similar to results published in other studies with nanomaterials.

While the increase in temperature greatly increased the rate of adsorption, the total amount of BPA adsorbed per gram adsorbent decreased in correlation with the increase in temperature (figure 3b). The decrease in adsorption capacity was substantially less than the increase in adsorption rate. Increasing the temperature of adsorption to 60 °C led to a 270% increase in reaction rate, but only a 35% reduction in adsorption capacity.
4.2.5 Thermodynamic analysis
The thermodynamic parameters such as changes in free energy; (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), calculated using Eqs. 5 and 6 are listed in Table 4.3. The negative values of ΔH° indicated that the adsorption process of BPA is exothermic and occurs mainly by physical process. The negative values of ΔS° suggested an increase in order and a decrease in randomness at the solid-solution interface occurs in the internal structure of the adsorption process of BPA [177]. The negative values of ΔG° indicated that the adsorption process of BPA is spontaneous while the spontaneity decreases at higher temperature indicating that the adsorption of BPA favors lower temperature. Similar results for exothermic and physical adsorption of BPA were observed from other studies on graphene [66]. Zaib et al. reported an increase in the rate of adsorption correlated to an increase in temperature. This increase in the rate of adsorption was also related to a decrease adsorption capacity of single walled carbon nanotubes [88]. Even non-nano materials exhibit a similar pattern of exothermic adsorption of BPA, favoring lower operating temperatures [65]

<table>
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<tr>
<th>Temperature (°C)</th>
<th>k2 (g/mg min)</th>
<th>Qe (mg/g)</th>
<th>ΔG° (KJ/mol)</th>
<th>ΔH° (KJ/mol)</th>
<th>ΔS° (J/mol)</th>
</tr>
</thead>
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<td><strong>MWCNT</strong></td>
<td></td>
<td></td>
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<tr>
<td>20</td>
<td>0.011</td>
<td>68.62</td>
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<tr>
<td>40</td>
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<td>64.29</td>
<td>-4.613</td>
<td>-16.300</td>
<td>-0.037</td>
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<tr>
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<td><strong>(50%) Fe3O4 -MWCNT</strong></td>
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<tr>
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<td>30.95</td>
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4.2.6 Mechanisms
The adsorption of BPA onto graphene based nanostructures e.g., graphene or carbon nanotubes, is often depicted as being predominated by π-π interactions between the benzene rings in BPA
and the carbon surface [88, 96, 178, 179]. The surface of MWCNT are predominated by C=C ring structures, allowing for a high concentration of π electrons. Joseph et al. (2008) used computer modeling to describe the mechanism of BPA adsorption onto the surface of single wall carbon nanotubes. In their model the one benzene ring in BPA lies horizontal to the CNT surface, while the other ring is rotated to be perpendicular. This rotation does not inhibit the adsorption of BPA onto the surface of the CNT. Though CNTs have a large surface area there is still only a finite number of available binding sites for BPA. The Langmuir isotherm also indicates that the BPA is only adsorbed as a single layer onto the MWCNT surface.

4.2.7 Column Based Adsorption Study

Table 4.4 summarizes the operation conditions for the Fe₃O₄-MWCNT/Sand fixed bed column. Four operating parameters were tested: influent flow rate; adsorbent loading; column bed height; and influent concentration (Figure 4.5). The data from the breakthrough curves were used to calculate the adsorption capacity (mg BPA/g adsorbent), zone of mass transfer (cm), the S-curve slope (ppm/min), and BPA removal efficiency (%).
Figure 4.5. Breakthrough curves of BPA in the Fe-MWCNT/sand fixed bed columns under varying conditions: a) flow rate [conditions] 100 mg Fe-MWCNT/18.3 g sand, 20 cm bed height, 20 ppm initial concentration; b) adsorbent loading [conditions] 1.2 mL/min flow rate, 18.3 g sand, 20 cm bed height, 20 ppm initial concentration; c) bed height [conditions] 1.2 mL/min flow rate, 200 mg Fe-MWCNT/18.3 g sand, 20 ppm initial concentration; d) initial BPA concentration [conditions] 1.2 mL/min flow rate, 200 mg Fe-MWCNT/18.3 g sand, 20 cm bed height.
<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>Adsorbent</th>
<th>F (mL/min)</th>
<th>Z (cm)</th>
<th>$t_{total}$ (min)</th>
<th>$V_{eff}$ (mL)</th>
<th>$m_{total}$ (mg)</th>
<th>$q_{total}$ (mg)</th>
<th>$Q_{e-exp}$ (mg/g)</th>
<th>$Z_m$ (cm)</th>
<th>dc/dt</th>
<th>E (%)</th>
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<tbody>
<tr>
<td><strong>Flow Rate</strong></td>
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<tr>
<td>20</td>
<td>100 mg</td>
<td>1.2</td>
<td>20</td>
<td>115</td>
<td>138</td>
<td>2.79</td>
<td>1.55</td>
<td>15.48</td>
<td>19.13</td>
<td>0.15</td>
<td>55.44</td>
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<tr>
<td>20</td>
<td>100 mg</td>
<td>3</td>
<td>20</td>
<td>70</td>
<td>210</td>
<td>4.25</td>
<td>2.09</td>
<td>20.91</td>
<td>19.14</td>
<td>0.30</td>
<td>49.20</td>
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<tr>
<td>21</td>
<td>100 mg</td>
<td>7</td>
<td>20</td>
<td>50</td>
<td>350</td>
<td>7.42</td>
<td>2.44</td>
<td>24.36</td>
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<tr>
<td>20</td>
<td>200 mg</td>
<td>1.2</td>
<td>20</td>
<td>365</td>
<td>438</td>
<td>8.66</td>
<td>6.50</td>
<td>32.49</td>
<td>19.56</td>
<td>0.09</td>
<td>75.07</td>
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<tr>
<td>19</td>
<td>150 mg</td>
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<td>240</td>
<td>288</td>
<td>5.58</td>
<td>3.24</td>
<td>21.59</td>
<td>19.36</td>
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<td>20</td>
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<td>1.55</td>
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<tr>
<td><strong>Column Length</strong></td>
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<tr>
<td>21</td>
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<td>438</td>
<td>8.66</td>
<td>6.50</td>
<td>32.49</td>
<td>19.56</td>
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<tr>
<td>20</td>
<td>400 mg</td>
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<td>852</td>
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<td><strong>Inlet Concentration</strong></td>
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<tr>
<td>10</td>
<td>100 mg</td>
<td>3</td>
<td>20</td>
<td>165</td>
<td>495</td>
<td>5.11</td>
<td>3.57</td>
<td>35.71</td>
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<td>20</td>
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<td>4.25</td>
<td>2.09</td>
<td>20.91</td>
<td>19.14</td>
<td>0.30</td>
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<tr>
<td>43</td>
<td>100 mg</td>
<td>3</td>
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<td>45</td>
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<td>5.82</td>
<td>3.16</td>
<td>31.58</td>
<td>19.44</td>
<td>1.30</td>
<td>54.29</td>
</tr>
</tbody>
</table>
While columns utilizing biochars have higher adsorbent capacities at lower flow rates, the adsorption capacity of BPA onto the MWCNT adsorbent actually increased with the flow rate. This is likely due to the fact that CNT based adsorbents are not restricted to the diffusion of contaminants into the pore space. Additionally CNTs need shorter retention times to achieve equilibrium. The time for MWCNT equilibrium for BPA was on the scale of minutes while adsorbents like biochar and GAC often require hours for equilibrium to be achieved. However the overall efficiency of the column (the amount of BPA adsorbed vs the total BPA) decreased as the influent flow rate increased. The slope of the S-curve increased with the increase of the flow rate. The breakthrough time decreased from 15 minutes down to 5 minutes, as the flow rate increased. Likewise the exhaustion time decreased from 115 minutes down to 50 minutes as the flow rate increased.

The (50%) Fe₃O₄-MWCNT were less efficient at adsorbing BPA when packed into the column. 100 mg of (50%) Fe₃O₄-MWCNT at a flow rate of 1.2 mL/min were only able to adsorb 15.5 mg BPA/g (50%) Fe₃O₄-MWCNT, about a third of the predicted maximum loading based on the Langmuir isotherm (45.7 mg BPA/g (50%) Fe₃O₄-MWCNT). However when increasing the loading of adsorbent in the column increased the adsorption capacity of the column, and greatly increased the overall efficiency (Table 4.3). Figure 4.5 compared the adsorption of BPA overtime with three different adsorbent loadings.

Increasing the loading of Fe₃O₄-MWCNT allows for longer break through times and the exhaustion time. However a side effect is an increase in the pressure drop due to the increased friction of the water over the adsorbent. This increase in pressure requires more pumping power to obtain higher flow rates and stronger materials to maintain the integrity of the column. While operating at 1.2 mL/min the pressure was measured at 11-13 psi. It was observed that at pressures near 15 psi the adsorbent breaks through the glass wool. Because of this the ideal operating pressure was capped at 10 psi. The higher loads of Fe₃O₄-MWCNT allowed for more BPA to be adsorbed. Not only was the total BPA adsorbed increased, but the amount of BPA/g adsorbent increased. Increasing the Fe₃O₄-MWCNT loading reduced the amount of empty space between the particles of sand. Reducing empty space increased BPA contact time with adsorbent.
Increasing the column length while maintaining the same adsorbent density, increased the breakthrough point and exhaustion time, but did not have a dramatic effect on the adsorption capacity. The mass transfer zone was likewise increased. Additionally shorter bed heights led to steeper S-curve slopes \( (dc/dt) \). There was still a trend of increasing adsorbent capacity, and overall removal efficiency as the column length increased. This implies that while operating at a maximum possible adsorbent loading, the removal efficiency and capacity can be further improved by increasing the column length.

4.3 Conclusions

The application of multiwall carbon nanotubes decorated with magnetite nanocrystals as an adsorbent for the removal of BPA from water was investigated. Experimental results indicate that Fe-MWCNT can be used to treat BPA under a variety of conditions. High pH (>10) inhibit BPA adsorption but at neutral and acidic pH the adsorption capacity remains constant. Temperature however reduces the adsorption capacity but increases the adsorption rate. Furthermore kinetic and thermodynamic studies indicate that the adsorption of BPA onto MWCNT surfaces is a spontaneous exothermic reaction. The adsorption is primarily \( \pi-\pi \) interactions between the BPA benzene rings and the MWCNT surface. The addition of Fe\(_3\)O\(_4\) nanocrystals inhibit these binding sites, reducing adsorption capacity. The iron decorated MWCNT were then applied to a fixed bed column utilizing sand as an inert support structure. Various factors were tested to observe their effect on the removal of BPA. One of the most dramatic factors was the adsorbent packing density. Higher densities resulted in higher adsorption capacities and efficiencies. However this is at the expense of increasing the pressure generated in the system. The adsorbent maintained high adsorption capacity at higher flow rates, but the overall efficiency of the system decreased substantially under the higher flow rate conditions. With this in mind further development and study could prove that the MWCNT/sand columns are effective treatment options for removing BPA and other EDCs for water systems.
Chapter 5 Adsorption and Fenton oxidation of BPA with non-conventional conditions and catalysts

5.1 Adsorption of Sub ppm BPA

In order to understand the adsorbent/catalyst in conditions more reflecting the real world a Waters 2475 fluorescence detector was implemented in conjunction with a 2695 separations module. The Fluorescence detector was able to provide superior detection down to about 50 ppb with potential after methods optimization to detect BPA in the single digit ppb levels. By maximizing the volume of BPA and minimizing the mass of adsorbent both Langmuir and Freundlich models were developed for the sub ppm concentrations of BPA (Figure 5.1). An interesting result of the isotherms is that the adsorption capacity was substantially reduced compared to isotherms developed at higher concentrations. This may be due to the low concentrations providing little driving force for the adsorption of BPA. It might also be that the sub ppm concentrations are operate well below the maximum adsorption capacity. The column study in chapter 4 showed an increase in the adsorption capacity. Running a column at 50-100 ppb may clarify the actual adsorption capacity of the MWCNTs at sub ppm concentrations.

![Figure 5.1. Langmuir (a) and Freundlich (b) for 50% Fe₃O₄-MWCNT at sub ppm conditions](image)

Conditions: 10 mg 50% Fe₃O₄-MWCNT adsorbent, 200 mL BPA (50-200 ppm), 20°C, conducted in duplicate.
5.2. In Column Fenton Oxidation

In column Fenton oxidation is a veritable hydra of complications, when one is solved two more appear. The first challenge was using the substrate to support the catalyst/adsorbent in the column. Initial attempts with sand showed that the natural minerals were highly reactive to the \( \text{H}_2\text{O}_2 \), but were not beneficial to the oxidation of BPA. To overcome this 1 mm glass beads were used in place of the sand. The glass beads were excellent at keeping the catalyst/adsorbent dispersed in the column and actually slightly improved the adsorption of BPA to the Fe\(_3\)O\(_4\)-MWCNT. When preforming Fenton oxidation however it was found that the H\(^+\) ions were being adsorbed to the surface of the Fe\(_3\)O\(_4\), increasing the local pH. With higher pH solutions the Fenton reaction did not occur (See chapter 3). To overcome the adsorption the H\(^+\) ions, the column was saturated with pH 2.65 H\(_2\)O until the pH stabilized. While the acidic conditions allowed for some column regeneration the column was only regenerated to about 25% capacity (Figure 5.2). Even though further optimization of the in column oxidation conditions could improve oxidation, another hurdle had to become overcome. The acidic conditions required for Fenton oxidation treatments allowed for the Fe\(_3\)O\(_4\)-MWCNT adsorbent to become more mobile in the column. Over the course of oxidation the adsorbent would migrate to the base of the column. The regular shape of the glass beads further compounded the problem. Sand with its irregularities has grooves and cavities for adsorbent to get trapped. These are not present on the glass beads, so the Fe\(_3\)O\(_4\)-MWCNT can pass around them relatively unimpeded. All of these obstacles can be overcome with proper time and development, but doing so greatly expands the complexity of this project.
Figure 5.2. Breakthrough curves for the Fe$_3$O$_4$-MWCNT and glass bead column before (blue) and after (orange and grey) oxidation [Conditions] 100 mg Fe-MWCNT/20 g 1 mm glass beads, 20 cm bed height, 20 ppm initial concentration, 1$^{st}$ oxidation: 60 mL H$_2$O$_2$ (108:1 mol H$_2$O$_2$:mol BPA), pH of solution: 3, cycled for 24 hr. 2$^{nd}$ oxidation: 150 mL H$_2$O$_2$ (36 mol H$_2$O$_2$:mol BPA), pH of solution: 3, cycled for 8 hr.

5.3. Zinc Ferrite Fenton Oxidation
The use of transition metal substitutions in magnetite have been shown by several authors to improve the Fenton potential of the catalyst. Some metals such as manganese or cobalt act as electron sources, reducing Fe$^{3+}$ to Fe$^{2+}$, increasing the regeneration rate of ferrous iron. The use of zinc as a doping metal has been a recent advancement. Zinc ferrite nanoparticles alone show low Fenton potential, but when attached to carbon surfaces, they become sensitized to visible light. These hybrid catalysts have been shown to effectively degrade dyes and produce hydroxyl radicals in the presence of visible light and H$_2$O$_2$.

5.3.1. Synthesis
Zinc was substituted for iron by replacing a portion of FeCl$_2$ for ZnCl$_2$. A downside to working with the zinc is that zinc hydroxide is soluble when high concentrations of hydroxyl radicles. To avoid this the NaOH was reduced to stoichiometric amounts, and added at a reduced rate to the
FeCl$_2$/ZnCl$_2$ solution. The initial synthesis produced an iron sludge when placed in pH 3 solution. This is likely due to poorly amended. By adding a wash of pH 3 water we were able to remove unattached particles. The resulting catalyst was stable in pH 3 solutions and did not produce a brown sludge. The thermal oxidation of the catalyst showed that it was about, by mass, 50% inorganics and 50% carbon.

### 5.3.2. Effect on Oxidation

The synthesized zinc ferrite-MWCNT catalysts had a drastic effect increasing the reaction rate. When operating at high doses of H$_2$O$_2$ (108:1 H$_2$O$_2$:BPA) and ambient temperatures the zinc ferrite MWCNT were able to oxidize all of the H$_2$O$_2$ 48 h (Figure 5.4). Compared to the Magnetite-MWCNT which took over 7 days at ambient temperatures. Furthermore, the zinc ferrites were still reactive pH 5 and 7 unlike the Fe$_3$O$_4$-MWCNT catalyst. The BPA of the pH 3 reaction was all completely removed after the oxidation and no BPA remained in the methanol extraction.

![Graph showing H$_2$O$_2$ removal rate](image)

**Figure 5.3.** H$_2$O$_2$ removal rate when reacted with zinc ferrite-MWCNT [Conditions]: 50 mg ZnFeO$_4$ Catalyst, 100 mL 70 ppm BPA, Temperature 20°C.
Chapter 6 Future Directions

6.1 Improving Adsorption Capacity
An important method to increasing the effectiveness of the Fe$_3$O$_4$-MWCNT catalyst is to increase the maximum capacity of the catalyst as an adsorbent. Improving the adsorption capacity for BPA onto MWCNTs is a difficult proposition. While polar contaminants such as dyes and antibiotics can interact with charged surface groups such as $-\text{COOH}$, BPA however has no charge at most pH, and therefore the predominant adsorption mechanisms are hydrophobic in nature. By adding functional groups which improve $\pi-\pi$ interactions such as hydroxyl groups, the adsorption capacity of the catalyst may be improved.

6.2 Improving Catalyst Reaction Rate
Improving the BPA oxidation rate is very important for developing a realistic treatment methods. While changing the initial Fenton Oxidation reaction conditions can be used to optimize the current catalyst, small physical changes to the catalyst could be used to further enhance the rate of BPA degradation. The most direct method is to decrease the Fe$_3$O$_4$ particle size, and thus increase the catalyst surface area. Switching to magnetite synthesis methods could show the benefit of smaller crystals. A common synthesis method is to start with a mixture of ferrous and ferric iron salts. The synthesis of magnetite is initiated by the addition of a base such as ammonia or sodium hydroxide. The size of the crystals can be tuned by; adjusting the addition rate of base, the stir speed, and the type of alkaline solution used.

6.3 Hybrid Treatment Methods
While the current method is a combination of physical adsorption and chemical oxidation, other treatment methods can be incorporated. For example reducing the amount of H$_2$O$_2$ used in the reaction leaves several by products in the system, which though less toxic than BPA may still be undesirable. A biological reactor could be implemented to further remove small organics, without the need for additional oxidant. Another method to reduce oxidant demand is to incorporate photo-Fenton reactions into the catalyst. Both $\gamma$-Fe$_2$O$_3$ and zinc ferrites have been shown to be effective photo-Fenton catalysts when amended to carbon supports. These photo catalysts are biologically safe and can be manipulated by magnetic fields. A difficulty with photo-Fenton reactions though is the need for light penetration. While this can be achieved with batch treatment methods, the sand columns would allow for minimal light to pass through.
6.4 Treatment of Other Emergent Contaminants

BPA is just one of several emerging contaminants concerning researchers. Compounds such as pharmaceuticals and personal care products are also showing impact on the environment. Their structures are often have similar moieties to BPA and may also be treatable by the same methods described in this thesis. By expanding the range of contaminants treatable by this method will further show benefit for this catalyst.

Appendix

1. Analytic Methods
   1.1. H₂O₂ measurement

   The magnetically separated samples were measured for H₂O₂ using a modified peroxytitanic acid colorimetric procedure with a detection limit of 0.1 mg/L [23]. 1 g of Ti(SO₄)₂ was dissolved in 10 mL of 10% H₂SO₄. The solution was heated to 80°C until all of the Ti(SO₄)₂ was completely dissolved. To measure the H₂O₂ concentration 900 µL of sample was treated with 100 µL of the Ti(SO₄)₂ solution. The solution was left for 15 minutes to allow for the color to develop. The absorbance was measured with a spectrophotometer at 407 nm.

   1.2. Iron Measurement

   Iron concentration was measured using the phenanthroline Method [23]. To measure Fe concentrations in water, 0.5 ml of the samples was added to 8.4 ml DI water. 0.1 ml 10% hydroxylamine solution and 1 ml 0.3% 1, 10-phenanthroline monohydrate was added to the samples. The color was then allowed to fully develop for 30 minutes. The absorbency was measured on a spectrophotometer at 510 nm.
Figure A-1. Iron measurement calibration curve for iron concentrations from 0.5 ppm to 50 ppm.

1.3. BPA measurement

BPA was measured using a UV/Vis spectrophotometer, HPLC with a photodiode array detector, and, for sub ppm detection, a HPLC separation module with a fluorescence detector.
Figure A-2. Calibration curve for BPA, as measured with the UV/Vis spectrophotometer. BPA concentration in water was measured on a Waters 2690 separations module with a Waters 996 photo diode array at 235 nm using a Phenomenex Aries Peptide column (3.6 µm XB-C18, 150x4.60 mm). The Aries Peptide columns are solid cores of silica encased in layers of pours silica, then coated with XB-C18 to produce a hydrophobic surface. The solid core style of packing material allows for reduced adsorption/desorption time onto the particles. The Aries Peptide packing material also has a narrower size distribution, allowing for more even packing in the column. The even packing further reduces spreading. The mobile phase was 42% water and 58% HPLC grade methanol applied as an isocratic run with a constant flow rate of 1 ml/min. The runs lasted for ten minutes with a five minute delay between injections to allow for the column to equilibrate.

Figure A-3. HPLC chromatogram of a 10 µL injection of 70 ppm stock BPA solution, 1.00 mL/min flow rate, 42% H₂O 58% Methanol solvent mixture, 10 minute runtime.
Figure A-4. HPLC chromatogram of a 10 µL injection of 15, 10, and 7.5 ppm stock BPA solution, 1.00 mL/min flow rate, 42% H2O-58% Methanol solvent mixture, 10 minute runtime.
Figure A-5. Calibration curve for BPA injected onto the HPLC, [Conditions] solvent composition= 42% H₂O and 58% HPLC grade Methanol, Flow rate= 1 mL/min,


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