CNT-based Electrochemical Filter for Water Treatment: Mechanisms and Applications

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CNT-based Electrochemical Filter for Water Treatment: Mechanisms and Applications

A dissertation presented
by
Han Liu

to
The School of Engineering and Applied Sciences

in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
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CNT-based Electrochemical Filter for Water Treatment: Mechanisms and Applications

Abstract

Water treatment is a critical global challenge requires innovated effective solution. Conventional treatment methods includes membrane filtration, adsorption and electrochemical oxidation of organics. This dissertation proposed a new hybrid of the three conventional technologies and investigated the mechanism and application potential for water treatment using carbon nanotube (CNT) based anodic filter. A qualitative reactive transport model consisting of mass transport, adsorption/desorption, electron transfer was developed to understand reaction mechanism and compare the filtration with the batch electrochemical system. The mass transport step is found to be the key advantage (>6-fold) of the electrochemical filtration over the batch system due to convective mass transport through the filter pores. This indicate synergy between the filtration and the electrochemistry. A quantitative model coupling the above three steps was also build to quantitatively simulate the reaction kinetics and probe information about reactive sites. The model simulation was successfully validated by experimental methyl orange oxidation data and was further used to identify kinetics from reactive sites. It was found that two types of reactive sites—the sidewall sites and oxy-defect sites are both reactive for ferrocyanide oxidation with a slightly different overpotential. Also, microscopic flux and streamline plot again verify the convective mass transport enhance reaction kinetics—synergy of the filtration and electrochemistry. To improve potential for organic oxidation applications, the CNT filter was coated with 3.9 ± 1.5 nm bismuth-doped tin oxide (BTO) nanoparticles. In the oxalate oxidation experiments, the current efficiency increased by 1.5–3.5 times and TOC removal increased by 2–8 times after coating. The BTO-CNT anode energy consumption was 25.7 kWh kgCOD\(^{-1}\) at ~93% TOC removal and 8.6 kWh kgCOD\(^{-1}\) at ~50% TOC removal, comparable to state-of-the-art oxalate oxidation processes (22.5–81.7 kWh kgCOD\(^{-1}\)). The anode stability also improved by extending the working potential range from 1.1 V of pure CNT to 2.2 V of BTO coated CNT. For inorganic ion removal applications, the CNT filter was coated by a 5.5 ± 2.7 nm layer of TiO\(_2\) for arsenic removal. Compared with the conventional adsorption column using granular adsorbents, the TiO\(_2\)-CNT filter is a highly dispersed nano-system allows forced convective transport through the pores whereas diffusive mass transport dominates and limits kinetics for granular adsorbents. As a result, adsorption kinetics of the TiO\(_2\)-CNT filter increased by two orders of magnitude due to structure improved site accessibility (20–30 fold), internal convection (4–6 fold) and electrosorption (0.15–2 fold). Groundwater samples containing 44 ppb As were treated by single-pass filtration, and 12500 bed volumes (residence time of 4.5 s; 127 L m\(^{-2}\) h\(^{-1}\); 5.8 mg m\(^{-2}\) h\(^{-1}\)). TiO\(_2\) filter was successfully regenerated by 5 mM NaOH for both As(III) and As(V).
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Dedicated to my family.
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Drinking water and wastewater treatment is a critical economic, environmental, and security issue that demands immediate attention and innovative solutions. More than 780 million people lack access to drinking water purification and about 4 billion lack access to water sanitation, resulting in millions of death per year.\[1\] Supplying safe water is simultaneously becoming more complicated due to population growth, industrial water contamination, and climate change. Membrane filtration, electrochemical oxidation and adsorption are widely used to meet the water treatment requirements throughout
the world. Each technology has unique benefits and drawbacks.

1.1 Membrane filtration

Membrane filtration is a fast physical separation process that prevent pollutants of a certain size from permeating through the membrane pores. Depending on the pore size (d) of the membrane, membrane filtration can be classified into four regimes: microfiltration (d = 50–500 nm), ultrafiltration (d = 2–50 nm), nanofiltration (d = 1–2 nm) and reverse osmosis (d <1 nm). Microfiltration is effective for suspended solids and bacteria removal (size >1 µm); ultrafiltration can remove colloids and viruses (30–300 nm); nanofiltration can remove organics (0.6–3 nm), and reverse osmosis is used for desalination to remove inorganic ions (0.2–0.4 nm). A smaller pore size allows better separation of pollutants and improved effluent quality, but also leads to lower permeability such that it consumes greater energy and operates at lower flux. A schematic of a representative reverse osmosis module is shown in Figure 1.1 as an example of membrane filtration according to Ref [2]. The pressurized feed volume, \( V_F \), is fed to a membrane module containing a semipermeable membrane where it is separated into a pure water permeate, \( V_P \), and a concentrate containing the retained salts, \( V_C \). Compared with other technologies, membrane filtration offers a rapid, compact and convenient water treatment solution. With proper design tailored to specific applications, membrane filtration technology has been successfully utilized at large scale in the field of drinking water, wastewater treatment, and desalination.

In the meantime, membrane filtration faces many challenges. First, the membrane filtration process creates a concentrated solution of pollutants after physically separating them from the water body. The concentrate itself still requires further treatment. Also, species in the water lead to membrane fouling, which significantly decreases permeability, increases energy cost, and eventually leads to membrane damage. To address fouling, membrane cleaning including backwash and chemical treatment.
are often completed periodically, increasing operation cost and complexity. Potentially, a membrane with reactivity towards foulants may help solve the problem. For example, a surface with strong oxidation power can mineralize the organic foulants to $\text{CO}_2$ to prevent organic adhesion and fouling. Microbes will also be inactivated by the oxidizing membrane so bio-fouling could also potentially be avoided. The electrochemical oxidation method may be helpful here and will be discussed in the next section.

### 1.2 Electrochemical oxidation

Electrochemical oxidation is an important technology in a wide range of industrial applications including chemical production and water treatment. In the chemical manufacturing industry, a primary method for generation of chlorine (a common disinfectant for drinking water) is electrolysis of sodium chloride solution, eq 1.1.

\[
\begin{align*}
\text{Cathode} : & \quad 2 \text{H}^+(\text{aq}) + 2 e^- \rightarrow \text{H}_2(\text{g}) \\
\text{Anode} : & \quad 2 \text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2 e^- 
\end{align*}
\]

To oxidize and remove organic pollutants, electrochemistry has long been studied for wastewater treatment due to its fast kinetics and effectiveness towards recalcitrant chemicals. The electrode
can oxidize organics at a given potential via either direct electrolysis or oxidative intermediate. Direct electrolysis is the direct oxidation of adsorbed species on the electrode without involving any intermediates. A typical example is the direct oxidation of phenol (eq 1.2):

\[ C_6H_5OH + 11 H_2O \rightarrow 6 CO_2 + 28 H^+ + 28 e^- \quad (1.2) \]

However, direct oxidation kinetics are usually slow and often accompanied by gradual fouling of the electrode due to polymer formation. The polymer is an intermediate oxidation product and may cover and passivate the electrode.

Electrochemical oxidation can also happen through producing oxidative intermediate species including \( \text{OH}^- \) (eq 1.3) and \( \text{SO}_4^{2-} \) (eq 1.4).

\[ \text{OH}^- + h^+ \rightarrow \text{OH}^- \quad (E^0 = 2.1 \, V, \, pH \, 7) \quad (1.3) \]

\[ \text{SO}_4^{2-} + h^+ \rightarrow \text{SO}_4^{2-} \quad (E^0 = 2.2 \, V) \quad (1.4) \]

The oxidative radicals further react with organics. These radicals are very strong oxidants such that electrode fouling may be reduced or eliminated.

Electrochemical oxidation for organic removal has many advantages compared with conventional oxidation methods. Conventionally, the organics in the water can be oxidized by aerobic or anaerobic bio-reactors. But these biological processes require significant organic concentrations, medium to high temperatures, and still tend to be quite slow, typically taking weeks to reach completion. In comparison, electrochemistry usually takes only minutes to hours. Also, many industrial wastewaters have significantly higher hazardous chemical content making biological processes ineffective. So electrochemical methods may offer a more rapid, green, and modular solution. Also, electrochemical
oxidation can achieve very strong oxidation power to degrade the otherwise recalcitrant chemicals for microbes.

Nevertheless, high energy consumption and mass transport limited kinetics are the key factors preventing the wide application of electrochemical organic oxidation. The main issue leading to the high energy consumption is competitive oxygen evolution reaction, eq 1.5:

\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{e}^- + 4 \text{H}^+ \quad (E^o = 1.03 \text{ V vs Ag/AgCl}) \quad (1.5) \]

The oxygen evolution reaction takes up energy and reduces the energy efficiency of organic oxidation. To improve energy efficiency, the electrode can be designed to achieve a high overpotential towards oxygen evolution to suppress the competing reaction.

Another limiting factor, the slow mass transport, often becomes the bottleneck of the overall kinetics because the subsequent oxidation step is usually fast. When mass transport is limiting the organic oxidation kinetics, higher energy input will only result in faster oxygen evolution and thus a waste of energy. Therefore, enhancing mass transport in the electrochemical system is another critical goal.

There are three modes of transportation: diffusion, convection and migration.[4] Diffusion is the movement of species from higher concentration to lower concentration along the concentration gradient. Convection is the hydrodynamic transport of species with forced convective flow. Migration is the movement of charged species in the electric field along the potential gradient. The holistic expression of mass transport to the electrode surface is shown in eq 1.6:[4]

\[ J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad (1.6) \]

where \( J_i(x) \) is the flux of species \( i \) (mol s\(^{-1}\) cm\(^{-2}\)) at distance \( x \) from the surface, \( D_i \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)), \( \partial C_i(x)/\partial x \) is the concentration gradient at distance \( x \), \( \partial \phi(x)/\partial x \) is the potential gradient, \( z_i \) and \( C_i \) are the charge and concentration (mol cm\(^{-3}\)) of species \( i \), and \( v(x) \) is the velocity.
of a volume element in solution moving along the axis. The three terms on the right-hand-side denote the contribution to the overall mass transport of diffusion, migration and convection, respectively.

For a given concentration \( C_i \), diffusional mass transport is hard to change by changing external conditions. In comparison, convective mass transport may be easily improved by increasing \( v(x) \) in eq 1.6. So utilizing the pressure forced flow of the filtration system to convectively transport target species to the electrode surface may significantly enhance mass transport and the overall electrochemical performance.

### 1.3 Adsorption

While organics can be removed by mineralization to \( \text{CO}_2 \), inorganic pollutants (e.g. heavy metals) must require alternatives for removal. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. It is widely used in water treatment due to its effectiveness towards low concentration hazardous species, cost-effectiveness, stability, and ease of operation. Many studies have demonstrated promising adsorptive removal results for hazardous inorganic ions including arsenic,\(^5\) copper,\(^6\) chromium\(^7\) and fluoride.\(^8\) For example, a Ce-Ti oxide adsorbent was demonstrated to effectively bring down the arsenic level to below drinking water standard limit (10 ppb) with As(III) and As(V) adsorption capacity of 7.5 and 6.8 mg g\(^{-1}\), respectively.\(^9\) The sorption mechanism is presented in Figure 1.2.

Briefly, the arsenate and arsenite adsorb onto the metal oxide surface by the hydroxyl ligand exchange mechanism and form monodentate or bidentate complexes with the adsorbent surface.

Many highly effective adsorbent are first made in powder and then converted into into large granules for sorption columns or beds to scale up for filtration. However, this scaling up method is inefficient because large aggregates and granules have significantly slower adsorption kinetics and decreased effective adsorption area. The adsorbents such as activated carbon are usually very porous to get max-
maximum sorptive surface area for adsorption. The main mass transport mode through the pores to reach the majority of sorption sites is only diffusion. Large aggregates and granules have great mass transport resistance because adsorbates have to travel a much longer path inside adsorbents. This slows down the overall kinetics and makes many reactive sites inaccessible. Nevertheless, if convective mass transport can be introduced within pores through proper material structure design, the adsorption kinetics as well as the adsorption technology would be significantly improved.

1.4 Electrochemical filtration

Previous studies have made many attempts to combine filtration processes with electrochemistry. Beginning in the 1960s, fluid bed electrodes[10] and packed-bed electrodes[11] were investigated for many electrochemical applications including removal of metal ions from dilute solutions. These electrodes consist of solid, electrically conducting particles packed on a porous support through which an electrolyte can be pumped. The setup of a packed bed cell is presented in Figure 1.3.

Nevertheless, the anode material consists of packed particles such as graphite or nickel that only allowed liquid to filtrate through spaces around the particles, thus having limited reactive surface
area and mass transport. Researchers then investigated flow-through electrodes where the liquid went through rather than around the electrode material.\cite{12} Porous carbon cloth or graphite felt consisting of 10 \( \mu \)m fibers were examples of flow-through electrode and were found efficient for metal recovery.\cite{13} But the pore size of those carbon materials are in millimeters and cannot take advantage of the size exclusion benefits of the membrane filtration. Also the fibers have limited surface area compared with other carbon materials, limiting the number of reactive sites. To further improve electrochemical filtration technology, a membrane-like anode material should be used to utilize the membrane filtration benefits. The material should also has high specific area, high porosity, good conductivity, and good chemical stability.

A hybrid membrane filtration and electrochemical reactor using carbon nanotube (CNT) as the anodic filter was proposed and studied first in 2010 to explore the potential for water treatment.\cite{14} The unique porous structure of CNT allows flow through the pores (the interstitial space between tubes). And the forced convective flow by filtration through the pores may enhance mass transport for electrochemistry and adsorption by bringing target species towards the electrode surface. Mem-
brane filtration with electrochemistry also achieves in-situ organic oxidation without generating a concentrate that requires additional treatment steps. Therefore, the CNT filter combines separation and oxidation technology into one effective step. An example of the electrochemical filtration device is displayed in Figure 1.4. A commercial 47 mm polycarbonate filtration casing (Whatman) was modified to allow for simultaneous electrochemistry (Figure 1.4B,C). Two holes were drilled in the upper piece of the filtration casing as openings for the cathodic and anodic leads. The main components of the electrochemical filter casing are the perforated stainless steel cathode (1) separated with an insulating silicone rubber seal (2) from the titanium anodic ring-connector (3). When the filtration casing is sealed, the anodic Ti ring (3) is pressed into the carbon nanotube filter (4) for electrical connectivity. The CNT anodic filter is critical for the electrochemical filtration process. Compared to other carbon-based alternatives, CNT has a unique combination of properties: high surface area, high conductivity, high porosity, good chemical stability and good mechanical stability that together yield a potentially promising electrochemical filter for water treatment purposes.

A preliminary study was first completed to demonstrate that the electrochemically active multiwalled carbon nanotube (MWCNT) filter is effective toward the adsorptive removal and electrochemical oxidation of the aqueous dyes, methylene blue and methyl orange, and the oxidation of the aqueous anions, chloride and iodide.[14] In the absence of electrochemistry, the MWCNT filter completely removed all dye from the influent solution until a near monolayer of dye molecules adsorbed to the MWCNT filter surface. Electrochemical filtration at 2 V resulted in >98 % oxidation of the influent dye during a single pass through the ~40 μm thin porous MWNT network with a <1.2 s residence time. The electrochemical MWCNT filter was also able to oxidize aqueous chloride and iodide with minimal overpotential. The results show the potential of an electrochemical MWCNT filter for the adsorptive removal and oxidative degradation of aqueous contaminants.
1.5 Thesis overview

Moving forward, both the mechanism and the application side of the CNT electrochemical filtration needs to be studied in greater detail to better develop this new technology for water treatment applications. In this dissertation, Chapter 2 investigates the qualitative mechanism behind the chemistry to understand the key reaction steps and drivers for performance. The mechanism leads to insights into synergies of filtration, adsorption and oxidation processes. Chapter 3 took the qualitative mechanism further to develop a quantitative model aiming at providing deep accurate insight into kinetics and reactive sites. The model used input from experimental measurements including initial concentration, anode potential, and CNT characteristics to generate a fundamental and quantitative picture of kinetics and reaction mechanisms. With regard to applications, CNT based material studies should be completed to tailor the technology to utilize the synergistic implications to improve performance.
for organic and inorganic pollutant removal. Chapter 4 focuses on organic electro-oxidation. We discussed preparation and performance of a 3–5 nm bismuth doped tin oxide coating that reduces competitive oxygen evolution on the CNT anode to improve energy efficiency and anode chemical stability. Chapter 5 focuses on (electro-)sorptive removal of inorganic species. An effective arsenic adsorbent (TiO$_2$) was uniformly coated onto the CNT walls for rapid arsenic adsorption through filtration of a very thin (<100 µm) membrane. The effect of mass transport, electrosorption, and filter structure on adsorption kinetics and adsorption capacity was discussed.
Reactive Transport Mechanism during Electrochemical Filtration
2.1 Abstract

An electrochemical carbon nanotube (CNT) filter has been reported to be effective for the adsorptive removal and oxidation of aqueous organic compounds. Here, we complete a detailed investigation of the aqueous dye oxidation reactive transport mechanism during electrochemical filtration. Similar to batch electrolysis, mass transfer, physical adsorption, and electron transfer are found to be three primary steps in the overall electrochemical filtration organic oxidation mechanism. Mass transfer was quantitatively examined by chronoamperometry and normal pulse voltammetry and determined to be increased 6-fold during electrochemical filtration as compared to batch electrochemistry. Convection-enhanced mass transfer to the electrode surface is determined to be the primary factor for increased current density and organic oxidation during electrochemical filtration. Physical adsorption of the organics onto the CNTs was evaluated using temperature-dependent batch adsorption and electrochemical filtration experiments. The electrochemical filtration kinetics were observed to have a minor negative temperature-dependence. Electron transfer was examined by challenging the electrochemical filter with a range of increasing dye concentrations until the mass transfer and adsorption processes were saturated. Upon surface site saturation, the electron transfer rates were determined to be $8.5 \times 10^5$, $6.3 \times 10^6$, and $1.3 \times 10^7 \, \text{e}^{-\text{s}^{-1}\text{m}^{-2}}$ at anode potentials of 0.35, 0.77, and 1.50 V, respectively. The electron transfer mechanism was also investigated and direct electron transfer was determined to be the dominant methyl orange oxidation mechanism at all evaluated anode potentials with an increasing contribution from indirect oxidation processes at potentials $\geq 1.0$ V. The anode potential dependent maximum electron transfer rate is also observed to be affected by the polarity of the organic charge indicating electromigration is also active. In summary, electrochemical filtration is advantageous as compared to batch electrolysis due to the liquid flow through the electrode resulting in convection-enhanced transfer of the target molecule to the electrode surface.
2.2 Introduction

Carbon nanotubes (CNTs) have attracted extensive attention since their discovery due to their combination of unique electronic, mechanical, and chemical properties.\cite{15} CNT-based materials may have potential for application in a variety of fields such as energy conversion,\cite{16} biomedical devices,\cite{17} and adsorptive water treatment.\cite{18} A promising general application is CNT-based electrodes.\cite{19–22} As compared to conventional carbon electrodes, CNTs are reported to have better electrocatalytic properties toward many electrochemical reactions.\cite{23} For example, CNT modified glass carbon electrode shows significantly lower overpotential and higher peak current compared to bare glass carbon electrode for several molecules including ascorbic acid, uric acid, and dopamine.\cite{24} These superior electrocatalytic properties may be attributed to the small dimensions of the tubes and channels in the tubes, the unique electronic structure, and the topological defects present on the tube surface.\cite{25} In addition, utilizing CNTs as either a bulk electrode or to modify a working electrode has been observed to increase electron transfer rates toward dyes\cite{14} and biomolecules.\cite{26} Thus, CNT-based electrodes may also have the potential for advanced environmental applications including wastewater treatment\cite{27} and micropollutant sensors,\cite{28} where minimal oxidative overpotentials are desired. Rational application of CNT-based electrodes for environmental applications will require an in depth physical chemical understanding of the fundamental electrochemical processes occurring at such electrodes.

The general electrochemical reaction mechanism is composed of four primary steps: (1) mass transfer to the electrode, (2) adsorption to and desorption from the electrode, (3) direct electron transfer at the electrode, and (4) bulk chemical reactions preceding and/or following electron transfer.\cite{4} While direct (3) or indirect (4) electron transfer is immediately responsible for electrochemical transformations, mass transfer (1) to the electrode surface is often found to limit the overall kinetics.\cite{29–31} Electrochemical mass transfer limitations arise since convection becomes negligible near the electrode-
Figure 2.1: Electrochemical filtration reactive transport mechanism. (1) Molecules are transported to electrode surface via convective and diffusive mass transfer as a function of flow rate, \( J \), and concentration, \( C \). (2) Molecules are adsorbed onto CNT surface as a function of temperature, \( T \). (3) Molecules diffuse on the CNT surface to electrochemically active sites and electron transfer occurs as a function of anode potential, \( V \).

Along with mass transfer, there are other processes that are also important to the overall electro-
chemical reaction kinetics and mechanism such as adsorption and electron transfer; Figure 2.1, steps 2 and 3, respectively. For example, physical and chemical adsorption of species to an electrode surface can significantly affect the electron transfer kinetics by altering its surface structure and chemistry resulting in a shift in the Gibbs free energy of reactants and/or products.\cite{33, 34} The adsorption-dependent reactivity is of importance to CNTs as they have a large specific surface area\cite{35} and have been shown to adsorb many chemical species. For example, CNTs have been observed to strongly adsorb aromatic compounds\cite{36} and natural organic matter\cite{37} via a combination of strong $\pi$-$\pi$ interactions and hydrophobic interactions.\cite{38} In turn, a CNT-based filter for adsorptive chemical removal has been proposed as a water treatment technology.\cite{38} An electrochemical CNT filter takes this concept one step further by not only adsorptively removing, but also electrochemically degrading the target contaminant. Thus, a fundamental understanding of organic sorption to the CNTs will result in an improved understanding of the overall electrochemical filtration mechanism.

Following molecular adsorption to the electrode, direct electron transfer will occur upon application of a sufficiently high potential. The electron transfer mechanism and kinetics will also be significantly affected by the electrode surface structure and chemistry. An accurate electrode model requires taking into account the total number and specific types of surface reactive sites because of their ability to substantially affect the electrochemical mechanism,\cite{39} kinetics,\cite{40} and overpotential.\cite{41} In regards to CNTs, the electrochemically reactive sites have been reported to be the conjugated sp$^2$ surface defect sites, similar to other elemental carbon-based electrodes. Specifically, these would be the edge-plane-like sites,\cite{42} which for CNTs are primarily located at the ends of the nanotubes, but may also be found on the tube sidewalls. For example, a stable carboxylic acid group redox couple was observed to be the electrochemically active site on a CNT electrode.\cite{43} Although specific surface chemistry effects on electrochemical processes have received widespread recognition, they are often overlooked by assuming surface homogeneity and disregarding existence of specific reactive sites.\cite{42} Kinetic methods overlooking specific chemical details can still yield insight into the maximum number
of electrochemically active sites and their overpotentials.

Here, we investigate the overall organic oxidative mechanism of an electrochemical CNT filter. We propose a primary three-step electrochemical filtration reactive transport mechanism: (1) mass transfer, (2) molecular adsorption, and (3) direct electron transfer to describe the oxidation of the dyes methyl orange and methylene blue, Figure 2.1. The hydrodynamically enhanced mass transfer of the electrochemical filtration system is studied by chronoamperometry and normal pulse voltammetry and is compared to a conventional batch bipolar electrochemical system. The physical adsorption of the dyes to the CNTs is investigated by temperature-dependent batch adsorption and electrochemical filtration experiments. The electron-transfer kinetics and mechanism during electrochemical filtration were studied by concentration- and voltage-dependent experiments. The electrochemical filtration oxidative efficiency is discussed in terms of experimental parameters such as flow rate, temperature, and voltage that mediate the overall reaction kinetics.

2.3 Experimental Materials and Methods

2.3.1 CNT Selection

In this study, we utilized multiwalled carbon nanotubes that had been made into preformed porous networks with an average depth of 40–50 µm (NanoTechLabs, Buckeye Composites, Yadinkville, NC). The CNTs were characterized here and previously in detail[14] and have a diameter distribution that agrees with the manufacturer specifications of \( <d> = 15–20 \text{ nm} \). Thermogravimetric analysis of the CNTs showed they are composed of 1–1.5% amorphous carbon and 4–5% residual metal catalyst, which was mostly Fe.[14]
2.3.2 SEM Analysis

Scanning electron micrography (SEM) was completed on a Zeiss FESEM Supra55 VP at Harvard’s Center for Nanoscale Systems. ImageJ (NIH) software was used to analyze the obtained scanning electron micrographs. The average CNT diameter was the average of at least 100 measurements from at least 2 images.

2.3.3 Chemicals

NaCl (EMD Chemicals, AR grade, >99%) was chosen as the background electrolyte and used at a concentration of 10 mM for all experiments. Methyl orange hydrate (MO; >95%) and methylene blue hydrate (MB; >97%) were purchased from Sigma-Aldrich. Methylene blue was quantified by its absorption at \(\lambda_{\text{max}} = 665\,\text{nm} \) \((\varepsilon = 74,100\,\text{M}^{-1}\text{cm}^{-1})\). Methyl orange was quantified by its absorption at \(\lambda_{\text{max}} = 464\,\text{nm} \) \((\varepsilon = 26,900\,\text{M}^{-1}\text{cm}^{-1})\).

2.3.4 Electrochemical Filtration

The CNT networks were supported by 5-μm PTFE membranes (Omnipore) and placed into the electrochemistry-modified filtration casing (Whatman), Figure 1.4. The weight of CNTs anode used in all of the experiments is 10 mg. After sealing the filtration casing and priming with water, a peristaltic pump (Masterflex) was used to flow water through the filter at \(1.5 \pm 0.1\,\text{mL min}^{-1}\) to rinse and calibrate the CNT filter. The liquid flow rate was calibrated with a graduated cylinder. Once the water rinse and flow rate calibration was complete, the pump was primed with the appropriate influent solution and then the experiment was started. The electrochemistry was driven by an Agilent E3646A DC power supply and connected to the external electrode wires with alligator clips. Effluent aliquots were collected at various time-points and analyzed by spectrophotometer to determine the effluent concentration of the target molecule. The temperature-dependent experiments were carried out by
putting the whole filtration set up including pump, filter, power supply, and influent container in an incubator set to the desired temperature. The temperature of influent was measured by a thermometer to confirm the temperature of solution is consistent with experimental design.

2.3.5 **Chronoamperometry and Normal Pulse Voltammetry**

The chronoamperometry and normal pulse voltammetry experiments were completed with a CHI604D electrochemical workstation; Ag/AgCl was used as the reference electrode, the perforated stainless steel shim was used as the counter electrode, and the prepared CNT network was used as the working electrode. For all experiments, the time-dependent current was continuously recorded by the electrochemical analyzer. For the normal pulse voltammetry experiments, the current was recorded at 100 s after each potential step and it was assumed that this time period was sufficient for the nonfaradaic current to become negligible. The electrochemical filtration system was operated at a flow rate of 1.5 mL min$^{-1}$ and the liquid flow was kept continuous for at least 5 min prior to a potential step. The batch system was operated in a beaker containing 0.5 L of 300 or 1000 µM methyl orange solution with 10 mM NaCl electrolyte. To ensure a consistent initial batch system state, the solution was stirred for at least 5 min prior to a potential step. The results were plotted as current density, which is calculated using the current recorded and the total surface area of CNT anode. The total CNT surface area is obtained by multiplying the mass of CNT anode by its specific surface area, 88 g m$^{-2}$.[14]

2.3.6 **Sorption Experiments**

The sorption experiments were carried out in 250 mL glass Erlenmeyer flasks containing 100 mL of aqueous methyl orange solution, 5–250 µM, and 0.015 g CNT powder. The flasks were shaken at 150 rpm in an incubator (New Brunswick Scientific) at temperatures of 15, 25, and −35 ºC for 24 h. Sample aliquots were filtered prior to analysis.
2.4 Results and Discussion

2.4.1 Electrochemical Filter Design and Operation

All filtration experiments were conducted with an electrochemically modified filtration casing as described in detail in our previous study[14] and depicted in Figure 1.4. Briefly, a 47-mm diameter carbon nanotube (CNT) network (NanoTechLabs, Buckeye Composites) was placed on top of a wetted 5.0-µm pore PTFE membrane (Omnipore). The CNT network was utilized as an anode and connected to the DC power supply via mechanical contact to a titanium ring. A perforated piece of stainless steel shim was used as the cathode and an insulating silicone rubber O-ring was used to separate the electrodes and seal the device. A polycarbonate 47-mm filter casing (Whatman) was modified to incorporate both anode and cathode materials. Images of the electrochemical filtration device and the CNT networks used in this study can be found in Figure 1.4. An aerial SEM image of the CNT network is presented in Figure 2.2. The macroporous filters had an average pore diameter of $90 \pm 40$ nm and the pore shape was quite heterogeneous.

Porous CNT anodes were selected to study the reactive transport mechanism during electrochemical filtration as they have desirable physical chemical properties that may lead to improved wastew-
ater treatment performance. For example, a recent study has shown an electrochemical CNT filter to operate with an energy efficiency of 4–16 kWh kg⁻¹ COD or <1 kWh m⁻³,[44] which is similar to or better than other state-of-the-art electrochemical oxidation processes.[27–29, 31] Similar to black carbon electrodes, CNTs have a high specific surface area[35] and are effective for the adsorptive removal of chemical contaminants.[18, 36–38] However, CNTs may show improved electrochemical performance as compared to traditional carbon materials due to their extended sp² structure[15] and reduced edge-like sites resulting in excellent 1-D conductivity and increased corrosion resistance. In regards to electrochemical filtration, the high-aspect ratio CNTs are easily formed into free-standing, thin-film, 3D networks of high porosity (85–90%), Figure 2.2 and 1.4, with liquid flow rates similar to microfiltration devices at 500 to 2000 LMH-bar.[14, 32, 44] This porous microstructure favors fast sorption and electrochemical oxidation due to the high number of easily accessible and reactive sites as compared to black carbon materials where many of the sites may be buried in the granules. Access to all of the surface sites within the anodic CNT network can be made by convectively flowing the liquid through the network. Thus, electrochemical filtration with porous CNT anodes may result in enhanced mass transfer and electrochemical energy efficiencies. However, since the liquid needs to be pumped through the filter, the pumping energy should also be considered to ensure overall improvement. If during electrochemical filtration \( V = 2.0 \) V and \( I = 5 \) mA, then the electrochemical energy necessary for 1 h of operation is 39 J. A common back pressure is 15 kPa[44] at a flow rate of 90 mL h⁻¹ and assuming a pump efficiency of 75%, the total energy cost for pumping is 1.5 J or 3.8% of the electrochemistry. Therefore, if the electrochemical efficiency is significantly increased during electrochemical filtration, the overall energy efficiency will also be significantly increased.
2.4.2 Mass Transfer: Hydrodynamic Enhancements during Electrochemical Filtration

The effect of hydrodynamically enhanced mass transfer, Figure 2.1, step 1, on the current density in the electrochemical filtration system versus a conventional batch electrochemical system was first compared by chronoamperometry over a series of anode potentials. Representative current (mA) versus time (s) plots for the filtration (red) and batch (black) systems obtained under the conditions of anode potential = 0.85 V, [MO]$_{in}$ = 300 µM, and [NaCl] = 10 mM are presented in Figure 2.3. The initial current of both filtration and batch systems was around 80 mA and decreased quickly over the first few seconds due to expansion of electrochemical diffusion layer.[4] After the initial sharp decline, the current of the filtration system leveled-off and reached a steady-state value of 5.5 mA. It is of note that there was a periodic oscillation to the filtration current that is likely due to electrolytic gas formation within the CNT network that effectively passivates a fraction of the electrochemically active sites. In contrast to the filtration system, the current of the batch system continually decreased to 0.8 mA after 100 s of electrolysis. The current of the filtration system was greater than the batch system for $t > 10$ s indicating a significantly greater molecular flux to the electrode surface. The increased flux in the filtration system can be explained by the non-negligible convective mass transfer to the electrode surface due to the hydrodynamic flow through the anode.[4]

The Cottrell equation, 2.1, describes the current-time relationship for diffusion-limited electrochemical systems such as the batch system in this study and can be used to estimate the molecular diffusion coefficient.[45, 46]

\[ I = \frac{nFA}{\sqrt{4\pi D t}} e^{-rac{1}{2} \pi t} \]  

(2.1)

In eq 2.1, $n$ is the number of electrons transferred, $D$ is the diffusion coefficient ($cm^2 s^{-1}$), $c$ is the bulk concentration of the molecule to be electrolyzed (mol cm$^{-3}$), $A$ is the geometric electrode area.
Figure 2.3: Chronoamperometry for the batch and filtration electrochemical systems. The batch system is in black and the filtration system in red. The conditions are $[\text{MO}]_0 = 300 \mu\text{M}$ and $[\text{NaCl}] = 10 \text{ mM}$ for both systems and $J = 1.5 \text{ mL min}^{-1}$ for the filtration system. The inset displays a linear plot of current versus time $^{-1/2}$ for the batch system.

$(7.1 \text{ cm}^2)$, and $I$ is the current at time $t$. An estimation of the maximum number of electrons oxidized from MO, $n$ in eq 2.1, can be made by comparing the MO molecular flux to the electron flux. It is assumed that anodic $\text{O}_2$ evolution is negligible at $0.85\text{V}$ vs SCE, which is below the potential for the 4-electron water oxidation. This assumption is confirmed by normal pulse voltammetry, Figure 2.4, where oxygen evolution is observed at anode potentials $\geq 1.1 \text{V}$. At an anode potential of $0.85 \text{V}$ and a flow rate of $1.5 \text{ mL min}^{-1}$, $\Delta[\text{MO}] = 130 \text{ microM}$ and $I_{S5}S = 5.5 \text{ mA}$ corresponding to the oxidation of $3.3 \times 10^{-9}$ moles of MO per second and $5.5 \times 10^{-8}$ mol of electrons$^{-1}$ flowing through the anode. Thus, a maximum of 17 electrons out of 80 total electrons could be oxidized from each MO molecule indicating incomplete oxidation. The current density versus time$^{-1/2}$ is plotted in the inset of Figure 2.3 and exhibits a linear relationship ($R^2 = 0.998$) over an intermediate at intermediate time range, i.e., 20–40 s. From the slope of this line, the diffusion coefficient, $D$, was calculated to be $8.5 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ for the batch system. An estimation of diffusion layer thickness, $\Delta$, can be made.
Figure 2.4: Normal pulse voltammograms for the batch and filtration electrochemical systems. (a) [MO]_{in}= 300 \mu M and (b) [MO]_{in}= 1, 100 \mu M. The batch system is in black and the filtration system in red. The experimental conditions are [NaCl] = 10 mM and the flow rate was $J = 1.5 \text{ mL min}^{-1}$ for the filtration system. The mass transfer limited regime is marked with a horizontal line.

using the following equation, eq 2.2:

$$\Delta = (2Dt)^{1/2}$$  \hspace{1cm} (2.2)

After 100 s of electrolysis, the diffusion layer thickness in the batch system was estimated to be 1.3 mm. However, natural convection may arise and reduce this thickness. Thus, a calculation of the diffusion layer thickness under natural convection was carried out using eq 2.3 derived by Levich[47] for the mean value of diffusion layer thickness $\delta$ of a vertical plate electrode under natural convection.

$$\delta \approx \frac{Z^{1/4}}{0.7Sc^{1/4}(\frac{g\Delta C}{4\rho})^{1/4}}$$  \hspace{1cm} (2.3)

where $h$ stands for electrode height, $Sc = \nu/D$ is the Schmidt number, with $\nu$ and $D$ being the solution kinematic viscosity and molecular diffusion coefficient, respectively, $g$ is gravitational acceleration, and $\Delta C$ is the numerical value of the concentration decrease across the diffusion layer in $\text{g cm}^{-3}$. For the batch system in the diffusion limited regime, the average MO concentration inside the CNT
network is expected to be near zero. Thus, the filter is acting like one planar electrode and eq 2.3 is applicable. The height of our electrode is 3 cm, $v = 1 \times 10^{-4}$ cm$^2$ s$^{-1}$, $D = 8.5 \times 10^{-5}$ cm$^2$ s$^{-1}$, and $\Delta C = 9.8 \times 10^{-5}$ g cm$^{-3}$, yielding a diffusion layer thickness from natural convection of $\delta = 1.45$ mm. Therefore, the 1.3 mm estimation of diffusion layer is reasonable and within the diffusion layer thickness limit associated with natural convection.

The thickness of diffusion layer in the filtration system is expected to be lesser than batch system under the same experimental condition due to the hydrodynamic compression of the diffusion layer. However, there is insufficient information for a quantitative estimation of the filtration system diffusion layer thickness as it cannot be considered diffusion-limited. Thus, normal pulse voltammetry experiments will be completed to provide more detailed and quantitative information about mass transfer in the filtration system.

Normal pulse voltammetry (NPV) was utilized to compare the mass transfer in the batch (black) and filtration (red) systems as presented in Figure 2.4. For the NPV experiments, the current was recorded 100 s after each potential step over a range of anode potentials from 0.4 to 1.3 V. Figure 2.4a displays the NPV for the batch and filtration systems at an influent methyl orange (MO) concentration of 300 $\mu$M. In both systems, as the potential was increased, the current exhibited a sigmoid transition i.e., at low potentials, <0.5 V, the current was near zero, then the current increased linearly with increasing potential from 0.5 to 0.8 V, and finally the current achieved a potential-independent, mass transfer limited plateau at potentials >0.8 V. The linear increase in current with increasing potential is representative of increasing direct electron transfer kinetics. Since MO electrooxidation is kinetically faster than MO diffusion, the CNT anode surface MO concentration will decrease resulting in the formation of a near surface concentration gradient. Eventually, the anode potential will increase to a point, in this case to >0.8 V, where the electrode surface MO concentration is zero and mass transfer to the interface becomes the limiting factor for MO electrooxidation. Thus, any further increase in anode potential should not lead to a further increase in current and a plateau will be observed due to
mass transfer limitations.\textsuperscript{[4]} The observed current increase at anode potentials \(>1.1\) V vs SCE, is attributed to oxygen evolution\textsuperscript{36} as electrolytic gas bubbles are visibly observed on CNT anode. Thus, any data collected at anode potentials \(>1.1\) V will not be discussed in detail at this moment since we only want to consider direct MO oxidation.

The mass transfer limited current regime, i.e., the current plateau in Figure 2.4a, is observed to begin at a greater potential in the filtration system, 0.8 V, as compared to the batch system, 0.6 V, indicating a hydrodynamic mass transfer enhancement likely due to the fluid flux through the electrode. Quantitatively, the mass transfer limited current density in the electrochemical filtration system is 6.1 mA m\(^{-2}\), and for comparison the mass transfer limited current density of conventional batch system is 0.97 mA m\(^{-2}\). Thus, at a liquid flow rate of 1.5 mL min\(^{-1}\) the electrochemical filtration design improves the current density and thus mass transfer by 6-fold as compared to the classical batch design under similar aqueous conditions. The thickness of the diffusion layer in the filtration system can be estimated to be approximately 1/6 of the batch system value, 1.3 mm, so a lower limit for estimation of diffusion layer thickness in the filtration system is 216 \(\mu\)m, about 5 times the thickness of porous CNT anode. The conclusion that mass transfer is significantly enhanced in the filtration system is supported by both the delay in mass transfer limited NPV regime from \(\sim 0.65\) V anode potential in the batch system to \(>0.8\) V in the filtration system and the 6-fold greater current density for the filtration system within the mass transfer limited regime, Figure 2.4a.

The NPV for the electrochemical filtration (red) system and the conventional batch (black) system at an MO concentration of 1,100 \(\mu\)M is presented in Figure 2.4b. The current density of the batch system again exhibited a sigmoid transition from zero to the mass transfer limited value of 3.5 mA m\(^{-2}\). The batch system mass transfer limited region was delayed from 0.65 V when \([\text{MO}]_{\text{in}} = 300\ \mu\text{M}\) to 0.85 V when \([\text{MO}]_{\text{in}} = 1100\ \mu\text{M}\) due to the increased diffusion rate at the higher MO concentration. In contrast, the current density of the electrochemical filtration system continually increased and did not appear to plateau and reach the mass transfer limited regime. This does not indicate the elim-
ination of the mass-transfer limitation, just that the start of the regime was shifted past the oxygen evolution potential and masked by the O$_2$ current density. Thus for the 1000 µM case in Figure 4b, the quantitative comparison will be completed by using the current density values at 1.0 V, just prior to oxygen evolution. The current density at 1.0 V anode potential for the electrochemical filtration system is \( \sim 20 \text{ mA m}^{-2} \) and for the batch system is 3.2 mA m\(^{-2}\). The current density and thus mass transfer is once again observed to be enhanced 6-fold for the filtration system as compared to the batch system due to convection through the electrode. However, even with such a large hydrodynamic enhancement, the anode potential can still be increased to a point where the electrochemical kinetics is significantly faster than the molecular flux.

A representative electrochemical diffusion layer profile is presented in Figure 2.5 to help explain the interaction between convection, the microstructure of CNT anode in the filtration system, and the resulting 6-fold increase in mass transfer as compared to batch system. In the batch system, Figure 2.5a, the diffusion layer is thicker than the anode, the concentration gradient is very low, and the MO concentration is zero within and at the surface of the CNT network. In this case, the microstructure of the porous CNT anode becomes irrelevant and the CNT network acts as a planar electrode due to averaging of the microstructure within the expanding diffusion layer.[4] In contrast, during electrochemical filtration, the CNT anode microstructure will be of significance. As depicted in Figure 2.5b, due to convective mass transfer through the CNT network, the average MO concentration at all of the filter cross sections is above zero i.e., always above effluent concentration, even if the system is in mass transfer limited regime. The concentration gradient between pore center and CNT surface and thus mass transfer is expected to be high, since the characteristic length, the average pore radius, is only 45 nm. Therefore, the convective flow through the CNT network allows for electrochemical oxidation at both the surface and the inner CNT surfaces and produces a high local concentration gradient resulting in an observed 6-fold increase of target molecule mass transfer to electrode interface.
2.4.3 **Physical Adsorption/Desorption: Temperature-Dependent Effects on Electrochemical Filtration.**

The nature of dye adsorption to the CNTs, Figure 2.1, step 2, and the influence of adsorption on the electrooxidation kinetics were investigated by temperature-dependent experiments as presented in Figure 2.6. For the experiments presented in Figure 2.6, the temperature was maintained at 15 (blue), 25 (black), and 35 °C (red) and prior to electrolysis the CNT surface was first saturated with MO, i.e., 300 µM MO was flowed through the CNT network in the absence of applied potential until the effluent MO concentration was equivalent to the influent concentration. Then an applied voltage of 2.0 V corresponding to an anode potential of 0.8 V was applied to the electrochemical filtration cell until a steady-state effluent MO concentration was observed for 30 min. The steady-state $[\text{MO}]_{\text{ef}} / [\text{MO}]_{\text{in}}$ is observed to slightly decrease with decreasing temperature, indicating that the extent of electrochemical oxidation increases with decreasing temperature. The inverse reaction kinetics temperature-dependence cannot be explained by effects on the electron transfer kinetics, i.e., the Arrhenius equation\[^{48}\] or transition state theory.\[^{49}\] According to these theories, the reaction rate constant should generally increase with increasing temperature.
Figure 2.6: Effect of temperature on electrochemical filtration oxidation kinetics. Effect of temperature on the extent of oxidation during electrochemical filtration where the applied voltage = 2 V, \( J = 1.5 \text{ mL min}^{-1} \), and \([\text{MO}]_{\text{in}} = 300 \mu\text{M}\).

One possible explanation to this interesting inverse temperature dependence may lie in the temperature effect on MO adsorption and desorption to the CNT electrode surface. To examine the nature of MO adsorption, batch temperature-dependent sorption experiments were conducted to investigate the adsorptive behavior of MO on CNTs. MO adsorption isotherms onto the CNTs at 15 (blue), 25 (black), and 35 °C (red) are displayed in Figure 2.7. In all cases, the adsorption capacity increased with increasing MO concentration until a plateau is reached. The temperature-dependent MO adsorption to the CNTs is quantitatively examined using the Langmuir isotherm. The Langmuir adsorption isotherm model has been successfully utilized to quantitatively describe monolayer sorption processes and determine sorption parameters such as the maximum sorption capacity, the partitioning coefficient and the adsorption thermodynamics via temperature-dependent isotherms.[50] Experiment data and fitting of data to the Langmuir isotherm are available in Supporting Information, Figure 2.7. In all cases, the Langmuir fitting had high correlation coefficients, i.e., \( R^2 > 0.97 \), and the correspond-
Figure 2.7: Effect of temperature on dye adsorption to the CNTs. Adsorption used 0.015 g CNTs, V = 100 mL, and allowed for 24 h to reach equilibrium. The points are experimental data and lines are fits to the Langmuir isotherm.

The fitting parameters are listed in Table 2.1.

**Table 2.1: Langmuir Isotherm Parameters for MO Adsorption onto CNTs.**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>b (L mg⁻¹)</th>
<th>q_m (mg g⁻¹)</th>
<th>R²</th>
<th>ΔG° (kJ mol⁻¹)</th>
<th>ΔH° (kJ mol⁻¹)</th>
<th>ΔS° (kJ mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>2.81</td>
<td>32.2</td>
<td>0.977</td>
<td>-35.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>2.33</td>
<td>28.5</td>
<td>0.983</td>
<td>-36.3</td>
<td>-11.2</td>
<td>0.0845</td>
</tr>
<tr>
<td>35</td>
<td>2.07</td>
<td>25.3</td>
<td>0.996</td>
<td>-37.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ q_e = q_mC_e/(1/b + C_e) \]

\[ \Delta G° = -RT\ln b; \quad \Delta G° = \Delta H° - T\Delta S° [47] \]

The maximum sorption capacity decreases by 10–20% for every 10 °C increase in temperature. Thermodynamic parameters for MO adsorption onto the CNTs were also calculated. The negative ΔG° values indicate...
that sorption of MO onto the CNTs is a spontaneous process under the experimental conditions. The \( \Delta S^\circ \) and \( \Delta H^\circ \) are calculated to be 0.085 kJ mol\(^{-1}\) K\(^{-1}\) and -11.2 kJ mol\(^{-1}\), respectively. The negative enthalpy value (\( \Delta H^\circ \)) indicates that the MO sorption process onto the CNTs is exothermic. Similar results were reported by Al-Johani et al.\([51]\) during their investigation of aniline adsorption to CNTs, where they found low temperature favors physical adsorption and reported a negative enthalpy of -24 kJ mol\(^{-1}\). The dominate interaction between MO and the CNTs is expected to be \( \pi \cdot \pi \) interaction as a recent literature review found \( \pi \cdot \pi \) to be the strongest intermolecular interaction between aqueous aromatic compounds and CNTs.\([38]\) According to the experimental adsorption isotherms and thermodynamic analysis, the equilibrium adsorption capacity decreases with temperature, in agreement with the observed results. However, we cannot attribute the temperature dependence of the overall electrochemical oxidation to this thermodynamic argument since electron transfer processes are too fast to assume equilibrium adsorption. Thus, an adsorption dynamics based hypothesis may provide a possible explanation. The equilibrium adsorption isotherm of methyl orange to CNTs, Figure 2.7, indicates an exothermic physical adsorption process. For physical adsorption processes, an increase in temperature generally results in an increase in desorption rate, thus reducing the residence time of molecules on the CNT surface and within the CNT network. Since the CNT electrocatalytic sites are predominantly found at the ends of the tubes,\([42]\) not all sorption sites will be near electron transfer sites and an increased desorption rate will reduce the likelihood of an adsorbed molecule finding an electron transfer site. As a consequence, the overall rate of reaction is decreased. In summation, although temperature and adsorption do effect the extent of oxidation during electrochemical filtration, the effect is relatively small at <10\% per 10 °C as compared to the previously discussed hydrodynamic enhancement and the anode potential effects to be discussed in the following section.
2.4.4 Electron Transfer: Concentration and Anode Potential Dependence

Although mass transfer and adsorption are important processes that affect the overall extent of oxidation during electrochemical filtration, the dye is ultimately transformed during the electron transfer step. Therefore, the nature and rate of electron transfer is of importance. The effect of influent dye concentration and anode potential on the electrooxidation rate was examined to determine the electron transfer kinetics and mechanism during electrochemical filtration. At high influent dye concentrations when the adsorption sites are saturated, the overall reaction rate will be limited by the electron transfer kinetics.

The concentration-dependent oxidation during electrochemical filtration of MO and MB at three different applied voltages; 1.0/1.6 (black), 2.0 (red), and 3.0V (blue), is presented in Figure 2.8, panels a and b, respectively. At each voltage, the electrochemical CNT filter was challenged with a range of influent concentrations from 25 to 5000 µM for MO and from 7 to 1200 µM for MB at a flow rate of 1.5 mL min$^{-1}$. For each concentration and voltage combination, the steady-state effluent dye concentration was measured and the molecules oxidized per unit time was calculated and plotted against influent concentration. In Figure 2.8a, the MO electrooxidation rate first increases with increasing influent concentration up to 110 µM for all three voltages. The voltage independent increase in electrooxidation rate indicates that the reaction is mass transfer limited when [MO]$_{in}$ ≤ 110 µM. The electrooxidation rate at 1 V reaches a maximum of 0.05 µmol min$^{-1}$ as indicated by the sharp transition when influent concentration exceeds 110 µM. The sharp transition indicates a shift from the mass transfer limited regime to the electron transfer limited regime. The 2 and 3 V curves stay in mass transfer limited regime until [MO]$_{in}$ > 500 µM. The greater transition concentration at 2 and 3 V as compared to 1 V indicates that a new and kinetically faster direct MO oxidation pathway has been activated. At [MO]$_{in}$ = 1000 µM the 2 V electrooxidation rate reaches a maximum of 0.37 µmol min$^{-1}$. The electrooxidation rate at 3 V was not observed to achieve an upper limit over the experimental con-
Figure 2.8: Concentration dependent oxidation of methyl orange and methylene blue during electrochemical filtration. (a) Methyl orange and (b) methylene blue. The conditions are [NaCl] = 10 mM, T = 25 °C, and J = 1.5 mL min⁻¹ for all experiments. Note the difference in the electrooxidation rate, y axis, scales of a and b.

Concentration range with a maximum oxidation rate of 1.04 µmol min⁻¹ at 5500 µM MO. If it is assumed that each MO molecule were to transfer 17 electrons to the anode as previously estimated, the maximum electron transfer rate is calculated to be $8.5 \times 10^{19}$ e⁻ per second at 1 V, $6.3 \times 10^{16}$ e⁻ per second at 2 V. At 3 V, indirect oxidation pathways are activated such that the contribution of direct oxidation toward total oxidation needs to be determined. From Figure 2.8a, at 3 V and an influent MO concentration of 300 µM, the $\Delta [MO] = 190$ µM and from calculation in later section direct oxidation contributes 140 µM of this total or 74% of total oxidation. By challenging the filter with 5500 µM MO to remove mass transfer limitation and saturate direct oxidation, the contribution of direct oxidation in total oxidation rate will increase to >74%. Thus, by assuming 74% of the total is direct oxidation, a lower limit for the direct electron transfer rate can be estimated to be $1.3 \times 10^{17}$ e⁻ per second at 3 V, which is still greater than $8.5 \times 10^{15}$ e⁻ per second at 1 V and $6.3 \times 10^{16}$ e⁻ per second at 2 V. As expected, the electron transfer kinetics increase with increasing potential.

The sharpness of the transition from mass transfer limited to electron transfer limited regimes yields insight into the electron transfer mechanism, i.e., direct versus indirect. A direct electrooxidation would be expected to have a sharper threshold than indirect electrooxidation as the direct mechanism
has a stronger surface site dependence. Thus, from the relative sharpness of the curves in Figure 2.8, we would expect the contribution of indirect oxidation to be minimal at 1 V and to increase with increasing voltage, becoming significant at 3 V where a plateau is not observed. More quantitatively, the applied voltages of 1, 2, and 3 V correspond to anode potentials of 0.35, 0.77, and 1.50 V vs SCE. At 3 V, the anode potential is 1.5 V, which is greater than the required potential for the 2-electron Cl⁻ oxidation ($E^0 = 1.2$ V vs SCE), producing reactive chlorine species that could indirectly oxidize MO.\textsuperscript{52} The coexistence of direct and indirect oxidation is also in agreement with the increased electrooxidation at 3 V. A similar trend of methylene blue oxidation rate versus influent MB concentration is observed in Figure 2.8b. A sharp transition region appears as early as 25 µM when 1.6 V was applied with a maximum oxidation rate of 0.016 µmol min\(^{-1}\). Increasing the applied voltage to 2 V elevates the maximum electrooxidation reaction rate to 0.072 µmol min\(^{-1}\) and a further increase of applied voltage to 3 V results in a maximum rate greater than 0.233 µmol min\(^{-1}\). Despite the similar voltage-and concentration-dependent electrooxidation rate trend of MB and MO, the absolute reaction rate of MB is significantly lower at a similar voltage. Quantitatively, the maximum electrooxidation rates for MB are 3.1, 5.1, and 4.5 times lesser than the corresponding MO oxidation rates at 1, 2, and 3 V, respectively. The significantly lower extent of MB oxidation could be attributed to either a difference in reduction potential, i.e., lower MO $E^0$ values and thus faster electron transfer rates, or the difference in molecular charge, i.e., MO is negatively charged and MB is positively charged and the resulting effects of electromigration on mass transfer. The $E^0$ for MO oxidation at influent pH 6.3 is reported to be 0.37 V,\textsuperscript{53} lower than that of MB, 1.1 V,\textsuperscript{54} indicating faster MO electron transfer kinetics at similar anode potentials. This is in agreement with the greater extent of MO oxidation at 1 and 2 V where the anode potential is less than the MB redox potential. However, it does not agree with the 3 V results, since at an anode potential of 1.5 V, both MO and MB should be completely oxidized. This suggests that the difference in MO and MB oxidation may be due to electromigration since a positive potential will be applied to the anodic CNT network resulting in the accumulation of positive
Figure 2.9: Voltage-dependent oxidation during electrochemical filtration. (a) Methyl orange and (b) methylene blue. For all experiments, the conditions are $[\text{MO}]_{in} = [\text{MB}]_{in} = 7 \mu\text{M}$, $[\text{NaCl}] = 10 \text{ mM}$, $J = 1.5 \text{ mL min}^{-1}$, and $T = 25 ^\circ\text{C}$ for all experiments.

surface charges. Thus, the negatively charged MO will diffuse more quickly to and be more favorably adsorbed onto the positively charged CNT anode than the positively charged MB molecule due to electromigration and electrostatic interactions, respectively. The electrostatic increase in MO diffusion and adsorption will increase the relative CNT electrode surface concentration of MO relative to MB and in turn increase the electron transfer rate. To investigate this hypothesis further, a more detailed examination of voltage-dependent effects on MO and MB electrooxidation were completed.

The voltage-dependent electrooxidation of low concentration MO and MB is presented in Figure 2.9 with the negatively charged methyl orange in Figure 2.9a and the positively charged methylene blue in Figure 2.9b. The influent concentration is $7 \mu\text{M}$ for both MB and MO and the minimum voltage applied is close to their reported $E^0$’s and increased by units of 0.2 V. In both Figure 2.9, panels a and b, it is observed that as the voltage is increased the steady-state effluent concentration after 200 min of electrolysis is decreased. As the applied voltage is increased above $E^0$, the standard free energy gap between anode surface and molecules is increased, resulting in faster electron transfer between the electron donors, MO and MB, and the CNT anode. It is of note that for the negatively charged
Figure 2.10: Effect of anode potential on MO oxidation and anodic current density during electrochemical filtration. Experimental conditions were [NaCl] = 10 mM, J = 1.5 mL min⁻¹, and [MO]₀ = 300 µM.

MO, the extent of oxidation, Figure 2.9a, grows more with increasing voltage. For example, the steady state concentration difference between 0.8 and 1.0 V is 2.2 µM and the difference between 1.0 and 1.2 V is 4.0 µM. In contrast, the inverse relationship is observed for the positively charged MB as the extent of oxidation is observed to grow less with increasing voltage. For instance, the concentration difference between 1.0 and 1.2 V is 2.2 µM and the difference between 1.4 and 1.6 V is 1.2 µM. The opposite trends of MB and MO support the hypothesis that electromigration and electrostatic interactions are responsible for the large difference in electrooxidation rates. Even though the rate of electron transfer is increased with increasing applied voltage in both cases, the effect of electrostatic interactions between the charged molecules and the positively charged CNT anode becomes more prominent with increasing voltage due to the increased positive-charge of the anode.[55] Thus, electromigration and electrostatics are responsible for the large difference in MO and MB oxidation rates, Figure 2.8.

The effect of anode potential on anodic current and MO oxidation at an influent MO concentration of 300 µM is presented in Figure 2.10. Insight into the predominant electron transfer pathway, i.e., direct electron transfer versus indirect electron transfer, can be inferred from the data. The effluent MO concentration initially decreases with increasing anode potential until 0.8 V and reaches a
plateau of 160 µM from 0.8 to 0.95 V. The current exhibits a corresponding increase until 0.8 V where it plateaus at a mass transfer limited current density of 6 mA m⁻² from 0.8 to 1 V. Therefore, it can be inferred that the initial decrease of MO concentration up to 0.8 V is due to the increasing rate of direct electron transfer as there are negligible thermodynamically viable indirect pathways. The effluent concentration plateau from 0.8 to 1.0 V, which overlaps with the mass transfer limited current plateau, is thus attributed to the mass transfer limited direct oxidation. In this regime, MO is oxidized only through direct oxidation pathway by CNT anode, eq 2.4.

\[
\text{MO}^- + n\text{h}^+ - \text{CNT} \longrightarrow \text{MO}_{\text{ox}}(\text{––nh}^+) + \text{CNT}
\]  

(2.4)

If direct oxidation is the only electron transfer mechanism, then the effluent concentration will not decrease with increasing anodic potential >0.8 V. However, this is not the case. Once the anode potential is increased to >0.95 V, the effluent MO concentration begins to decrease with increasing potential indicating indirect and direct oxidation are occurring simultaneously. The activation of the indirect oxidation pathway negates the mass transfer limitation since the electrogenerated oxidants may diffuse to the bulk solution and react with MO molecules that are not directly oxidized. According to the literature, at 1.01 V vs SCE, the four electron water oxidation to produce oxygen, eq 2.5, becomes viable.[52]

\[
\text{H}_2\text{O} \longrightarrow 4 \text{H}^+ + \text{O}_2 + 4\text{e}^-
\]  

(2.5)

The \(E^0\) of eq 2.5 is similar to the experimentally observed anode potential, 0.95 V, at which indirect oxidation becomes active. The produced oxygen will immediately react with the radicals generated from direct oxidation of MO and form reactive oxygen species such as peroxy radicals that could indirectly oxidize MO.[56] At anode potentials >1.2 V vs SCE, the two-electron oxidation of Cl⁻ to Cl₂ becomes thermodynamically viable resulting in another possible indirect oxidation pathway. The
contribution of the direct and indirect oxidation pathways can be determined from Figure 2.10. For example, at an anode potential 1.2 V, the total MO oxidized is 180 µM and the contribution from the direct electron transfer pathway is 140 µM or 78% and the contribution from the indirect electron transfer pathway is 40 µM or 22%. In summary, at low potentials, ≤0.8 V, direct oxidation is the dominant pathway and as the anode potential is increased above 1.0 V, the contribution from indirect oxidation increases proportionally as new indirect pathways become viable.

2.5 Conclusions

This study investigated the overall reaction mechanism for organic oxidation during electrochemical filtration. The overall electrochemical filtration process is described by a reactive transport mechanism consisting of three primary steps: (1) hydrodynamically enhanced mass transfer, (2) temperature-dependent physical adsorption/desorption, and (3) voltage-dependent direct electron transfer. The key to effective oxidation in the electrochemical filtration system is the 6-fold increase in mass transfer due to convection of the target molecule through the electrode. Following mass transfer in the overall mechanism is physical adsorption onto the CNT anode, which was determined to be an exothermic process with enthalpy of -11.2 kJ mol⁻¹. Higher temperatures were observed to decrease the overall rate of organic oxidation during electrochemical filtration possibly due to increased desorption kinetics and thus a decreased likelihood for oxidation. Once sorbed to the CNT anode, direct oxidation of the organic occurs and the rate of electron transfer is proportional to the applied voltage. The electrooxidation rate is also observed to be a function of the molecular charge due to electromigration. Direct oxidation is observed to be the predominant electron transfer mechanism at all anode potentials evaluated with indirect oxidation making a fractional contribution at anode potentials ≥1.0 V. The electrochemical filtration reactive transport mechanism discussed here yields an improved fundamental understanding of hydrodynamically enhanced electrochemical systems and will be utilized to
optimize the device design and construct an accurate model of the system. Future studies will delve deeper into the effects of the liquid flow rate on the electrochemical diffusion layer.
Quantitative 2D electrooxidative carbon nanotube filter model: Insight into reactive sites
3.1 Abstract

In this study, the electrooxidative carbon nanotube (CNT) filtration of sorptive methyl orange (MO) and non-sorptive ferrocyanide was investigated by both experiment and numerical simulation. The two-dimensional numerical model includes target molecule; mass transport, adsorption, and electron transfer and product desorption. For MO, the model was calibrated with experimental reaction rates from the mass- and electron-transfer limited regimes and accurately predicted effluent concentrations over a much larger range of conditions. For ferrocyanide, five CNT electrodes of various specific surface area and surface oxygen content were utilized and a similar single reaction site model to MO accurately predicted kinetics at low anode potentials while a two-site model was necessary at higher potentials yielding insight into the CNT reactive sites. For example, at low anode potentials (≤0.2 V), the kinetics have a linear correlation with CNT surface area indicating the sp² conjugated sidewall sites are dominant. In contrast, at higher anode potentials (≥0.3 V), the kinetics were significantly greater than expected from CNT surface area and the differential kinetics have a linear correlation with the CNT surface oxygen content indicating the CNT tips were also electroactive. The spatial distribution of internal electrode mass transport and surface reactivity is discussed.

3.2 Introduction

Electrochemical filtration has great potential for a number of applications such as advanced microbial, gas, and water separations. For example, electrochemical filtration has been reported to be effective towards oxidation of organics and ions\cite{14, 27} and inactivation of virus (MS2) and bacteria (Escherichia coli),\cite{32, 57} and can be coupled with microbiology\cite{58} or hydrolysis\cite{59} to enhance pollutant degradation. The electrochemistry and filtration are synergistic as the fluid flow through the electrode can increase electrochemical kinetics by over 10-fold\cite{60} and the electric field can enhance electroosmotic flow efficiency by over 100-fold.\cite{61} Elemental carbon-based materials such as carbon
cloths or felts have been classically utilized as electrochemical filters.[62] Recently, carbon nanotubes (CNT) have drawn attention as electrochemical filters[63] due to their unique combination of conductivity, chemical stability, and ability to form high porosity networks. Many current research studies are focused on improving our fundamental understanding of the individual processes that mediate the overall performance of an electrochemical CNT filter.

Qualitatively, the reactive transport mechanism describing Faradaic electrochemical CNT filtration has four primary steps: target molecule mass transport, adsorption, and electron transfer and product desorption, with the flow through the electrode significantly increasing mass transport and product desorption.[64] However, an in-depth understanding of the effect of target molecule & CNT physical-chemical properties requires not only a qualitative, but also a quantitative understanding of the aforementioned mechanisms. For example, there is a vast number of aqueous electrochemical target molecules ranging from inorganics such as nitrite,[65] halides[14], and heavy metals[66, 67] to organics such as aromatics[68] and biomolecules[69, 70] that significantly differ in physical-chemical properties. There are also a wide range of CNT[71] in terms of diameter that will affect surface area and pore size,[72] length that will affect number of reactive sites and network mechanical stability,[42] and surface chemistry such as N/B-doping[73] or surface oxidation that will affect CNT conductivity and reactivity. Therefore, the development of a quantitative electrochemical filtration model would allow for a more rapid examination of the innumerable combinations of experimental conditions.

Quantitative electrochemistry modeling studies typically utilize simple reactors with controlled hydraulic convection[74–76] such as the rotating disk electrode (RDE)[77, 78] where the homogenous flow pattern and concentration field can be analytically solved. For more complex and practical electrode configurations, numerical simulation will be necessary. For example, Zhang et al.[79] recently reported an experimental and simulation study of CO oxidation in a thin-layer flow cell using a reactive transport mechanism qualitatively similar to that for electrochemical filtration.[64] The experimental electrooxidative reaction current and CO concentration field were accurately simulated with both
2D and 3D models. Thus, a similar multi-dimensional model may be able to quantitatively simulate electrochemical CNT filtration.

In regards to the CNT characteristics that control electrochemical kinetics, the location and type of the CNT surface reactive sites are of particular interest. The two plausible major CNT reactive sites are (1) the sp² conjugated CNT sidewalls and (2) the surface oxy defect sites found predominantly at the CNT tips as displayed in Figure 3.1. The prevailing hypothesis on CNT reactive sites is that the CNT sidewall is inert and the CNT tips with high oxy-functional group defect site density dominate electrochemistry, analogous to the inert basal plane and the reactive edge-steps of highly oriented pyrolytic graphite.\[80\] For example, cyclic voltammetry (CV) studies of epinephrine oxidation and ferricyanide reduction on a multiwall carbon nanotube electrode indicated the CNT tips were the predominant reactive sites.\[81\] However, a recent CV study observed that the oxygenated species formed on free-standing CNT tips after acid treatment did not measurably change the heterogeneous charge transfer kinetics.\[82\] Another CV study, in which either the CNT sidewall or tips were coated by insulating polystyrene reported that the CNT sidewalls were also active and that the location of the

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**Figure 3.1:** Schematic representation of the predominant CNT electro-active sites. CNT sp² conjugated sidewall sites (S-sites) versus CNT oxy-defect tip sites (T-sites).
dominant electro-active site, sidewall versus tip, was a function of target molecule physical–chemical properties. To date, CV has been the predominant electrochemical method to investigate the specific identity of CNT electroactive sites. To fully explore the interplay of CNT tip versus sidewall electro-activity, there is a need for experimental methodologies that go beyond CV analysis. Thus, investigations of the CNT reactive sites using experimental reaction rates from a randomly-oriented CNT network are needed and will require a quantitative electrochemical kinetics model to gain insight into reaction site identity.

In this study, we developed and validated a 2D quantitative electrochemical CNT filtration model that includes mass transport, adsorption, and electron transfer processes. The model is used to numerically simulate the electrooxidation kinetics of (1) methyl orange (MO), a sorptive species that undergoes a multi-electron transfer oxidation, and (2) ferrocyanide, a non-sorptive species that undergoes a single electron transfer oxidation. The electrooxidation filtration rate for both species was experimentally and numerically examined as a function of both the influent concentration ($C_{in}$) and anode potential ($E$). The ferrocyanide electrooxidation experiments and modeling was completed for five CNT anodes that are characterized in detail by scanning electron microscopy (SEM), transmission electron microscopy (TEM), BET specific surface area analysis (BET), and X-ray photoelectron spectroscopy (XPS). The CNT specific surface area and surface oxygen content dependent ferrocyanide electrooxidation kinetics are used to gain insight into the predominant CNT electro-active sites. The 2D electrochemical filtration model was used to gain insight into the microscopic target molecule concentration and convection–diffusion flux fields within the electrochemical CNT filter.
3.3 **Experimental**

3.3.1 **Chemicals**

Methyl orange hydrate (>95%), potassium hexacyanoferrate (II) trihydrate \((K_4Fe(CN)_6\cdot3H_2O; 98.5–102.0\%)\), and sodium sulfate \((Na_2SO_4; >99\%)\) were purchased from Sigma-Aldrich (St. Louis, MO). Methyl orange was quantified by its absorption at \(\lambda_{\text{max}} = 464\,\text{nm}\) \((\varepsilon = 26,900\,\text{M}^{-1}\text{cm}^{-1})\) and ferrocyanide was quantified by its absorption at \(\lambda_{\text{max}} = 420\,\text{nm}\) \((\varepsilon = 1000\,\text{M}^{-1}\text{cm}^{-1})\) using an Agilent 8453 UV-visible spectrophotometer.

3.3.2 **Anodic CNT Filter**

In this study, we utilized multiwalled carbon nanotubes that had been made into preformed porous networks with an average depth of 64–96 \(\mu\text{m}\) (NanoTechLabs, Buckeye Composites, Yadinkville, NC). Five CNT types were used in this study are of different diameter, wall number, specific surface area, and oxygen content and are referred as A-CNT, B-CNT, C-CNT, D-CNT, and E-CNT. The A-CNT networks were used as the anode material in the MO kinetics study and all five CNT networks were used as anode materials in the ferrocyanide study.

3.3.3 **CNT Characterization**

The five different multi-walled carbon nanotubes were characterized in detail by TEM, SEM, XPS, and BET to determine diameter \((d)\), number of walls, surficial O/C ratio, and specific surface area. Characterization details can be found in the Appendix A.
3.3.4 Electrochemical Filtration

Sodium sulfate (Na$_2$SO$_4$) was utilized as the background electrolyte and methyl orange and ferrocyanide were used as the target molecules for electrochemical filtration. The sodium sulfate concentration was 0.1 M for methyl orange experiments and 1 M for ferrocyanide experiments to minimize the effects of electro-migration (<5% overall mass transport; calculations in the Appendix A). Influent solutions were peristaltically pumped (Masterflex) through the electrochemical CNT filter of area 7.06 cm$^2$ at 3.0 mL min$^{-1}$ and the electrochemistry was driven by a CHI604D electrochemical workstation. A detailed description of the electrochemical filtration system has been previously reported in Section 2.3.4 and a schematic and images of the apparatus are displayed in Figure 1.4. Before every experiment, the titanium ring was polished with sandpaper to optimize the electrical connectivity between the Ti and the CNT network. For all filtration experiments, effluent aliquots were collected after 180 s to ensure steady-state and the concentration was measured by UV-vis to calculate the electrooxidation rate.

3.4 CNT Characterization

The five CNT networks were characterized by XPS to determine surface oxygen content, BET to determine specific surface area, and TEM to determine diameter distribution and number of walls. Representative TEM images of the A-CNT network and an individual A-CNT with a tube wall spacing of 0.33 nm are displayed in Figure 3.2a and b, respectively. Similar TEM images of the B-E CNT networks are displayed in Appendix Figure A.1. The CNT diameter and wall number distribution were determined by TEM image analysis (ImageJ) and are summarized in Table 3.1. The average CNT diameter ranged from 23.5 (A-CNT) to 93.3 nm (D-CNT) and the average number of walls ranged from 20 (A-CNT) to 119 (D-CNT) per nanotube with the number of walls increasing monotonically with CNT diameter. Since the CNT diameter distributions are variable, histograms of the CNT diameters

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and wall numbers are presented in Figures A.2 and A.3, respectively. The CNT XPS survey scans are displayed in Figure A.4 and the CNT surface oxygen percentage is listed in Table 3.1. The CNT surface oxygen atomic percentage ranged from 0.55% (A-CNT) to 2.16% (D-CNT) and the SSA ranged from 20.0 (D-CNT) to 88.5 m² g⁻¹ (A-CNT). The total surface areas (S) were calculated using the filter weight and SSA as summarized in Table 3.1. The total CNT filter surface area ranged from 0.35 (D-CNT) to 1.47 m² (A-CNT). The CNT physical-chemical parameters are the basis for the model geometry design that will be discussed in detail later.
Table 3.1: Physical-chemical characteristics of the CNT networks.

<table>
<thead>
<tr>
<th>CNT</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>23.4±7.3</td>
<td>27.7±17.1</td>
<td>71.4±58.5</td>
<td>93.3±69.5</td>
<td>36.0±4.3</td>
</tr>
<tr>
<td>Number of walls</td>
<td>20±11.5</td>
<td>32±26</td>
<td>102±93</td>
<td>119±92</td>
<td>40±5</td>
</tr>
<tr>
<td>Oxygen (%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.55±0.05</td>
<td>0.77±0.24</td>
<td>1.06±0.2</td>
<td>2.16±0.15</td>
<td>1.55±0.17</td>
</tr>
<tr>
<td>SSA (m&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>88.5</td>
<td>34.6</td>
<td>30.3</td>
<td>20.0</td>
<td>55.9</td>
</tr>
<tr>
<td>Filter weight (mg)</td>
<td>17.1</td>
<td>22</td>
<td>21.2</td>
<td>17.5</td>
<td>19.2</td>
</tr>
<tr>
<td>S (m&lt;sup&gt;2&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.47</td>
<td>0.76</td>
<td>0.64</td>
<td>0.35</td>
<td>1.07</td>
</tr>
<tr>
<td>Filter depth (µm)</td>
<td>83.0±3.5</td>
<td>96.3±4.2</td>
<td>88.8±2.3</td>
<td>64.0±4.0</td>
<td>92.3±3.8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Surface oxygen content measured by XPS.

<sup>b</sup> BET specific surface area.

<sup>c</sup> Total surface area calculated by the weight of CNT networks × SSA.

3.5 Methyl Orange Electrooxidative Filtration Kinetics

3.5.1 Modeling Approach

Electrochemical CNT filter 2D model geometry

The A-CNT network (depth ~83 µm; d<sub>A-CNT</sub> = 23.4±7.3 nm) was used as the anode material for the methyl orange (MO) electrooxidation experiments. The model geometry consists of a 5-µm headspace followed by the 83-µm anodic CNT filter and another 5-µm space after the filter bed as shown in Figure 3.3a. An SEM image of the 83-µm CNT filter cross-section is presented in Figure 3.3b and the thin (~µm) CNT layers stacked along z direction indicate an individual CNT (~100-µm in length) is
randomly-oriented in the x-y plane. In the model, the CNT are assumed to be randomly-distributed, similar diameter circular slices in the x-z plane to reduce computation time. These assumptions have a negligible effect on the simulation results (see Appendix A). Since the CNT are closely packed in the x-z plane, the 2D model geometry width was set to be 8.5 times the tube diameter and to have periodic boundary conditions in the x-direction for a representative presentation of the entire width to reduce computation time. The total number of CNT in the model is calculated by the CNT surface area to filter volume ratio and the geometric area of the model domain (see Appendix A).

**Hydraulic field model**

The hydraulic field within the 2D CNT filter (Figure 3.3a) is laminar (Reynolds number \( R = 1.6 \times 10^{-6} \)). The steady state fluid velocity field can be numerically solved using the 2D Navier–Stokes equation and mass conservation of an incompressible fluid, Eqs 3.1 and 3.2, respectively:

\[
\frac{\partial \mathbf{u}}{\partial t} = -\nabla p + \rho \mathbf{g} + \mu \nabla^2 \mathbf{u} \quad (3.1)
\]

\[
\nabla \cdot \mathbf{u} = 0 \quad (3.2)
\]

where \( \mathbf{u} \) is the velocity vector, \( \rho = 1.0 \text{ g cm}^{-3} \) is the density of water, \( p \) is the pressure in Pa, \( g \) (9.8 m s\(^{-2}\)) represents gravity, and \( \mu = 8.9 \times 10^{-4} \text{ Pa s} \) is the dynamic viscosity of water at 25 °C. The flow field boundary conditions are summarized in Table 3.2: the average influent flow rate \( (u_{\text{ext in}} = 70.8 \times 10^{-6} \text{ m s}^{-1}) \) is the domain inlet boundary condition (green Figure 3.3a), the no-slip condition is used at CNT electrode surfaces (black), and a periodic boundary condition is applied at the sides (purple) of the model geometry.
Figure 3.3: A-CNT network model geometry. (a) 2D CNT geometry used in numerical simulation where the CNT are assumed to be randomly distributed, of the same diameter, and the vertical cross-sections are assumed to be circles. Figure includes the domain inlet (green), domain outlet (blue), periodic boundary on the left and right (purple) and CNT electrode surfaces (black). (b) Cross-sectional SEM image of the A-CNT network used for electrochemical filtration.

Table 3.2: Governing equations and boundary conditions for hydraulics and species transport.

<table>
<thead>
<tr>
<th>Governing equations</th>
<th>Boundary conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydraulic field</strong></td>
<td><strong>CNT surface</strong></td>
</tr>
<tr>
<td>( \rho \frac{D}{Dt} \mathbf{u} = -\nabla p + \rho g + \mu \nabla^2 \mathbf{u} )</td>
<td>( \mathbf{u} = \mathbf{0} )</td>
</tr>
<tr>
<td>( \nabla \cdot \mathbf{u} = 0 )</td>
<td></td>
</tr>
<tr>
<td><strong>Species transport</strong></td>
<td></td>
</tr>
<tr>
<td>( D \nabla^2 C = \nabla \cdot \mathbf{u} )</td>
<td>( -D \nabla \cdot \mathbf{n} = r )</td>
</tr>
</tbody>
</table>

Species transport model

The fluid velocity field is the initial input for calculating the target molecule concentration field by the convection-diffusion equations, Eqs 3.3 and 3.4:

\[ D \nabla^2 C = \nabla \cdot \mathbf{u} \text{ in the bulk solution} \quad (3.3) \]
\[-D \nabla C \cdot \mathbf{n} = r\] on the electrode surface \hspace{1cm} (3.4)

where \(D = 8.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\) is the estimated diffusion coefficient for methyl orange, \(\mathbf{n}\) is the normal vector to the CNT cylinder surface, \(C\) is the target molecule concentration in mol m\(^{-3}\), and \(r\) is the reaction rate in mol m\(^{-2}\) s\(^{-1}\). The movement of a fluid through a porous material may give rise to mechanical mixing resulting in a greater effective diffusivity. However, in this study the fluid velocity is extremely low such that ordinary diffusion dominates i.e., the flow rate would need to be increased 4 orders of magnitude to drive advective dispersion. Detailed discussion is available in Appendix A.

The boundary condition at domain inlet is the influent molar flux \((C_{\text{in}} \times u_{\text{in}})\) and a periodic concentration field is assumed for the left and right boundaries. The summary of the governing equations and boundary conditions for the species transport model can be found in Table 3.2. Detailed information on COMSOL model construction, simulation, and boundary condition selection are available in Appendix A.

**MO electrochemical filtration mechanism**

The organic electrochemical filtration reaction mechanism\(^{[64]}\) follows a multi-step process:

-(R0) mass transport to the electrode surface. Convection-Diffusion; Eqs 3.3 and 3.4

-(R1) adsorption to the electrode surface,

\[M + \text{CNT}^+ \xrightarrow{k_1} M - \text{CNT}\]

-(R2) direct electron transfer and molecular transformation,

\[M - \text{CNT} \xrightarrow{k_2} P - \text{CNT} + n_e e^-\]
(R₃) and oxidation product desorption,

\[ P - \text{CNT} \xrightarrow{k₃} P + \text{CNT}^* \]

where CNT* is a vacant reactive site, M is the reactant, in this case MO, P is the oxidation product, and M-CNT and P-CNT are adsorbed species, \( n_t \) is the total number of electron transferred per molecule. In regards to R₁, negatively-charged MO adsorption will be increased on a positively-charged CNT anode. If the product is negatively-charged, the same electrostatic interaction may lead to slow product desorption blocking electron-transfer sites. Product readsorption will be embedded in the desorption rate (slower assuming no readsorption). The highest anode potential used in the MO experiments was 0.9 V, much lower than the aromatic ring cleavage potential 2.1 V,\(^84\) thus all MO electrooxidation products will be aromatic and have similar strong interactions with a CNT surface.

Rate constants of MO adsorption, electron transfer, and product desorption are \( k_1 \), \( k_2 \), and \( k_3 \), respectively. The surface area normalized reaction rate \( r \) (µmol m\(^{-2}\) s\(^{-1}\)) can be expressed by:

\[ r = k_2 \omega \delta_M \]  

(3.5)

where \( \delta_M \) is the MO fractional surface coverage and \( \omega \) is the absolute surface reactive site density. The electron transfer rate constant, \( k_2 \), is determined by the Butler–Volmer relation,\(^85\) Eq 3.6:

\[ k_2 = A e^{naF(E-E_0)} \]  

(3.6)

where \( A \) (m\(^2\) s\(^{-1}\)) is the pre-exponential factor, \( n \) is the number of electrons transferred in the rate determining step, \( a \) is the transfer coefficient, \( f = F/RT \) where \( F = 96500 \) C mol\(^{-1}\) is Faraday’s constant, \( R = 8.314 \) J K\(^{-1}\) mol\(^{-1}\) is the gas constant, and \( T = 298 \) K is the temperature, \( E \) denotes the
anode potential, and $E_o$ is the standard reduction potential. The standard MO reduction potential is a function of pH ($E_o = 0.3 \ V$ (vs. Ag/ AgCl) at pH$_{in} = 7$).[53]

The evolution of surface MO ($\theta_M$) and product ($\theta_P$) coverage is described by the following mass balance Eqs 3.7 and 3.8, respectively:

\[
\frac{d\theta_M}{dt} = k_1 C_M \omega (1 - \theta_M - \theta_P) - k_2 \omega \theta_M
\]

\[
\frac{d\theta_P}{dt} = k_2 \omega \theta_M - k_3 \theta_P \omega
\]

where $C_M$ denotes the MO concentration in the near CNT surface solution. Assuming steady-state for Eqs 3.7 and 3.8, solving for $\theta_M$, and substituting $\theta_M$ into Eq 3.5, we receive the electrooxidative reaction rate, $r$, at the electrode surface, Eq 3.9:

\[
r = \frac{k_1 k_2 C_M \omega}{k_1 C_M + \frac{k_2}{k_1} k_1 C_M + k_2} = \frac{k_1 A e^{n_1 \frac{F}{RT} (E - E_0)} C_M \omega}{k_1 C_M + (\frac{k_2}{k_1} + 1) A e^{n_1 \frac{F}{RT} (E - E_0)}}
\]

The electrochemical filtration model will be calibrated, validated, and discussed in the following sections.

3.5.2 Results and Discussion

Influent concentration and anode potential dependent kinetics

Electrooxidative MO filtration experiments were completed with an anodic A-CNT network. The concentration change ($\Delta C = C_{in} - C_{out}$) between influent and effluent as a function of influent concentration ($C_{in}$) was measured at anode potentials of 0.45, 0.6, and 0.7 V and is presented in Figure 3.4a as open and closed symbols, where the closed symbols are used to calibrate the model and
the open symbols to validate the model. The $\Delta C$ value first increases with increasing $C_{in}$ because of enhanced mass transport and adsorption kinetics and plateaus due to electron transfer limitations. The threshold concentrations $C_{T}(E)$ for electron transfer rate plateau increases with increasing anode potential $E$: $C_{T}(0.45 \text{ V}) = 17 \mu M < C_{T}(0.6 \text{ V}) = 2000 \mu M < C_{T}(0.7 \text{ V}) = 4500 \mu M$, and the plateau height, $\Delta C$, can be used to calculate the $k_2$ in Eqs 3.6 and 3.9.

**Figure 3.4:** Simulated and experimental influent-to-effluent MO concentration change. Concentration change, $\Delta C = C_{in} - C_{out}$, of MO during electrochemical filtration as a function of (a) influent concentration and (b) anode potential. Symbols are experimental measurements: solid to calibrate and open to validate. The electrochemical filtration was carried out with 100 mM Na$_2$SO$_4$ as electrolyte and a flow rate $J = 3 \text{ mL \ min}^{-1}$. Solid curves are model simulation results generated by COMSOL. The kinetic parameters used in simulations are $A_\omega = 5.21 \times 10^{-6} \text{ \mu mol m}^{-2} \text{s}^{-1}$, $n_{at} = 0.774$, $k_1 \omega = 1.2 \times 10^{-7} \text{ m s}^{-1}$, $k_3 \omega = 0.0696 \text{ \mu mol m}^{-2} \text{s}^{-1}$.

For the second set of experiments, the $\Delta C$ is measured over a range of anode potentials (0.3–0.9 V) at fixed $C_{in}$ of 300 $\mu M$ and 875 $\mu M$, Figure 3.4b, where the symbols are experimental data points (solid to calibrate and open to validate). A similar trend is observed for potential dependent $\Delta C$, i.e., $\Delta C$ first increases due to an increasing electron transfer rate then plateaus due to mass transport limitations likely due to adsorption rather than convection limitations. The mass transport limited regime occurs at 0.6 V for $C_{in} = 300 \mu M$ and at 0.7 V for $C_{in} = 875 \mu M$ and the plateau height can be used to calculate the sorption kinetic parameters ($k_i$ and $k_j$) in Eq 3.9.
Kinetic Parameters Calculation

Kinetic parameters for MO adsorption \( (k_1) \), electron transfer \( (k_2, A\omega, na) \), and product desorption \( (k_3) \) are calculated using closed symbol data (Figure 3.4) to calibrate the model. The density of reactive sites \( (\omega) \) and number of electrons transferred in the rate determining step \( (n) \) are difficult to determine individually and thus are determined in combination with the other constants e.g., \( A\omega, na \), and \( k_3\omega \). At high influent MO concentrations, Eq 3.9 reduces to Eq 3.10:

\[
\lim_{C_{M} \to \infty} r = \frac{A\omega e^{na \frac{F}{RT} (E - E_0)}}{1 + \frac{e^{na \frac{F}{RT} (E - E_0)}}{k_3}}
\]

(3.10)

where \( r \) corresponds to the maximum reaction rate in the electron transfer limited regime and is calculated from the \( \Delta C \) plateau values by Eq 3.11:

\[
r = \frac{J \Delta C}{S}
\]

(3.11)

where \( r \) has units of \( \mu \text{mol m}^{-2} \text{s}^{-1} \), \( S \) stands for total CNT filter surface area (1.47 m\(^2\)), \( \Delta C \) is the plateau value in \( \mu \text{mol m}^{-3} \), and \( J \) is \( 5.0 \times 10^{-8} \text{ m}^3 \text{s}^{-1} \). From Eq 3.11 and Figure 3.4a, the electron transfer limited reaction rates \( (r) \) are \( 0.45 \text{ V} \) (\( 4.76 \times 10^{-4} \mu \text{mol m}^{-2} \text{s}^{-1} \)) \( \ll \) \( 0.6 \text{ V} \) (\( 2.70 \times 10^{-2} \mu \text{mol m}^{-2} \text{s}^{-1} \)) \( \ll \) \( 0.7\text{ V} \) (\( 6.46 \times 10^{-2} \mu \text{mol m}^{-2} \text{s}^{-1} \)). The kinetic parameters: \( A\omega = 5.21 \times 10^{-6} \mu \text{mol m}^{-2} \text{s}^{-1} \), \( na = 0.774 \), and \( k_3\omega = 0.0696 \mu \text{mol m}^{-2} \text{s}^{-1} \), were solved with Matlab using the anode potential \( (E) \), electron transfer limited rates, and Eq 3.10. The \( na \) value is the number of electrons transferred in the rate-determining step, \( n \), multiplied by the charge transfer coefficient, \( a \). The latter is typically in the range of 0.3–0.7, thus \( n \) here is likely 1 or 2 and consistent with the literature i.e., although MO electrooxidation is a multi-electron transfer, the elementary rate-determining electron-transfer is the initial one-electron transfer.[4]

For the anode potential dependent experiments (Figure 3.4b), the data points marked with closed
symbols denote the adsorption rate limited ΔC plateau and were used to calculate the MO adsorption rate constant ($k_i\omega$) and product desorption rate constant ($k_3\omega$). At high anode potentials, Eq 3.9 reduces to:

$$\lim_{E \to \infty} r = \frac{k_1C_M\omega}{k_1C_M + 1}$$  \hspace{1cm} (3.12)

where $C_M$ is the average concentration within the filter and is calculated assuming concentration decreases linearly from the inlet of the diffusion layer to the filter outlet and that $C_M$ is the concentration in the middle of the filter. Given that the filter thickness is $l = 83 \, \mu m$ and assuming the bulk concentration begins to decrease at $\delta = \sim 200 \, \mu m$ prior to entering the filter[64] and a linearly decreasing concentration profile, $C_M$ can be approximated by Eq 3.13:

$$C_M = \frac{(l/2)C_{in} + (l/2 + \delta)C_{out}}{l + \delta}$$  \hspace{1cm} (3.13)

From Eqs 3.11 and 3.12, the adsorption limited reaction rates ($r$) are $300 \, \mu M \ (8.3 \times 10^{-3} \, \mu mol \, m^{-2} \, s^{-1}) < 875 \, \mu M \ (2.21 \times 10^{-2} \, \mu mol \, m^{-2} \, s^{-1})$ and $k_i\omega$ is determined to be $1.2 \times 10^{-7} \, m \, s^{-1}$.

COMSOL Multiphysics V 4.2 was used to simulate the coupled hydraulics, species transport, and electrochemical reaction using a finite element method. In the finite element model, nanotubes are simplified as voids with reactive surfaces in the fluid domain. The solution domain is discretized into approximately 200,000 (value is geometry dependent) first order triangular elements and at least 8 boundary layer elements are inserted around the voids (around 56,000 quadrilateral elements in total) for finer resolution of the near surface processes. The COMSOL simulation first determines the hydraulic field that is then used as input together with the above kinetic parameters to simulate the 2D concentration field. The simulated hydraulic field is displayed in Figure A.8 and discussion is available in the Appendix A.
Figure 3.5: Simulated MO concentration electrochemical filter depth profile. (a) Spatial concentration field with geometry with red color being highest concentration, 300 µM and blue color being lowest concentration, 74.2 µM and (b) average concentration along flow direction showing the CNT filter from z = 5 to 88 µm. Simulations are generated by COMSOL and conditions are C_in = 300 µM, inlet velocity u_in = 7.08 × 10^{-7} m s^{-1}, and E = 0.6 V.

Spatial concentration field and effluent concentration prediction

A simulation of the 2D concentration field for C_{extin} = 300 µmol L^{-1} and E = 0.6 V is displayed in Figure 3.5a. Due to the high model aspect ratio of 8000, the geometry is straight and narrow, so magnified insets are plotted for: the domain inlet, the center of CNT filter and domain outlet. The color bar on the right denotes concentration in mol m^{-3}, with red highest (0.3 mM) and dark blue lowest (0.074 mM). The simulated average MO concentration profile along the direction of the flow is displayed in Fig 3.5b. Prior to entering the CNT filter, the MO concentration decreases from 300 to 140 µM, accounting for 71% of the total concentration decrease. The remaining 29% of the concentration decrease occurred inside the CNT filter. Interestingly, the simulation indicates that the majority of the absolute concentration drop occurs before the filter bed. The filter effluent concentration profile rapidly flattens as expected for a direct surface electrooxidation process.

The quantitative electrochemical filtration model was validated by simulating over the whole range of Figure 3.4a and b and the results were plotted as solid lines. It is of note that in both Figure 3.4a
and b, the simulated effluent target molecule concentrations (lines) agree well with the experimental measurements (points) under all conditions. For example, the simulation correctly describes not only the increasing trend of the reaction rate with influent concentration, but also the position and height of electron transfer limited plateau.

In summary, the quantitative reactive transport model accurately simulated the effluent concentration of the strongly-sorbing, multi-electron transfer methyl orange during electrooxidative filtration as a function of both influent concentration and anode potential. To evaluate the reactive transport model in terms of varying target species physical chemical properties and varying CNT physical chemical properties, the following sections will discuss the electrooxidative filtration experiments and simulation of the non-adsorbing, single-electron-transfer ferrocyanide by five different CNT networks.

3.6 Ferrocyanide Electrooxidative Filtration Kinetics

Since the overall ferrocyanide electrooxidative filtration mechanism is simpler than methyl orange i.e., single-electron transfer and negligible adsorption, more emphasis can be placed on examining the effects of individual CNT properties. Five different individual CNT of varying specific surface area and surficial oxygen content (Table 3.1) were used as porous flow-through anodes to investigate the effect of the CNT sp² conjugated sidewall and oxy-defect tip reactive sites on the overall electrooxidation kinetics.

3.6.1 Influent concentration dependent ferrocyanide electrooxidation kinetics

Experiments were completed to examine the ferrocyanide electrooxidation kinetics as a function of influent concentration (Cₘᵢₙ = 0.1 to 35 mM), anode potential (ₚ = 0.15 (black), 0.2 (red), 0.3 (blue), and 0.4 V (pink)), and specific CNT anode (A–E) with the steady-state effluent Fe(III) concentrations
Figure 3.6: Experimental and simulated effluent Fe(III) concentration during ferrocyanide electrooxidative filtration. The oxidation product concentration Fe(III) during electrochemical filtration with (a) A-CNT, (b) B-CNT, (c) C-CNT, (d) D-CNT, and (e) E-CNT. Symbols are experimental measurements and solid lines were model predictions generated by COMSOL considering only sidewall sites. The electrochemical filtration was carried out with 1 M Na\textsubscript{2}SO\textsubscript{4} as electrolyte and a flow rate of J = 3 mL min\textsuperscript{-1}. The kinetic parameters used in simulations are listed in Table 3.3.

(C\textsubscript{Fe(III)}) presented as open squares in Figure 3.6. For all experiments, the background electrolyte was 1 M Na\textsubscript{2}SO\textsubscript{4} to minimize electromigration and the flow rate was 3 mL min\textsuperscript{-1}. The electrooxidation kinetics for all CNT increased with increasing anode potential. At lower potentials, 0.15 and 0.2 V, the C\textsubscript{Fe(III)} first increases with increasing influent concentration due to enhanced mass transport, but eventually levels off due to electron transfer rate limitations, similar to the MO experiments. The threshold concentration for reaction rate plateaus occur at C\textsubscript{in} = 5–10 mM for 0.15 V, and 10–17 mM for 0.2 V. Since mass transport/adsorption effects are minimal, the plateau height can be used to calculate the electron transfer kinetic parameters. The plateau C\textsubscript{Fe(III)} for the A-CNT, B-CNT, C-CNT, D-CNT, and E-CNT at 0.15 V were 1.21, 0.6, 0.45, 0.33, and 0.7 mM, respectively, and at 0.2 V were 5.91, 2.72, 2.39, 1.48, and 3.5 mM, respectively. In contrast, at 0.3 and 0.4 V, the electron transfer limited regime was never observed either because the regime was beyond the experimental C\textsubscript{in} range or another electron transfer reaction mechanism was activated.
3.6.2 Ferrocyanide electrooxidative filtration modeling approach

Geometry, hydraulic field, and species transport

A similar modeling approach to methyl orange was used for ferrocyanide electrooxidative filtration. The model geometry consists of a 5-µm headspace, a porous CNT filter anode with specific CNT diameter, thickness, and tube number density that were calculated with the specific CNT physical parameters (Table 3.1), and finally a 5-µm effluent space. The detailed calculation of the CNT number density is available in the SI and the domain width was set to be 8.5 times the tube diameter. The diffusion coefficient of ferrocyanide is $6.67 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$. The hydraulics, Eqs 3.1 and 3.2, and species transport, Eqs 3.3 and 3.4, were the same as for methyl orange (Table 3.2 for governing equations and boundary conditions). The primary difference in the ferrocyanide model is the reaction mechanism since sorption is negligible.

Ferrocyanide electrochemical reaction mechanism

Previous CV studies investigating the nature of CNT electrochemically-active sites have indicated that CNT sp² sidewalls and/or defect tips (Figure 3.1) may be active and the relative activity depends on the target molecule properties. For MO, a one-site model accurately described the kinetics, thus no information could be obtained regarding the dominant CNT reactive sites. For the ferrocyanide electrooxidation model, a one-site model was initially applied. The mechanism and kinetics were similar (R1, R2, and R3), with M = ferrocyanide and P = ferricyanide. The corresponding kinetic coefficients are denoted $k_4$, $k_5$, and $k_6$ for ferrocyanide in place of $k_1$, $k_2$, and $k_3$ for MO. Since ferrocyanide is non-adsorbing, desorption is assumed to be very fast and happens immediately after electron transfer, thus R2 and R3 are combined into a single step, R2':

$$M - \text{CNT} \overset{k_1}{\rightarrow} \text{CNT}^* + P + e^- \quad (R2')$$
The surface area normalized reaction rate is given by Eqs 3.5 and 3.6, with a ferrocyanide standard potential of $E^\circ = 0.134 \text{ V}$ (vs. Ag/AgCl).[87] Similar to Eq 3.7, the ferrocyanide surface coverage can be described by the following mass balance equation:

$$\frac{d\theta_M}{dt} = k_4 C_M \omega (1 - \theta_M) - k_5 \omega \theta_M$$

(3.14)

where $C_M$ denotes the ferrocyanide concentration in the near CNT surface solution. Applying the steady-state condition to $\theta_M$ in Eq 3.14, solving for $\theta_M$, and then substituting into Eq 3.5, we receive the ferrocyanide surface area normalized reaction rate expression, Eq 3.15:

$$r = \frac{k_5 \omega k_4 \omega C_M}{k_4 \omega C_M + k_5 \omega} = \frac{A \omega e^{\frac{aF}{RT}(E-E_0)} k_4 C_M}{k_4 C_M + A e^{\frac{aF}{RT}(E-E_0)}}$$

(3.15)

Comparison of the surface area normalized reaction rates for ferrocyanide (Eq 3.15) to MO (Eq 3.9), it is noted that Eq 3.15 is a special case of Eq 3.9, where $k_6 \gg k_4$ such that $k_4 / k_6$ vanishes and desorption never limits the overall reaction. The electron transfer limited reaction rate is given in Eq 3.9 and is reached at both 0.15 and 0.2 V:

$$\lim_{C_{Fe(III)} \rightarrow \infty} r = A \omega e^{\frac{aF}{RT}(E-E_0)}$$

(3.16)

**Reactive site identification and kinetic parameter calculation**

If a second CNT reactive site does become active at higher anode potentials, questions arise to the identity of the two sites (sp² sidewall vs defect tips) and the potential-dependent relative contribution of each site. Anode potential dependent electron transfer limited reaction rates, $r_o$ (mol s⁻¹), were calculated by Eq 3.17 using the Fe(III) plateau values for 0.15 and 0.2 V, and the highest $C_{Fe(III)}$ values

61
for 0.3 and 0.4 V where no plateau was observed:

\[ r_0 = J C_{Fe(III)} \]  \hspace{1cm} (3.17)

The electron transfer limited or maximum reaction rates (mol s\(^{-1}\)) at 0.15, 0.2, 0.3, and 0.4 V were plotted in Figure 3.7a as a function of total anode surface area. There is a linear relationship (solid lines) between the total reaction rate and the surface area of the anode for 0.15 and 0.2 V with \(R^2 > 0.99\) indicating a homogeneous reactive site distribution on the CNT sidewalls at these potentials. In contrast, there is no correlation between reaction rate and total surface area at the higher anode potentials of 0.3 and 0.4 V suggesting a second CNT reactive site that is not homogeneously distributed has been activated.

To complete this comparison, the kinetic parameters for ferrocyanide adsorption \(k_4\) and electron transfer \(k_5\) must be determined. However, the mass transport limited reaction rate plateau values for the one-site model cannot be determined since the anode potentials necessary activate a second reaction. Thus, the adsorption \(k_4\) and electron transfer \(k_5\) kinetic parameters were estimated using only the data at 0.15 and 0.2 V (Table A.1. The \(k_4\) values at anode potentials 0.15 and 0.2 V (Fig 3.7b) were used to calculate the \(A\omega\) and \(a\) values by the Butler-Volmer relation (Eq 3.6). The \(k_4\) value was the average of the 0.15 and 0.2 V results. The estimated \(k_4\), \(A\omega\), and \(a\) values for S-sites of all five CNT anodes are summarized in Table 3.3.

The \(k_5\) values are plotted against the CNT anode surface oxygen content in Figure 3.7b. The surface oxygen ratio is related to the number of CNT oxygen defect sites largely present at the tips. At 0.15 and 0.2 V, the surface oxygen ratio has no effect on the \(k_5\) values. In contrast, at 0.3 and 0.4 V there is an effect suggesting the second reaction site is related to CNT surficial oxygen. To test this hypothesis, a two-site model will be evaluated towards distinguishing the kinetic contribution of sp\(^2\) sidewall (S-sites) and the oxy-defect tip (T-sites) assuming that the S-sites are dominant at 0.15 and 0.2
Figure 3.7: Ferrocyanide electrooxidation kinetics versus total surface area and surface oxygen ratio. (a) Maximum total reaction rate (mol s⁻¹) as a function of anode surface area. The open squares for 0.15 (black) and 0.2 V (red) are electron transfer limited reaction rates. Then open squares for 0.3 (blue) and 0.4 V (pink) are maximum reaction rates measured under experimental conditions. The straight lines are linear fittings for 0.15 (black) and 0.2 V (red). (b) k₅ω values at anode potentials 0.15 (black), 0.2 (red), 0.3 (blue), and 0.4 V (pink). Horizontal lines denote the average values at 0.15 and 0.2 V.

V and that the T-sites contribute at 0.3 and 0.4 V.

Table 3.3: Summary of S-site kinetic parameters for ferrocyanide model simulation.

<table>
<thead>
<tr>
<th>CNT anode</th>
<th>Aω (mol m⁻² s⁻¹)</th>
<th>a</th>
<th>k₅ω (m s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.85 × 10⁻⁸</td>
<td>0.90</td>
<td>2.61 × 10⁻⁸</td>
</tr>
<tr>
<td>A</td>
<td>2.82 × 10⁻⁸</td>
<td>0.85</td>
<td>3.60 × 10⁻⁸</td>
</tr>
<tr>
<td>B</td>
<td>2.44 × 10⁻⁸</td>
<td>0.90</td>
<td>2.10 × 10⁻⁸</td>
</tr>
<tr>
<td>C</td>
<td>3.24 × 10⁻⁸</td>
<td>0.79</td>
<td>3.54 × 10⁻⁸</td>
</tr>
<tr>
<td>D</td>
<td>2.37 × 10⁻⁸</td>
<td>0.84</td>
<td>1.63 × 10⁻⁸</td>
</tr>
</tbody>
</table>

3.6.3 Results and discussion

S-site Electrooxidation Kinetics

Numerical simulation of ferrocyanide electrooxidation was completed for all CNT at the same influent concentration/anode potential combination as Figure 3.6 to predict effluent ferricyanide concentrations. The ferricyanide simulation results at 0.15, 0.2, 0.3, and 0.4 V were plotted as solid lines in
Figure 3.6a–e, for A-CNT, B-CNT, C-CNT, D-CNT, and E-CNT, respectively. The simulation accurately described the increase of reaction rate with influent concentration and anode potential as well as the position and height of the electron transfer limited plateau at 0.15 and 0.2 V, but significantly underestimated the kinetics at 0.3 and 0.4 V. Comparison of the experimental and simulation results indicates there are two distinct CNT reaction sites with S-sites dominant at lower potentials and T-sites activated at higher potentials. Although the second site has a higher ferrocyanide electrooxidation overpotential, the difference between experimental and simulation kinetics at ≥ 0.3 V indicates that it also has faster electron transfer kinetics.

**T-site electrooxidation kinetics**

The T-site contribution (light bars) to electrooxidation was estimated by the difference between experimental and simulation effluent ferricyanide concentration results (Figure 3.6) and plotted with the contribution of S-site electrooxidation (dark bars) at 0.3 (green) and 0.4 (blue) V in Figure 3.8a–e for A-CNT, B-CNT, C-CNT, D-CNT, and E-CNT, respectively. Generally, for all CNT, faster kinetics was observed for both S- and T-sites with increasing influent ferrocyanide concentration and anode potential. For example, in Figure 3.8a the ferrocyanide electrooxidation via T-sites increased from 1.3 mM at Cin = 6 mM to 6.0 mM at Cin = 35 mM when V_anode = 0.3 V, and increased further to 9.6 mM at Cin = 35 mM when V_anode = 0.4 V. However, the fractional contribution of the S- and T-sites with increasing anode potential varied for each individual CNT type. For instance, the fractional contribution of T-sites to electrooxidation for the A-CNT (lowest O content; 0.55%) at Cin = 25 mM was 0 at 0.2 V, increased to 0.19 at 0.3 V, and increased again to 0.41 at 0.4 V. For the D-CNT (highest O content; 2.17%), the fractional T-site contribution was significantly greater, increasing to 0.67 at 0.3 V and 0.77 at 0.4 V even though the \( S_{A-CNT} = 4 \times S_{D-CNT} \), indicating that the higher potential T-sites are likely the oxy-defect sites at the CNT tips. Although the T-sites had a slightly higher ferrocyanide electrooxidation overpotential than the S-sites (+66 mV), the T-site electrooxidation kinetics increase
with anode potential was greater than the S-sites. This result is consistent with the ferrocyanide CV study by Gong et al.\cite{83} where an insulating polymer was used to expose only sidewalls (S-CNT) or tips (T-CNT) and a smaller $\Delta E_p$ was observed for the T-sites indicating faster electron transfer kinetics. For methyl orange, a one-site model was likely successful due to the T-sites dominating at the higher anode potentials ($\geq 0.3$ V) used for electrooxidation.

To further support the CNT electroactive site identification, the T-site electron transfer kinetic parameters are compared to the measured CNT surficial oxygen ratio. It is assumed that the same governing S-site kinetic equations also apply to the T-sites. The T-site $k_1\omega$ values for all CNT networks as a function of anode potential (0.3 and 0.4 V) were estimated using Eqs 3.15, 3.17 and Figure 3.8 through fitting of $r$ to $C_M$ from Eq 3.15 and the results are plotted in Figure A.9a and b. The estimated T-site $k_1\omega$ values for the various CNT at 0.3 and 0.4 V were then plotted versus the CNT anode surface.
Figure 3.9: T-sites electron transfer kinetics as a function of anode oxygen ratio. The symbols are the T-site electrooxidation data in Figure 3.8. The solid lines are linear fittings for 0.3 (black) and 0.4 V (red).

Oxygen ratio in Figure 3.9. The $k_5$ vs. $\omega$ values exhibited a linear relationship with the CNT surface oxygen ratio at both 0.3 V ($R^2 = 0.84$) and 0.4 V ($R^2 = 0.87$) providing further support for the conclusion that the higher overpotential and faster kinetic T-sites are represented by oxy-defects at the CNT tips.\[83\] In addition the lack of correlation to S and correlation to surficial oxygen supports the assumption that CNT oxy-defects are predominantly located at the CNT tips. The slight deviations of $k_5$ vs. CNT surface oxygen from linearity is likely because the number of surface oxygen atoms may not be perfectly correlated to the number of oxy-defect groups e.g., a hydroxyl group contains 1 O-atom and a carboxylate group contains 2 O-atoms. In conclusion, the ferrocyanide electrooxidation kinetic modeling revealed the CNT networks have two distinct reactive sites of the sp$^2$ conjugated sidewalls (S-sites) and the oxy-defect tips (T-sites) with the latter having a higher overpotential (+66 mV) and faster electron transfer kinetics.

The anodic onset potential (+0.2–0.3 V vs. Ag/AgCl) observed for the T-sites may be associated with the CNT electronic properties. A study on single-walled CNT observed that there was a threshold potential (+0.2 V for metallic and +0.7 V for semiconducting) for transfer of static positive charge to the CNT. Multi-walled CNT are a mixture of metallic (1/3) and semiconducting (2/3) CNT with the metallic tending to dominate electronic properties.\[88\] The anodic T-site onset potential here may
be necessary to activate the oxy-containing defect sites via positive charging prior to electrochemical ferrocyanide oxidation.[89]

**Single CNT spatial reaction rate distribution**

The simulated concentration and diffusional flux fields, Figure 3.10a and b, respectively, provide insight into the spatial distribution of mass transport and electrochemical kinetics within the CNT network. The concentration decreased by 0.1 mM (~0.5% of influent concentration) in the direction of the fluid flow after passing through 5 µm of filter depth or had a concentration gradient of 2.4 µM µm⁻¹ in the z-direction. There was minimal concentration gradient in the x-direction with the exception of lines passing through a region near the top/bottom of an individual CNT. There was minimal concentration field variation (~0.01%) on the scale of a single CNT (100 nm) as expected since the simulation conditions are in the electron transfer limited regime i.e., mass transport is sufficient since diffusion is rapid at the nanoscale. The average distance between the CNT is <200 nm and small compared to the filter thickness of ~90 µm. The estimated time for a target molecule to diffuse ~100 nm, the maximum distance to a CNT surface, is $4 \times 10^{-7}$ s and significantly lesser than the hydraulic residence time of 1.2 s. The homogenous near CNT surface concentration indicates that the spatially distributed reaction rate around an individual CNT perimeter is also homogeneous as expected for a surface area dependent reaction according to Eq 3.15.

In contrast, the spatial distribution of the 2D diffusional flux was quite heterogeneous (up to 90%) around an individual CNT perimeter. The diffusional flux is directly proportional to and thus representative of the concentration gradient. Although the absolute concentration difference around a single CNT in Figure 3.10a is quite small (~0.01% of bulk concentration), its gradient (dC/dz = 2.4 µM µm⁻¹) is not insignificant due to the extremely small scale (<100 nm). Diffusional fluxes were the lowest (minimum of $7 \times 10^{-6}$ mol m⁻² s⁻¹) at the CNT top/bottom, in regards to fluid flow, and were the highest (maximum of $7 \times 10^{-5}$ mol m⁻² s⁻¹) at the sides. The large spatial range of diffu-
Figure 3.10: Microscopic concentration field, diffusional flux, and streamline simulations for C-CNT. (a) Concentration field, concentration ranging from 23.3 mM on top to 23.2 mM at the bottom, (b) diffusional flux magnitude field, ranging from $4.7 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ (red) to $7 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ (blue). (c) Overlapped concentration contours and streamlines. Concentration contours ranging from 23.259 (blue) to 23.287 µM (red). The streamlines are in black. The representative patterns inside the CNT filter are shown from $z = 35$ to 40 µm for (a) and (b), and $z = 39.4$ to 40.6 µm for (c). Simulations are generated by COMSOL and conditions are ferrocyanide at $C_{in} = 25$ mM, $V_{in} = 7.08 \times 10^{-4}$ m s$^{-1}$, and $E = 0.2$ V.

The streamlines were mostly perpendicular to the concentration contours near each single CNT indicating the concentration gradient/diffusional flux is maintained by advection and that the diffusional flux is predominantly in a similar direction to the fluid flow. The fluid stagnation points at the top/bottom of an individual CNT results in slow convective target molecule replenishment; whereas the high fluid velocity near the sides of an individual CNT results in rapid target molecule replenishment, high concentration gradients, and high diffusional flux. Thus, within the electrochemical CNT network the rate of mass transport can be enhanced up to 10-fold within regions of rapid fluid flow that in turn maintains a high concentration gradient resulting in faster diffusion.
In summary, the electrochemical filter simulation allows for examination of microscopic flux and concentration gradients around an individual CNT that are experimentally difficult to probe.

3.7 Conclusion

The electrooxidative filtration kinetics of methyl orange and ferrocyanide were investigated by both experiment and simulation. The target molecules were selected to cover a range electrochemical activity; ferrocyanide is non-adsorptive and undergoes a single outer-sphere electron transfer and in contrast MO is strongly adsorptive and undergoes a multi-electron transfer. The physical model used to quantitatively describe the experimental data consists of four primary mechanistic steps: target molecule mass transport, adsorption, and electron transfer as well as product desorption. For methyl orange, a single-site model simulation was able to accurately predict effluent concentrations over a range of solution and electrochemical conditions. For ferrocyanide, the single-site model simulation could only predict effluent concentrations at low anode potentials (≤0.2 V) and a two-site model was necessary for prediction at higher anode potentials (≥0.3 V). Ferrocyanide electrooxidative filtration was completed using five different individual CNT of varying SSA and O/C ratio. The single site ferrocyanide electrooxidation kinetics correlated well with the SSA of the CNT networks indicating the sp² sidewalls were the predominant reaction site at low anode potential. The differential (total – sidewall site) ferrocyanide electrooxidation kinetics correlated well with the O/C ratio of the CNT networks indicating the oxytips also contributed at higher anode potentials. The tip differential kinetics had a greater increase with potential than the sidewall kinetics, thus although the sp² sidewalls had a lower ferrocyanide electrooxidation overpotential than the oxy-tips, once activated the oxy-tips had faster electrochemical kinetics. Finally, the simulation was used to probe the internal CNT electrode spatial concentration, concentration gradient, and diffusional flux distribution and it was observed that although the concentration is quite homogeneous in x at each depth z, the gradient and diffusional
flux can be 10-fold greater at the sides of a CNT as compared to the top/bottom due to convective replenishment.
Bi-Doped Tin Oxide-Coated Carbon Nanotube Network for Flow-Through Organic Electrooxidation
4.1 Abstract

In this study, a binder-free, porous, and conductive 3D carbon-nanotube (CNT) network uniformly coated with bismuth-doped tin oxide (BTO) nanoparticles was prepared via a simple electrosorption-hydrothermal method and utilized for the electrooxidative filtration of organics. The BTO-CNT nanocomposite was characterized by scanning electron microscopy, thermogravimetric analysis, transmission electron microscopy, X-ray photoelectron spectroscopy, linear sweep voltammetry, and Tafel analysis. The submonolayer BTO coating is composed of $3.9 \pm 1.5$ nm diameter nanoparticles (NPs). The oxygen-evolution potential of the BTO-CNT nanocomposite was determined to be 1.71 V (vs Ag/AgCl), which is 440 mV higher than an uncoated CNT anode. Anodic stability, characterized by CNT oxidative corrosion to form dissolved species, indicated that the BTO-CNT incurred negligible corrosion up to $V_{\text{anode}} = 2.2$ V, whereas the uncoated CNT was compromised at $V_{\text{anode}} = 1.4$ V. The effect of metal oxide-nanoparticle coating on anodic performance was initially studied by oxalate oxidation followed by total organic carbon (TOC) and chemical oxygen demand (COD) analysis. The BTO-CNT displayed the best performance, with $\sim 98\%$ oxalate oxidation (1.2 s filter residence time) and current efficiencies in the range of 32 to $>99\%$. The BTO-CNT anode energy consumption was 25.7 kWh kgCOD$^{-1}$ at $\sim 93\%$ TOC removal and 8.6 kWh kgCOD$^{-1}$ at $\sim 50\%$ TOC removal, comparable to state-of-the-art oxalate oxidation processes (22.5–81.7 kWh kgCOD$^{-1}$). The improved reactivity, current efficiency, and energy consumption are attributed to the increased conductivity, oxygen-evolution potential, and stability of the BTO-CNT anode. The effectiveness and efficiency of the BTO-CNT anode as compared to the uncoated CNT was further investigated by the electrooxidative filtration of ethanol, methanol, formaldehyde, and formate, and it was determined to have TOC removals 2 to 8 times greater, mineralization current efficiencies 1.5 to 3.5 times greater, and energy consumption 4 to 5 times less than the uncoated CNT anode. Electrooxidation and anode passivation mechanisms are discussed.
4.2 Introduction

Carbon nanotubes (CNTs) are widely used in electrochemical applications including batteries,[90, 91] super-capacitors,[92, 93] and fuel cells[94, 95] because of their unique physical and chemical properties. One promising general electrochemical application of CNTs is anodic organic oxidation, which is relevant to water treatment, fuel cells, and sensors. Because of their high aspect ratio, large specific surface area, excellent conductivity, and stable chemical structure, CNTs can potentially form porous, conductive, and 3D structures for effective, efficient, and rapid electrochemical oxidation.[14, 27] For example, recent studies have shown that a porous CNT electrochemical filter, where the solution to be treated flows through the electrode, can effectively remove organic dyes, phenol, and ions via adsorption and electrooxidation.[14] The flow-through filter configuration results in electrochemical kinetics up to 10 times greater as compared to the conventional batch electrochemical reactor configuration because of increases in the convective mass transfer of the target molecules to the electrode surface.[64, 84] Nevertheless, the electrochemical filter CNT anode still faces the same universal anode development challenge: low current efficiencies at high anode potentials as a result of competition with anode corrosion and water oxidation (eq 1.5).[64, 96]

The oxygen-evolution reaction will substantially reduce the current efficiency (CE) because the solvent water (55 M) will always be in great excess relative to the target molecules, limiting electrochemical oxidation applications at anode potentials over their oxygen evolution overpotential (OEP). For example, the electrochemical oxidation of recalcitrant perfluorinated molecules such as perfluorooctanoate (PFOA) required anode (Ti/SnO$_2$-Sb-Bi) potentials >3.4 V for rapid oxidation, resulting in a current efficiency of less than 1%.[79]

A low OEP may be problematic for uncoated CNT anodes. For example, a CNT OEP of ~1.0 V (vs Ag/AgCl) has been reported, indicating a negligible oxygen-evolution overpotential and resulting in significant decreases (~70%) in dye oxidation current efficiency at ~200 mV > OEP.[64] In addition,
a recent study on the durability of single-wall carbon nanotubes indicated that high anode potentials (>4 V) caused severe CNT degradation in deionized water,[97] which would significantly deteriorate anode conductivity and performance. Therefore, the development of novel anode materials with increased OEP (and in turn target-molecule current efficiency) as well as stability is of great importance, in particular for organic oxidation processes requiring high anode potentials.

Fortunately, CNTs are not only effective as a homogeneous anode material but can also serve as an excellent high surface area catalyst substrate. Surface modification with selected organic,[98] inorganic,[79, 99] and biological species[100, 101] dramatically influences the CNT chemical and physical properties and can improve device performance for many electrochemical applications such as fuel cells,[102, 103] super-capacitors,[92, 104] and Li-ion batteries.[105–107] For example, a range of inorganic nanoparticle (NP)-CNT composites such as Fe$_3$O$_4$-CNT,[108] MnO$_2$-CNT,[109] and SnO$_2$-CNT (TO-CNT)[110] have been synthesized by reactive sputtering or hydrothermal methods and evaluated for Li-ion battery applications. In regards to electrochemical organic oxidation applications, SnO$_2$ and doped-SnO$_2$ are common inorganic anode-coating materials because SnO$_2$ has one of the highest reported OEPs at 1.7 V versus Ag/AgCl.[3] For example, a TiO$_2$ nanotube (TiO$_2$-NT) loaded with Sb-doped SnO$_2$ (ATO) NPs of 20 nm in diameter demonstrated an OEP of 1.6 V versus Ag/AgCl and was effective for the mineralization of benzoic acid:[111]

$$C_6H_5COOH + 12 H_2O \rightarrow 7 CO_2 + 30 H^+ + 30 e^-$$ (4.1)

The mineralization current efficiency (MCE) was greatly improved from 0.4% for the TiO$_2$-NT anode to 14.2% for the ATO coated TiO$_2$-NT anode. Therefore, one strategy to improve the current efficiency of high-potential CNT anode applications may be to coat a thin layer of high-OEP-doped tin oxide nanoparticles onto the CNT network.

Although a significant number of interesting works have been published on the coating of tin oxide
or doped tin oxide nanoparticles (NPs) onto a carbon-nanotube substrate, we could not find any reported material synthesis method that met all of the requirements for a CNT anode operating in the flowthrough configuration. Because of the nature of high-potential Faradaic electrochemical filtration, three key challenges in CNT-metal oxide anode preparation must be addressed: (I) a binder-free conductive CNT network, (II) a mechanically stable 3D porous structure viable for fluid filtration, and (III) a high-OEP CNT-metal oxide nanocomposite with minimal toxicity. First, many hydrothermal or sol-gel methods for SnO$_2$-coated CNT synthesis depend on conductive additives, such as carbon black and polymer binders, to lower the electrical resistance and increase mechanical stability. However, additives may result in competitive oxidation and block reactive sites, so binder-free and conductive CNT-metal oxide network materials are of great interest (key challenge I). Second, although there are few studies that successfully developed binder free and conducting SnO$_2$-CNT networks, a thin layer of CNTs must first be deposited on a metal substrate such that the NP coating can be formed via chemical vapor deposition. The final product is a network attached to the metal substrate that cannot be used as a flow-through electrode (key challenge II). Third, tin oxide is a semiconductor with a large band gap of 3.5 eV and is typically doped with Sb (toxic substance with an EPA drinking water limit of 6 µg L$^{-1}$) to increase the conductivity and electrochemical oxidation kinetics (key challenge III). Therefore, it is of interest to develop a highly conductive, stable, binder-free, non-toxic, and porous 3D CNT network to improve the anodic performance of highpotential, flow-through, organic oxidation applications.

In this study, we have prepared a porous CNT network coated with Bi-doped tin oxide (BTO) NPs and investigated its potential to overcome the three key challenges discussed above. Initial experiments compared the anodic performance of the uncoated CNT, tin oxide-coated CNT (TO-CNT), antimony-doped tin oxide-coated CNT (ATO-CNT), and bismuth-doped tin oxide-coated CNT (BTO-CNT) to determine if Bi was an effective and non-toxic alternative to Sb by measuring OEP, Tafel slope, and organic mineralization current efficiency. The composite is prepared using the
electrosorption of metal ions at the desired mole ratio onto a preformed 3D porous CNT network to ensure CNT–CNT contact followed by thermal hydrolysis at 80 °C for 1 h in pure water to precipitate the metal oxide coating. After hydrolysis, the metal oxide-CNT composite anode can be immediately used for electrochemical filtration. The metal oxide-CNT anodes were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA). The oxygen evolution of the metal oxide-CNT composites was examined by linear sweep voltammetry (LSV) and Tafel analysis. The anodic performance of the composite materials were examined by challenging with 1 mM oxalate, a recalcitrant organic.[118] Once enough evidence was collected demonstrating that the nontoxic BTO-CNT anode was as effective and efficient as the ATO-CNT anode, further experiments were completed only with the uncoated CNT control and BTO-CNT anodes. A stability test of the uncoated CNT and BTO-CNT anodes was completed by challenging the anode with only electrolyte or no electrolyte and measuring the effluent total carbon (TC) and inorganic carbon (IC), which are indicators of CNT electrooxidative corrosion. The anode materials before and after the stability test were also analyzed by XPS. Finally, the CNT and BTO-CNT anodic performance towards a range of small organics was evaluated. Electrooxidation and anode passivation mechanisms are discussed.

4.3 Materials and Methods

4.3.1 Chemicals and Materials

Sodium sulfate (Na$_2$SO$_4$, ≥98.0%), sodium persulfate (Na$_2$S$_2$O$_8$, ≥98.0%), tin chloride dihydrate (SnCl$_2$·2H$_2$O, ≥98.0%), antimony chloride (SbCl$_3$, ≥99.0%), bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O, ≥98.0%), hydrochloric acid (HCl, 36.5–38.0%), phosphoric acid (H$_3$PO$_4$, 85%), sodium oxalate (Na$_2$C$_2$O$_4$, ≥99.5%), ethanol (EtOH, ≥99.5%), methanol (MeOH, 99.8%), formaldehyde (HCHO, 36.5–38% in H$_2$O), and sodium formate (HCOONa, ≥99.0%) were purchased from Sigma-Aldrich.
(St. Louis, MO). All chemicals were reagent grade. All aqueous solutions were made with water from a Barnstead Nanopure Infinity purification system that produced water with a minimal resistivity of 18 MΩ cm⁻¹. The multiwalled carbon-nanotubes networks were purchased from NanoTechLabs (Buckeye Composites, Yadkinville, NC) in circles that were 47 mm in diameter, 41 ± 8 µm in depth, ~85% pore volume, and had an average pore size of 104 ± 39 nm, as have been characterized previously in detail.[84]

4.3.2 Electrooxidative Filter Preparation

The NP-CNT nanocomposite anode was prepared via a simple electrosorption-hydrothermal method. To prepare the TO-CNT, 1 g of SnCl₂·2H₂O was dissolved in 33 mL of 37% HCl followed by the addition of 67 mL of deionized water. The solution was bath sonicated for 15 min and used as the electrolyte for electrosorption. The CNT network (40 mg) was first wetted with ethanol prior to electrosorption. The electrosorption process utilized a conventional bipolar electrochemical cell that was placed into the electrolyte solution using the CNT network as the cathode and a titanium plate (3 × 2 cm²) as the anode. The total applied voltage was 1 V for 1 h. During the electrosorption process, the CNT cathode becomes negatively charged and in turn electrosorbs the positively charged metal cations. After electrosorption, the CNT network was placed in a hot (80 °C) DI water bath for 1 h to precipitate the metal oxides. The coated CNT filter was then removed from the hot water bath and dried in air at 60 °C for 2 h. The ATO-CNT and BTO-CNT preparation processes were exactly the same as that of the TO-CNT except that 0.050 g SbCl₃ or 0.107 g Bi(NO₃)₃·5H₂O was also added to the electrolyte solution such that the molar ratio of dopant (Sb or Bi) to Sn was 0.05. The anodic filter was then loaded into a filtration casing modified for electrochemistry, as described in detail in a previous study (Figure 1.4).[14]
4.3.3 SEM

SEM was completed in Harvard's Center for Nanoscale Systems (CNS) on a Zeiss FESEM Ultra Plus. Micrographs were analyzed with ImageJ (NIH) software to determine CNT diameter and aerial pore diameter, which is the distance between CNTs. Reported diameters were the average of at least 100 measurements from at least two network images.

4.3.4 TEM

TEM was completed at Harvard's Center for Nanoscale Systems on a JEOL 2100TEM with an accelerating voltage of 200 kV. Prior to imaging, BTO-CNT powder was scratched from the BTO-CNT filter and spread onto a copper grid for analysis. Nanoparticle size measurements were the average of at least 100 measurements from at least two network images.

4.3.5 XPS

XPS was completed on a Thermo Scientific K-Alpha XPS with a monochromatic Al Kα X-ray source in Harvard’s Center for Nanoscale Systems. Survey spectra were scanned for all samples from 0 to 1400 eV to determine the elemental composition near the CNT network surface. Individual element scans were also completed for C 1s (274–294 eV), O 1s (522–542 eV), Sn 3d (477–500 eV), and Bi 4f (154–169 eV). Avantage software was used to determine the integrated peak areas for the individual elements and to estimate the surficial carbon-nanotube network elemental ratios.

4.3.6 TGA

TGA was completed in Harvard’s Material Research Science and Engineering Center (MRSEC) on a Q5000-IR Thermogravimetric Analyzer (TA Instruments). Samples were ground into powder and placed in a platinum pan. The initial sample weight was ~5.2 mg for the uncoated CNT network.
and ~6.4 mg for the BTO-CNT network. The pan was heated from room temperature to 150 °C at 10 °C min⁻¹, held at 150 °C for 30 min to remove any residual water, heated to 800 °C at 10 °C min⁻¹, held at 800 °C for 30 min, and was finally brought back to room temperature at 20 °C min⁻¹. A second identical run was completed immediately after the first and used as a background. The percent of residual material was determined using the initial mass and the mass remaining after a complete thermal cycle.

4.3.7 Electrochemical Characterization

The LSV and Tafel experiments were completed with a CHI604D electrochemical workstation (CH Instruments, Inc.) utilizing a Ag/AgCl reference electrode, a perforated titanium shim counter electrode, and an uncoated CNT or a metal oxide coated CNT network as the working electrode in the conventional batch (no flow) configuration. The electrochemical cell was placed into 500 mL of 0.5 M H₂SO₄ for LSV and Tafel analysis. Scan rates of 0.02 and 0.01 V s⁻¹ were used for LSV and Tafel analysis, respectively. The anode used for electrochemical characterization had an active geometric area of 7 cm² and a mass of 16 mg CNT plus metal oxide. The total surface area was obtained by multiplying the CNT mass by its BET specific surface area, 88.5 m² g⁻¹,[14] which in this case was 1.4 m².

4.3.8 Electrooxidative Filtration

A background electrolyte of 10 mM sodium sulfate in water was used for all experiments unless otherwise noted. Oxalate, ethanol, methanol, formaldehyde, and formate at different concentrations were used as target molecules for electrooxidative filtration. Although the uncoated or coated CNT networks were circles of 47 mm in diameter, only an inner circle with a diameter of 30 mm was in contact with solution, with the rest buried by the rubber seal. Thus, in all experiments, the effective anodic filter was composed of 16 mg of CNT and any additional NPs. The exposed geometric area was 7 cm²,
and the total surface area was 1.4 m². The flow rate (J) in the oxalate experiments was 1.5 mL min⁻¹ and for all other electrooxidative filtration experiments was 3 mL min⁻¹. The thickness of the CNT filter was 45 µm, so the residence time was ~1.2 s for oxalate experiments and ~0.6 s for all other electrooxidative filtration experiments. The electrooxidative filtration was completed at a number of controlled currents ranging from 1 to 60 mA. The controlled-current method was used here such that the current efficiency can be easily calculated and compared to previous organic electrooxidation studies that utilize constant-current methods. The steady-state effluent total organic carbon (TOC) was measured after the current was constant for 20 minutes, and the mineralization current efficiency (MCE) was calculated by the following equation

\[
MCE = \frac{(TOC_{inf} - TOC_{eff})n_e F J}{12 I} \quad (4.2)
\]

where \(TOC_{inf}\) and \(TOC_{eff}\) stand for the influent and effluent TOC in mg L⁻¹, \(n_e\) is the average number of electrons transferred per carbon to oxidize to carbon dioxide, \(F = 96485 \text{ C mol}^{-1}\) is Faraday’s constant, \(J\) is the flow rate in L s⁻¹, and \(I\) is the current in mA. The time-averaged voltage at each current was also recorded and used to calculate the energy consumption (EC) in kWh kgTOC⁻¹ by the following equation

\[
EC = \frac{UI}{3600(\text{TOC}_{inf} - \text{TOC}_{eff})J} \quad (4.3)
\]

where \(U\) and \(I\) denote the measured voltage (V) and current (mA).

4.3.9 Anode Stability Test

The anode stability tests of the uncoated CNT and BTO-CNT networks were completed with a CHI604D electrochemical workstation using an Ag/AgCl reference electrode, a perforated titanium shim counter electrode, and an uncoated CNT or metal oxide coated CNT network as the working
electrode. For the stability experiments, either DI water or 10 mM electrolyte (Na₂SO₄ or NaF) was flowed through the working electrode at a set anode potential and a flow rate of 1.5 mL min⁻¹. The anode potential was increased stepwise from 0.6 to 3.0 V and kept at each potential for a time interval of 10 min. The time dependence of the effluent concentration for the CNT stability test was measured, and the results (Figure B.1) indicate that a measurement at 10 min represents an extended time average. The steady-state current, TC, and IC measurements of the effluent were taken at the end of each interval.

4.3.10 TOC Measurement

The TOC analyses were completed on a Shimadzu TOC-VW analyzer equipped with a UV/thermal persulfate oxidizer. The calibration was completed over a concentration range of 1 to 100 mg C L⁻¹ using a six-point curve with potassium terephthalate as a carbon source. The TC injection was 1.5 mL per sample with the addition of 75 μL of 0.5 M sodium persulfate and 75 μL of 17% phosphoric acid. The IC injection was 2.5 mL per sample with the addition of 125 μL of 17% phosphoric acid.

4.4 Results and Discussion

4.4.1 Anode Material Characterization

The uncoated CNT and BTO-CNT networks were characterized by SEM and TEM for surface morphology, XPS for surface elemental composition analysis, and TGA for NP loading as well as electrochemical characterization for OEP and Tafel slopes. The surface morphology of the BTO-CNT nanocomposite prepared is of interest because the size and uniformity of the NP coating may significantly alter the physical and chemical properties of the material and in turn its effectiveness. An SEM image of the uncoated CNT network is displayed in Figure 4.1a. The CNTs have an average diameter of 19.6 ± 9.9 nm, exhibit a clean and smooth surface, are randomly oriented in a 2D plane,
Figure 4.1: Electron microscopy images of representative anode networks. (a) Aerial SEM image of the uncoated CNT network. (b) Aerial SEM image of the BTO-CNT network. (c) TEM image of the BTO-CNT nanocomposite analyzed for NP size and coating thickness. (d) Magnified view of BTO crystals on the CNT surface with the inset showing the lattice spacing of a BTO particle in the red square.

And form a porous and conductive 3D network viable for electrochemical filtration. An aerial SEM image of the CNT network after BTO NP deposition is displayed in Figure 4.1b. The CNT surfaces are uniformly coated by the BTO NPs as they become significantly rougher, and no bulk (>10 nm) tin oxide particles are observed.

TEM images of the BTO-CNT nanocomposite network are displayed in Figure 4.1c,d. The BTO coating on the CNT networks has a thickness of <10 nm and a uniform particle size of 3.9 ± 1.5 nm. There is also a large particle of ~20 nm located inside one of the CNTs, which can be attributed to the residual Fe catalyst because similar particles were also observed inside the uncoated CNTs. A magnified view of a BTO NP (Figure 4.1d) at the surface of a CNT indicates that the NPs are crystalline with
distinct lattice fringes. The adjacent spacing of aligned lattice fringes is 0.33 nm, slightly larger than the spacing of the (110) plane of a pure SnO$_2$ crystal, 0.32 nm, possibly due to the Bi doping because Bi has a slightly larger atomic radii (1.60 Å) than Sn (1.45 Å).[120] Together, the SEM and TEM images show that the uniformly coated BTO-CNT network prepared in this study is free-standing, binder-free, and porous and is thus suitable for electrochemical filtration (key challenges I and II).

The uncoated CNT and BTO-CNT networks were also characterized by XPS and TGA analysis. The surficial elemental compositions (XPS) are summarized in Table 4.1, and the XPS survey scans can be found in Figure B.2. XPS indicates that the uncoated CNT surface elemental composition is 0.51% O, 0.14% Fe, and 99.35% C. The observed iron is attributed to the residual iron catalyst from the CNT synthesis.[14] For comparison, the BTO-CNT surface elemental composition is 11.6% O, 83.6% C, 4.7% Sn, and 0.1% Bi, and no surface iron was detected, possibly due to dissolution in the acidic (pH 2 to 3) electrosorption solution. From the surficial elemental composition, the Sn/C atomic ratio is 0.056. The nanocomposite Bi/Sn atomic ratio is 0.02, which is lower than the electrosorption solution Bi/Sn atomic ratio of 0.05. The mass of the nanoparticle coating was evaluated by TGA (Figure B.3 and Table 4.1). The remaining mass of the uncoated CNT sample after combustion (800 °C) was 2.5% of its original weight and can be attributed to the residual Fe catalyst. This result is consistent with previous reports,10 but it is much higher than the Fe content as determined by XPS analysis (0.14% atomic ratio or 0.65% weight), indicating that most of the residual catalyst is within tubes, in agreement with the large internal particles observed by TEM in Figure 4.1c. The BTO-CNT sample had a significantly greater residual mass of 17.4%, as expected because of the addition of the inorganic BTO NP coating. Assuming the same iron oxide/carbon weight ratio of the uncoated CNT sample holds in BTO-CNT, the actual weight ratio of BTO nanoparticles/carbon is determined to be 0.185. The TGA burn temperature of the BTO-CNT network is 630 °C, which is slightly (5 °C) higher than the burn temperature of the uncoated CNT, 625 °C, indicating negligible degradation of the CNT stability during the coating process. In summary, the BTO NP loading on the CNT network was
Table 4.1: Material Characterization by XPS and TGA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C %</th>
<th>O %</th>
<th>Fe %</th>
<th>Na %</th>
<th>S %</th>
<th>Sn %</th>
<th>Bi %</th>
<th>res %</th>
<th>burn peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>99.35</td>
<td>0.51</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>625</td>
</tr>
<tr>
<td>CNT 1.8 V</td>
<td>87.41</td>
<td>9.82</td>
<td>0.61</td>
<td>1.57</td>
<td>0.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BTO-CNT</td>
<td>83.62</td>
<td>11.56</td>
<td></td>
<td>4.72</td>
<td>0.10</td>
<td>17.4</td>
<td>0.08</td>
<td></td>
<td>630</td>
</tr>
<tr>
<td>BTO-CNT 3 V</td>
<td>70.26</td>
<td>17.92</td>
<td>5.78</td>
<td>1.77</td>
<td>4.18</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Determined by XPS, atomic percentage.
b Determined by TGA, weight percentage.

18.5% with regards to carbon weight, and the Bi doping was 2% with regards to Sn.

As previously discussed, the OEP is an important operational parameter for anode materials used in high-voltage applications such as organic oxidation.[121] The oxygen-evolution potential and kinetics of the four electrodes, uncoated CNT, TO-CNT, ATO-CNT, and BTO-CNT, were examined by both LSV and Tafel analysis. The linear sweep voltammograms (scan rate = 0.02 V s⁻¹ in 0.5 M H₂SO₄ solution) for the four anode materials are presented in Figure refamifig2a (solid lines). The subsequent extrapolations (dashed lines) of the current waves to 0 A was used to determine the oxygen-evolution potentials (vs Ag/AgCl) of the uncoated CNT (black, 1.27 V) < ATO-CNT (blue, 1.51 V) < BTO-CNT (pink, 1.71 V) < TO-CNT (red, 1.85 V) anodes. The OEP of TO-CNT is 150 mV higher than the reported OEP of bulk SnO₂, 1.7 vs Ag/AgCl,[3] which not only verifies that the NP deposition method used here leads to an effective and uniform coating on the CNT surface but also indicates that the SnO₂ NPs may have a higher OEP than bulk SnO₂. As the particle size decreases to the nanoscale (<10 nm), the band gap will increase because of quantum confinement as compared to the bulk material and may in turn affect the material OEP by lowering the valence band edge. For example, SnO₂ NPs with
a diameter of 3–5 nm were reported to have band gap of 4.05 eV, which is 0.35 eV larger than that of the bulk SnO$_2$ band gap of 3.7 eV.\cite{122} The OEP (vs Ag/AgCl) of the TO-CNT (1.85 V) and BTO-CNT (1.71 V) network anodes produced here (1.85 V) are also higher than many other common anode materials, including PbO$_2$ (1.7 V), Pt (1.4 V), and IrO$_2$ (1.32 V), but are still lower than borondoped diamond (BDD, 2.1 V).\cite{3}

To further understand the oxygen-evolution kinetics, a Tafel analysis of the four electrodes was completed and is presented in Figure 4.2b. The Tafel plot, eq 4.4, describes the linear relationship between the anode potential $E$ (mV) and the logarithm of the current $I$ (A):\cite{4}

$$E = a + b \log (I) \quad (4.4)$$

The slope $b$ (V dec$^{-1}$) is known as the Tafel slope and is inversely related to the oxygen-evolution kinetics (i.e., a larger Tafel slope indicates slower oxygen-evolution kinetics). The unit, V dec$^{-1}$ represents volts per decade of current. The Tafel slopes for the four materials follow the order uncoated CNT (black, 0.5 V dec$^{-1}$) < ATO-CNT (blue, 0.88 V dec$^{-1}$) < BTO-CNT (pink, 1.05 V dec$^{-1}$) < TO-CNT
The Tafel slopes of the TO-CNT and BTO-CNT are higher than many common anode materials including BDD (0.29 V dec\textsuperscript{−1}) and PbO\textsubscript{2} (0.18 V dec\textsuperscript{−1}),\textsuperscript{123} indicating relatively slow oxygen-evolution kinetics. The LSV and Tafel analysis both indicate that the tin oxide and doped tin oxide nanoparticle coatings on the CNT networks can effectively increase the OEP and the Tafel slope relative to the uncoated CNT anode, resulting in both a delayed onset of water oxidation and slower oxygen-evolution kinetics (key challenge III).

4.4.2 Effect of Metal Oxide NP Coating on Organic Oxidation Performance.

Although high-anode-material OEP usually indicates higher current and energy efficiency towards organic oxidation, rapid kinetics is also necessary for an effective electrooxidative processes. Thus, here, the recalcitrant organic oxalate was utilized as a target molecule for the initial oxidation experiments. Electrochemical anodic oxidation as well as other advanced oxidation processes (AOPs) have been previously studied for oxalate degradation\textsuperscript{118, 124–126} because it is the most common non-CO\textsubscript{2} end product during aromatic oxidation\textsuperscript{118} as a result of its slow reaction with the \textbullet OH radical (C\textsubscript{2}O\textsubscript{4}\textsuperscript{2−} + \textbullet OH → CO\textsubscript{2} + CO\textsubscript{3}\textsuperscript{−} \cdot ; k = 7.7 × 10\textsuperscript{6} M\textsuperscript{−1} s\textsuperscript{−1}.\textsuperscript{127}) Oxalate and oxalic acid can undergo a two-electron oxidation process to carbonate/CO\textsubscript{2} according to the following equations:

C\textsubscript{2}O\textsubscript{4}\textsuperscript{2−} + 2 OH\textsuperscript{−} → 2 CO\textsubscript{3}\textsuperscript{−} + 2 H\textsuperscript{+} + 2 e\textsuperscript{−} \hspace{1cm} \left(E^\circ = 1.18 \text{ V}\right) \hspace{1cm} (4.5)

H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} → 2 CO\textsubscript{2} + 2 H\textsuperscript{+} + 2 e\textsuperscript{−} \hspace{1cm} \left(E^\circ = 0.345 \text{ V}\right) \hspace{1cm} (4.6)

The uncoated CNT, TO-CNT, ATO-CNT, and BTO-CNT were challenged by an aqueous oxalate solution (C\textsubscript{in} = 100 mg L\textsuperscript{−1}, [Na\textsubscript{2}SO\textsubscript{4}] = 10 mM, J = 1.5 mL min\textsuperscript{−1}, and residence time 1.2 s). The TOC removal percentage and average total cell voltage of the uncoated CNT (black), TO-CNT (red), ATO-
CNT (blue), and BTO-CNT (pink) as a function of the steadystate current (0–60 mA) are presented in Figure 4.3, panels a and b, respectively. The solid line (yellow) in Figure 4.3 is the theoretical maximum TOC removal, and the points are the experimental measurements. The TOC removal for the uncoated CNT anode first increases with increasing current to 62 ± 2.5% at 15 mA and then decreases significantly to only 26 ± 12.4% at 40 mA. A similar trend was observed for the TOC-CNT anode, with TOC removal peaking at 40 mA (71 ± 4.4%) and then decreasing to 32 ± 23% when the current was increased to 60 mA. In contrast, the TOC removal for the ATO-CNT and BTO-CNT anodes increased until 89 ± 4 and 94 ± 4% TOC removal was achieved at ≥40 mA, respectively, and no TOC removal decrease with increasing current was observed. In regards to the maximum TOC removal rate over the current range of 0–60 mA, the ATO-CNT and BTO-CNT were 1.3 times greater than the TO-CNT because the Sb/Bi doping improved the conductivity and they were 1.5 times greater than the uncoated CNT anode because of a lesser oxygen evolution and improved anode stability, as will be discussed in detail later.

In Figure 4.3b, the total cell voltage of the electrochemical filter was observed to increase with increasing current for all four anode materials, and the voltage response was quite similar for all four anodes below 15 mA. For the uncoated CNT anode, the total cell voltage increased significantly at both 15 and 20 mA to 5.5 ± 0.5 V, which is the greatest among all of the materials, and reached 6.1 ± 1.9 V at 40 mA. The TO-CNT anode total cell voltage increased to values greater than the ATO and BTO at currents ≥40 mA, achieving 6.3 ± 1.7 V at 60 mA. In contrast, only a slight increase (slope 20–60 mA < slope 0–20 mA) in total cell voltage was observed for the ATO-CNT and BTO-CNT anodes when the current was >20 mA, reaching 4.7 ± 0.3 and 4.3 ± 0.2 V, respectively, at 60 mA.

The anodic TOC removal behavior in Figure 3a and the total cell voltage data in Figure 4.3b must be combined and compared with the anode electrochemical characterization results for a clear understanding of the material effect on anode efficacy and efficiency. At currents up to 10 mA, all four electrodes displayed similar performance: ~50% TOC removal and >99% current efficiency near the
Figure 4.3: Electrochemical filtration of oxalate with the various anode materials as a function of steady-state current. (a) TOC removal (%). (b) Total cell voltage (V). (c) Current efficiency (%). (d) Energy consumption (kWh kg TOC$^{-1}$).

The uncoated CNT results are in black, TO-CNT, red, ATO-CNT, blue, and BTO-CNT, pink. The dark-yellow line in panel c represents the theoretical maximum of current efficiency assuming 100% TOC removal. TOC$_{inf}$ = 100 mg C L$^{-1}$, $J$ = 1.5 mL min$^{-1}$, residence time 1.2 s, and [Na$_2$SO$_4$] = 10 mM.
Figure 4.4: Representative CNT Passivation Mechanisms. (a1) The produced oxygen bubbles block surface reactive electron transfer sites. (a2) The produced oxygen bubbles break CNT–CNT network contacts. (b1) Direct CNT oxidative corrosion resulting from surface hole accumulation, releasing small organics and CO$_2$. (b2) CNT oxidative corrosion resulting from hydroxyl radical and sulfate radical production at >2.2 V, releasing small organics and CO$_2$.

Theoretical maximum. The total cell voltage when I $\leq$ 10 mA was always $<$ 2.7 V, and this voltage results in an anode potential $<$ 1.1 V on the basis of previous CNT anode open-circuit potential measurements.\[^{44}\] A 1.1 V anode potential is higher than the two-electron standard reduction potential of oxalate to carbonate ($E^\circ = 0.98$ V, pH 14; eq 4.5), but it is less than the OEP for all of the anode materials examined in this study (1.27–1.8 V vs Ag/AgCl), indicating the oxygen evolution reaction is not active, which is in agreement with the similar oxidation performance of the four electrodes when I $\leq$ 10 mA. However, when the current was increased to $\geq$ 15 mA, the cell voltage for the uncoated CNT anode increased significantly to 4 V, indicating a dramatic decrease of anode conductivity with a corresponding decrease in TOC removal, as presented in Figure 4.3a. The increase of total cell voltage from 2.7 to 4 V will increase the anode potential to $\sim$ 2 V and over the OEP of the uncoated CNT, 1.27 V, activating oxygen evolution.
The passivation mechanism of the uncoated CNT anode at \( \geq 4 \) V cell voltage may be attributed to two types of processes shown in Figure 4.4: (a) electrochemical production of oxygen, eq 1.5, and subsequent formation of bubbles that can (a1) block reactive sites and (a2) mechanically break the CNT-CNT contacts and network and (b) CNT oxidative corrosion because of (b1) direct oxidation via the build-up of a high surface hole concentration and (b2) indirect oxidation via the production of homogeneous or surface-bound free radicals. In regards to mechanism a1, at potentials higher than the CNT OEP, significant oxygen evolution will produce a large amount of gas bubbles, which can be trapped in the porous CNT network and block the reactive surface for electrooxidation, leading to a decrease in the TOC removal rate. In regards to mechanism a2, at extended operation times, the bubbles will grow and expand in the porous network, resulting in the loss of CNT-CNT contact and the breakdown of network mechanical-stability, and both in turn will reduce network conductivity. The decrease of the uncoated CNT anode conductivity (i.e., significant increase in the total cell voltage with current) and TOC removal rate at \( \geq 4 \) V cell voltage is likely due to mechanisms a1 and a2 because it coincides with the onset of the oxygen-evolution reaction. In regards to mechanisms b1 and b2, a high total cell voltage resulting from decreased network connectivity and conductivity will result in a high anode potential that will inevitably lead to CNT corrosion.[126] The CNT corrosion will decrease anode conductivity, resulting in a positive feedback that may rapidly aggravate anode passivation. Another consequence of CNT corrosion is the release of small organics into solution. CNT corrosion mechanisms b1 and b2 will be discussed in detail in the next section. In summary, the decrease in TOC removal by the uncoated CNT when I \( \geq 15 \) mA is likely due to one of the previously discussed passivation mechanisms and is most likely a complex combination of the processes.

The TO-CNT displayed a better TOC removal rate than the uncoated CNT at \( \geq 15 \) mA and had a similar TOC removal percentage as the ATO and BTO-CNT until I \( > 40 \) mA. The increased stability of the TO-CNT as compared to the uncoated CNT is due to the high OEP and preferential hole transfer to the tin oxide coating, reducing passivation. However, a significant loss of electrochemical activ-
ity still occurred at 60 mA. The total cell voltage versus steady-state current did not display a sudden increase similar to the uncoated CNT, indicating bubble formation via oxygen evolution (mechanism a2) is not greatly affecting the conductivity because of the high OEP of TO-CNT. However, the cell voltage still increased up to 6.3 V and may have led to CNT corrosion and anode passivation. The higher total cell voltage of the TO-CNT at 60 mA as compared to ATO-CNT and BTO-CNT can be attributed to the semiconductive nature of the TO coating, which increases the overall electrical resistance of the anode network (i.e., SnO$_2$ is a semiconductor with a large band gap of 3.7 eV and limited conductivity if it is not doped). For example, pure tin oxide has a low conductivity (0.01–1 $\Omega^{-1}$ cm$^{-1}$) that can be increased by doping with Sb (1–200 $\Omega^{-1}$ cm$^{-1}$) because of the creation of oxygen vacancies that increase the charge carrier concentration. For comparison, fabricated CNT yarns with a porosity of 75% have a conductivity of 200 $\Omega^{-1}$ cm$^{-1}$.[3] The low conductivity of SnO$_2$ indicates that at high steady-state currents the holes may preferentially flow through the more conductive CNTs, resulting in passivation. Therefore, as compared to the uncoated CNT and TO-CNT, the ATO-CNT and BTO-CNT benefited from both their high OEP and increased conductivity (e.g., at 40 mA, the ATO-CNT achieved an 89 $\pm$ 4% TOC removal with a cell voltage of 4.7 $\pm$ 0.4 V and the BTO-CNT achieved a 94 $\pm$ 4% TOC removal with a cell voltage of 4.3 $\pm$ 0.4 V without any indication of anode passivation).

The oxalate electrooxidation current efficiency as a function of the steady-state current for the CNT (black), TO-CNT (red), ATO-CNT (blue), and BTO-CNT (pink) anodes is displayed in Figure 4.3c (same experimental conditions as panels a and b). The bars represent the experimental measurements, and the solid line is the theoretical maximum current efficiency. The theoretical maximum current efficiency is calculated by setting TOC$_{eff}$ = 0 in eq 4.2 and a maximum efficiency of 100%. All four anode materials had a current efficiency of >90% when $I \leq 10$ mA, indicating minimal oxygen evolution, which is in agreement with the results presented in Figure 4.3a,b, and at higher steady-state currents ($\geq 15$ mA) the current efficiencies for all four anodes decreased relative to the theoretical maximum.
current efficiency. The oxalate oxidation current efficiency of the uncoated CNT anode decreased rapidly to 12.9% at 40 mA. Improvement was observed for the TO-CNT anode where the current efficiency was 34.3% at 40 mA, but it decreased to 10.3% at 60 mA. The ATO-CNT and BTO-CNT anodes had the highest oxalate oxidation current efficiency, which approached the theoretical maximum at all steady-state currents. At 40 mA, the current efficiency for the ATO-CNT and BTO-CNT anodes was 38.6 and 48.7%, respectively, which are more than 3 times greater than the uncoated CNT anode, 12.9%, and slightly less than the theoretical maximum CE of 60%. At 60 mA, the current efficiency of the ATO-CNT and BTO-CNT anodes was 30 and 32.2%, respectively, which again are more than 3 times the less conductive TO-CNT anode, 10.3%, and close to the theoretical maximum CE of 33%.

The energy consumption (kWh kgTOC⁻¹) for oxalate oxidation at the uncoated CNT (black), TO-CNT (red), ATO-CNT (blue), and BTO-CNT (pink) anodes are plotted in Figure 4.3d (same experimental conditions as a–c). All electrodes showed similar energy consumption (2.8–10.3 kWh kgTOC⁻¹) at currents ≤15 mA, but the ATO-CNT and BTO-CNT anodes had significantly lower energy consumption at higher steady-state currents. At 40 mA, the energy consumption of the ATO-CNT and BTO-CNT anodes are 24.4 and 17.1 kWh kgTOC⁻¹, respectively, which are 4 to 5 times less than the energy consumption of the uncoated CNT, 105.3 kWh kgTOC⁻¹. At 60 mA, the energy consumption of the ATO-CNT and BTO-CNT anodes were 35.2 and 30.4 kWh kgTOC⁻¹, respectively, which again are 4 to 5 times less than the energy consumption of the TO-CNT, 130.5 kWh kgTOC⁻¹. In practical applications, high current densities (>40 mA cm⁻²) may be necessary to ensure rapid oxidation kinetics, and the ATO-CNT and BTO-CNT anodes significantly reduce (4 to 5 fold) the energy consumption under the highest current conditions utilized here by reducing competitive water oxidation. A comparison of oxalate oxidation kinetics and energy consumption by various anode materials and methods is presented in Table B.1 along with detailed discussion in the Appendix.

Both ATO-CNT and BTO-CNT displayed similar efficacy and efficiency towards oxalate oxida-
tion; however, antimony is a regulated toxic chemical. The EPA National Primary Drinking Water Regulations regulates a maximum contaminant level for antimony of $6 \ \mu g \ L^{-1}$, whereas Bi is not regulated and can be found in common over the counters medicines such as Pepto-Bismol. Therefore, the BTO-CNT network was the most effective and efficient anode material because of the combination of high OEP, increased conductivity, and nontoxicity (key challenge III), and thus will be evaluated in greater detail relative to the uncoated CNT anode as a control.

4.4.3 Anode Stability Test

Anode corrosion stability is a critical factor in high-potential electrochemical applications. Many studies indicate that CNT anode corrosion will likely occur at increased anode potentials ($>1.7$ V for MWCNT and $>1.0$ V for SWCNT vs Ag/AgCl) in electrolyte solutions because of direct electrolyte-mediated oxidation (mechanism b1) or indirect free-radical oxidation (mechanism b2).[97, 131, 132] Anodic corrosion will decrease the CNT conductivity by damaging their sp² conjugation, leading to decreased current efficiencies and organic oxidation rates. It was reported that the resistivity of an SWCNT increased by over 4 orders of magnitude from $120$ to $1.6 \times 10^6 \ \Omega \ \text{sq}^{-1}$ after being etched at an anode potential of $2.0$ V.[132] To mineralize or even oxidize recalcitrant organics, high anode potentials are inevitable and thus the anode stability acts as an upper limit to the anode potential.

The anodic stability of the BTO-CNT and uncoated CNT network was evaluated by electrochemical filtration experiments with $10$ mM Na$_2$SO$_4$, deionized water, and $10$ mM NaF solutions (TC $\leq 0.1 \ \text{mg} \ \text{L}^{-1}$), and the results are displayed in Figure 4.5a−c, respectively. The left vertical axis is the effluent TC and IC concentration in milligrams per liter, the right vertical axis is the percent anode mass loss per liter filtered, and the x axis is the anode potential (0.6−3.0 V). The percent anode mass loss per liter filtered was calculated by effluent TC (mg L$^{-1}$) divided the total weight of filter, 16 mg. The maximum filtration volume can then be calculated as the inverse of the percentage anode mass loss per liter filtered.
During the anode stability test, the TC and IC in the effluent should be minimal under potentials where the anode is stable because neither is in the influent. In the Na$_2$SO$_4$ experiments (Figure 4.5a), the uncoated CNT anode was stable (TC$\text{eff} <$0.6 mg L$^{-1}$) when V$_{\text{anode}} <$1.4 V and displayed two regimes of oxidative corrosion between 1.4–2.2 V and >2.2 V. Interestingly, between the anode potential range of 1.4–2.2 V, the uncoated CNT effluent TC (2.5 mg L$^{-1}$) and IC (1.6 mg L$^{-1}$) values peaked at 1.8 V, indicating a finite amount of electro-active reactant, such as the CNT surface functional groups, in agreement with previous literature where direct MWCNT etching was observed at >1.7 V.$^{[132]}$ At anode potentials $\geq$2.2 V, the effluent TC and IC increased rapidly to maxima of 15.6 and 4.2 mg L$^{-1}$, respectively, at 3.0 V. At this corrosion rate, it would take only 34 min to lose 5% of
the CNT anode mass, and the maximum filtration volume would be only ~1 L before near complete anode corrosion.

The corrosion mechanism must be considered in two ways: the predominant corrosion sites and the predominant corrosion reaction. The oxidation peak at 1.8 V can be attributed to mostly direct electrooxidation of the CNT surface oxyfunctional groups because of the high inorganic carbon (64%) and low organic carbon content of the effluent (e.g., surface carboxylates would be oxidized to CO₂ and surface carbonyls would be oxidized to CO). In contrast, at anode potentials ≥2.2 V, a high organic carbon (73%) and low inorganic carbon effluent content was observed and may be attributed to bulk corrosion of the CNTs via direct and indirect oxidation pathways.

From the perspective of the predominant corrosion reaction, the oxidative corrosion mechanisms proposed in Figure 4.4, b₁ and b₂, the surface hole accumulation (>1.4 V), and the oxidative radicals production (>2.2 V), respectively, can explain the anodic processes responsible for the TOC and IC production. In regards to mechanism b₁, the electrolyte/semiconductor interface plays an important role in the anodic hole stabilization and the subsequent corrosion process[132] (i.e., under an anodic bias, the electrolyte forms a charged layer at the semiconductor surface that stabilizes interfacial charge carriers such as holes, resulting in anode corrosion) (Figure 4.4, mechanism b₁). In regards to mechanism b₂, oxidative radicals produced from the water (HO·) and electrolyte (SO₄²⁻) oxidation may also contribute to CNT bulk corrosion at higher potentials (>2.2 V). At the neutral pH used in this study, anode potentials >2.2 V (vs Ag/AgCl), similar to the onset of the second oxidation regime, would be sufficient to produce hydroxyl radicals following eq 4.7.[133, 134]

\[
\text{OH}^- + h^+ \rightarrow \text{OH} \cdot \quad (E^o = 2.1 \, V, \, pH \, 7) \tag{4.7}
\]

Similarly, at anode potentials >2.2 V (vs Ag/AgCl), the sulfate radical can be produced following
Therefore, to test our hypothesis, stability tests for an uncoated CNT anode were completed in deionized water without electrolyte (only mechanism b2 via eq 4.7) and in an inert NaF electrolyte (only mechanisms b1 and b2 via eq 4.7). Fluoride is considered to be an oxidatively inert electrolyte at anode potentials <3 V because of its high standard reduction potential, eq 4.9:

\[
\text{F}^- + \text{h}^+ \rightarrow \text{F} \cdot \quad (E^\circ = 3.4 \text{ \textit{V}})
\]  

(4.9)

During the stability test in deionized water (Figure 4.5b), the TC was equivalent to the IC, and both peaked at 3.0 V at 0.7 mg L⁻¹ (~4% anode mass loss per liter filtered), indicating minimal corrosion in the absence of electrolyte. Only 4.4% of filter weight was lost per liter filtered at 3.0 V, and the maximum filtration volume would be 22.7 L before complete corrosion. Anodic water oxidation and hydroxyl radical production, eq 4.7, is also observed to be inactive and may be inhibited because of the high resistance of deionized water. The stability test in the inert electrolyte NaF in Figure 4.5c (in black) displayed a two oxidation regimes (1.5–2.2 and >2.2 V) similar to that of Na₂SO₄, and the peak TC concentration at 3 V was ~50% less (8 mg L⁻¹) than Na₂SO₄, indicating a strong contribution of sulfate oxidation, eq 4.8, to CNT corrosion at high potentials. Therefore, the no electrolyte/Na₂SO₄/NaF experiments indicate that CNT corrosion because of high surface hole concentration (Figure 4.4; mechanism b1) is the dominant corrosion mechanism at 1.4 to 2.2 V because the TC/IC are similar in the sulfate and fluoride electrolytes but are negligible in the absence of electrolyte. At >2.2 V, free-radical production, eqs 4.7 and 4.8, (Figure 4.4; mechanism b2) also contributes significantly to CNT oxidative corrosion (e.g., at 3 V sulfate contributes to ~50% of the corrosion). Therefore, the maximum stable working potential for the uncoated CNT anode is 1.4 V and may be acceptable up to 2.2 V. The maximum filtration volume for the most extreme case (10 mM Na₂SO₄)
of a 16 mg uncoated CNT anode was 15 L at 1.4 V and 7.4 L at 2.2 V.

In contrast, the BTO-CNT anode displayed significantly improved anode stability under all solution conditions (blue symbols in Figure 4.5a–c). For the 10 mM Na$_2$SO$_4$ electrolyte, the effluent TC and IC remained <0.6 mg L$^{-1}$ up to anode potentials of 2.2 V, indicating minimal CNT corrosion at potentials necessary for the oxidation/mineralization of most species. The anode mass loss per liter filtered was only 3.75%, and the volumetric life span was increased to 26.7 L; 3-fold greater as compared to the uncoated CNT anode. The improved BTO-CNT anode stability at $V_{\text{anode}} <$2.2 V indicates that the BTO-NPs preferentially accumulate generated holes because they are at the outermost surface of the anode material and have a smaller radii of curvature (i.e., a higher local charge density, the tip effect).[135] A slight increase of effluent TC and IC for the BTO-CNT was observed between 2.2 and 3.0 V, but even at 3.0 V, the TC$_{\text{eff}}$ = 2.7 mg L$^{-1}$ and IC$_{\text{eff}}$ = 1.4 mg L$^{-1}$. The anode mass loss per liter filtered was only 16.9%, and the volumetric life span was increased to 5.9 L, a 6-fold increase as compared to the uncoated CNT anode. The blue symbols in Figure 4.5b are the effluent TC and IC for the BTO-CNT corrosion in deionized water. Similar to the CNT stability test, the BTO-CNT corrosion in deionized water was minimal, with TC$_{\text{eff}} <$0.4 mg L$^{-1}$ at $V_{\text{anode}}$ = 3.0 V, indicating again that hole accumulation and radical formation (mechanisms b1 and b2) were inhibited in the absence of electrolyte. Similar to the uncoated CNT results, the BTO-CNT anode stability in 10 mM NaF (blue, Figure 4.5c) displayed two corrosion regimes at anode potentials from 1.4–2.2 and >2.2 V, with a maximum TC$_{\text{eff}}$ = 3.1 mg L$^{-1}$ at $V_{\text{anode}}$ = 3 V. This TC$_{\text{eff}}$ maximum was similar to that for Na$_2$SO$_4$, TC$_{\text{eff}}$ = 2.7 mg L$^{-1}$, indicating that CNT oxidation by the sulfate radical did not contribute significantly to BTO-CNT corrosion. Thus, the BTO-CNT exhibited negligible corrosion up to 2.2 V (0.8 V higher than uncoated CNT anode) and significantly reduced corrosion up to 3.0 V.

The mass-normalized volumetric lifespan of the BTO-CNT anode is 2.6 m$^3$ gCNT$^{-1}$ when $V_{\text{anode}}$ = 1.4 V and 1.7 m$^3$ gCNT$^{-1}$ when $V_{\text{anode}}$ = 2.2 V. The energy consumption in this study for treating 1.7 m$^3$ water with [Oxalate]$_{\text{in}}$ = 100 mg C L$^{-1}$ at a steady-state current of 40 mA was 3.06 kWh (a
total electricity cost of $0.41 assuming an electricity price of $0.134 kWh⁻¹; US Energy Information Administration). The cost of 1 g of CNTs is <$0.1 and thus <25% of the energy costs.[136] Therefore, the major cost of high-potential water treatment using CNT-based anodes is the energetic operational costs. Nevertheless, the relatively short lifespan of the CNT-based anode is a drawback, and the development of CNT materials with greater anode stability should be a direction of future research.

The steady-state current, over a similar potential range of 0.4–3.0 V, is presented in Figure 4.5d. The uncoated CNT anode had a higher current than the BTO-CNT anode at V_{anode} >1 V, and the current difference increased with increasing potential. The higher uncoated CNT current is due to faster oxygen evolution (>1.27 V) and CNT corrosion kinetics (>1.4 V, mechanisms b1 and b2). The uncoated CNT anode current started to increase significantly at >1.2 V, around its OEP, and the current of the BTO-CNT started to increase at >2 V, again close to its OEP. Two regimes were labeled in Figure 4.5a,b according to the nature of the CNT sites that undergo oxidation, as previously discussed, with regime 1 (1.4–2.2 V) being predominantly mechanism b1 and regime 2, mechanisms b1 and b2 acting simultaneously. In regime 2 (V_{anode} >2.2 V), the max effluent TC was 15.6 mg C L⁻¹ for the uncoated CNT anode, which is around 5.8-fold greater than the BTO-CNT at 2.7 mg C L⁻¹. Similarly, the max current for the uncoated CNT was ~80 mA, which is around 5.7-fold greater than the BTO-CNT anode at ~14 mA. In summary, the BTO-CNT exhibited significantly improved anode stability, extending the working potential upper limit to 2.2 V (800 mV higher than the CNT anode at 1.4 V) and increasing the anode lifetime by 6-fold at an anode potential of 3.0 V. The BTO-CNT anode also displayed a significantly lower water oxidation and corrosion current at all potentials.

To examine anodic CNT corrosion further, the surface elemental ratios of the uncoated CNT anode after oxidation at 1.8 V for 5 min and the BTO-CNT anode after oxidation at 3.0 V for 5 min were determined by XPS analysis and are listed in Table 4.1. For the oxidized and uncoated CNT anode, the surface was composed of 87.41% C, 9.82% O, 0.61% Fe, 1.57% Na, and 0.58% S by atomic ratio. The S and Na were attributed to residual electrolyte salt deposited on CNT network, and the Fe was the
Figure 4.6: Electrooxidative filtration of various small dissolved organics. (a) TOC removal (%) on the CNT anode. (b) TOC removal (%) on the BTO-CNT anode. (c) Mineralization current efficiency (%) on the uncoated CNT anode. (d) Mineralization current efficiency (%) on the BTO-CNT anode. J = 3 mL min⁻¹, residence time 0.6 s, and influent TOC were [EtOH] = 7 mg C L⁻¹, [MeOH] = 5 mg C L⁻¹, [formaldehyde] = 11 mg C L⁻¹, [formate] = 20 mg C L⁻¹. [Na₂SO₄] = 10 mM was used as the background electrolyte.

residual catalyst. Assuming that the O/S ratio in deposited salt is 4 and that the remainder is oxygen bound to carbon, the CNT surficial oxygen content is 7.5%. If we denote the oxygen bound to carbon as O-C, then the O-C/C ratio is 7.5%/87.41%, or 0.086. For comparison, the fresh CNTs have an O-C/C ratio of 0.005, indicating a significant amount of uncoated CNT anode surface oxidation. A similar O-C/C ratio calculation was carried out for the BTO-CNT anodes assuming the O/Sn ratio for tin oxide is 2, the O/Bi ratio for bismuth oxide is 1.5, and the O/S ratio for sulfate is 4. The estimation yields an O-C/C ratio of 0.023 for the fresh BTO-CNT and 0.034 for the BTO-CNT after the application of a 3.0 V anode potential for 10 min, indicating minor anode corrosion and oxidation as compared to the uncoated CNT. The improved stability against anodic corrosion/oxidation of BTO-CNT is a result of preferential hole accumulation in the SnO₂ nanoparticles reducing mechanism b1. The increased BTO-CNT OEP will also result in lesser water electrolysis, oxygen bubble
formation, and oxidant production (mechanisms a1, a2, and b2). In summary, the XPS data supports the improved BTO-CNT anode stability (e.g., there is a minimal increase, 0.011, of CNT surface oxygen content increase with a BTO coating at 3 V in comparison to the increase, 0.081, observed for the uncoated CNT at 1.8 V).

4.4.4 General Organic Electrooxidative Filtration

The initial experiments have now shown the BTO-CNT anode to be a stable, environmentally friendly, and effective/efficient towards oxalate oxidation. To study the efficacy and efficiency of the BTO-CNT anode towards organic electrooxidation further, the anodic filter was challenged with a series of small organic molecules: ethanol, methanol, formaldehyde, and formate. Their selected physical/chemical properties are listed in Table B.2 together with those of oxalate. Electrooxidation experiments were completed with \([\text{Na}_2\text{SO}_4] = 10 \text{ mM}, J = 3.0 \text{ mL min}^{-1}\), residence time = 0.6 s, and steady-state currents ranging from 10 to 60 mA. As a control, similar oxidation experiments were also conducted with an uncoated CNT anode. The influent concentrations for ethanol, methanol, formaldehyde, and formate were 7, 5, 11, and 20 mg C L\(^{-1}\), respectively, such that they require a similar total number of electron transfers for mineralization. In the mineralization processes, ethanol and methanol require 6 e\(^-\) transfers per carbon (3.5 and 2.5 mmol L\(^{-1}\)), formaldehyde, 4 e\(^-\) per carbon (3.67 mmol L\(^{-1}\)), and formate, 2 e\(^-\) per carbon (3.33 mmol L\(^{-1}\)). The effluent TOC was measured after the electrooxidation reached steady state (20 min) and was used to calculate the TOC removal percentage and mineralization current efficiency, as presented in Figure 4.6. For the uncoated CNT anode, the TOC removal of ethanol, methanol, and formate first increased with steady-state current because of faster reaction kinetics but then decreased because of the CNT anode passivation at high current/potential, in agreement with the oxalate results (Figures 4.3 and 4.5). The peak TOC removal by the uncoated CNT anode of ethanol, methanol, and formate are 27.5, 17.5, and 12.9%, respectively. The formaldehyde TOC removal peaked at 4% (10 mA), decreased to 1% at 20 mA, and then became
negative because the effluent TOC was greater than the influent TOC because of anode corrosion (Figure 4.5).

These experimental results yield insight into the anode passivation mechanisms during CNT electrochemical filtration and support the proposed mechanism in Figure 4.4. The gradually decreasing TOC removal with increasing current for all four organic molecules studied here as well as oxalate provide evidence for oxygen evolution being a primary anode passivation mechanism. Oxygen evolution will not only compete with organic oxidation for current, eq 1.5, but will also produce oxygen bubbles that block reactive sites (Figure 4.4; mechanism a1) and strain the CNT network structure, breaking the integrity and conductivity of the network (Figure 4.4; mechanism a2). In addition, should oxygen evolution be the only passivation mechanism, the TOC in effluent should never exceed the influent TOC. However, the formaldehyde experiment displayed that the effluent TOC became greater than the influent TOC at over 20 mA (V_{anode} \sim 2 V, Figure 4.5d), clearly indicating that CNT corrosion is also an important passivation mechanism (Figure 4.4; mechanisms b1 and b2).

The electrooxidation results of ethanol, methanol, formaldehyde, and formate by the BTO-CNT anode are presented in Figure 4.6b. In the ethanol and methanol electrooxidation experiments, a monotonic increase in TOC removal is observed with increasing steady-state current. At 60 mA, the BTO-CNT anode TOC removal was 85.7% (1.5 \times 10^{-4} \text{ mg C s}^{-1}) for ethanol and 88.7% (1.1 \times 10^{-4} \text{ mg C s}^{-1}) for methanol, a 3-and 5-fold increase in the mineralization rate, respectively, as compared to the uncoated CNT anode. The highest formaldehyde BTO-CNT TOC removal was 33.5% (0.92 \times 10^{-4} \text{ mg C s}^{-1}) at 60 mA, an 8-fold increase relative to the uncoated CNT anode. Formate electrooxidation by the BTO-CNT anode peaked at 25% removal (1.2 \times 10^{-4} \text{ mg C s}^{-1}) at both 50 and 60 mA, a 2-fold increase in the TOC removal relative to the uncoated CNT anode. In summary, the BTO-CNT anode displayed excellent TOC removal rate towards methanol, ethanol, and oxalate and improved TOC removal rates towards formaldehyde and formate, with a 2–8-fold increase in mineralization kinetics as compared to uncoated CNT anode. The origin of such performance may be attributed to three
important factors: the conductivity of the BTO-CNT network, the high overpotential for and slow kinetics of oxygen evolution, and the improved anode stability towards CNT corrosion (key challenge III).

Some interesting findings were revealed by comparing the oxidation kinetics of oxalate, ethanol, methanol, formaldehyde, and formate on the BTO-CNT anode. Although all of the organic solutions have similar electron demands for mineralization, the TOC removal rates were quite different. Interestingly, oxalate, ethanol, and methanol had the highest TOC removal rate followed by formate and then formaldehyde, despite the fact that formate and formaldehyde have a smaller number of electrons per molecule for mineralization. The maximum electron transfer rates on the BTO-CNT anode were oxalate \((2 \times 10^{-7} \text{ mol s}^{-1}) > \text{ethanol} \ (1.5 \times 10^{-7} \text{ mol s}^{-1}) > \text{methanol} \ (1.1 \times 10^{-7} \text{ mol s}^{-1}) > \text{formaldehyde} \ (6.2 \times 10^{-8} \text{ mol s}^{-1}) > \text{formate} \ (4.2 \times 10^{-8} \text{ mol s}^{-1})\). In addition, the maximum TOC removal rates on the BTO-CNT anode were oxalate \((2.4 \times 10^{-3} \text{ mg C s}^{-1}) > \text{ethanol} \ (3 \times 10^{-4} \text{ mg C s}^{-1}) > \text{formate} \ (2.4 \times 10^{-4} \text{ mg C s}^{-1}) > \text{methanol} \ (2.2 \times 10^{-4} \text{ mg C s}^{-1}) > \text{formaldehyde} \ (1.8 \times 10^{-4} \text{ mg C s}^{-1})\), respectively. The significantly higher TOC removal rate of oxalate oxidation indicates that oxalate strongly sorbs to the anode surface, which would increase effective filter residence time and reduce the barrier to direct electron transfer. The similar electron transfer rates of methanol and ethanol to oxalate suggest that they also sorb well to the tin oxide surface. Similar to our observation, Stucki reported that the oxidation rate and current efficiency of ethanol was higher than formic acid on an ATO anode. This result indicates the formaldehyde and formate molecules are not intermediates during mineralization of methanol (i.e., methanol is oxidized through a multi-electron transfer mechanism directly to \(\text{CO}_2\) on the BTO-CNT anode).

To understand the predominant oxidation pathways further, kinetic calculations of the pseudo-first-order rate coefficient observed \((k_{\text{obs}})\) at different currents \((10–60 \text{ mA})\) for the four organics were completed and then normalized with respect to the ethanol oxidation rate coefficient, \(k_{\text{obs}}^0 = k_{\text{obs}} / k_{\text{obs}}^{\text{EtOH}}\). At each current, the \(k_{\text{obs}}^0\) values of the organics are compared with normalized bimolecular reaction
rate constants (with respect to ethanol) of OH\( \cdot (k_{\text{OH}}^{0} = k_{\text{OH}}^{0} + S/k_{\text{EtOH}}^{0}) \) and SO\(_4^{2-}\) \( (k_{\text{SO}_4^{2-}}^{0} = k_{\text{SO}_4^{2-}}^{0} + S/k_{\text{EtOH}}^{0}) \). The detailed calculation steps can be found in the Appendix. The kinetic rate coefficients are listed in Table B.3, and the relationships of \( k_{\text{obs}}^{0} \) versus \( k_{\text{OH}}^{0} + S \) and \( k_{\text{obs}}^{0} \) versus \( k_{\text{SO}_4^{2-}}^{0} - S \) are plotted in Figure B.4. There is neither a correlation between \( k_{\text{obs}}^{0} \) and \( k_{\text{OH}}^{0} + S \) data nor a correlation between \( k_{\text{obs}}^{0} \) and \( k_{\text{SO}_4^{2-}}^{0} - S \). This indicates that direct organic oxidation on the anode surface is the dominating oxidation pathway in the electrochemical filtration system examined here and supports the conclusion that stronger organic-metal oxide sorption results in faster and more effective mineralization kinetics.

The mineralization current efficiency (MCE) for organic oxidation on the CNT and BTO-CNT anodes are presented in Figure 4.6, panels c and d, respectively. Similar trends to the TOC removal results are observed for both the CNT and BTO-CNT anodes as discussed in the Supporting Information. Overall, the BTO NP coating on the CNT improved the MCE of anode by 50 to 1100% in the organic electrooxidation experiments. Of note is that the TOC removal and MCE increase rapidly with increasing current for alcohols but not as rapidly for formate and formaldehyde on the BTO-CNT anode, indicating that another process other than electron or mass transfer is mediating the overall oxidation kinetics. A previous study demonstrated a three step reactive transport mechanism during CNT electrochemical filter organic electrooxidation consisting of (1) mass transport, (2) sorption, and (3) electron transfer. Should electron transfer be the only rate limiting step in the direct anodic oxidation of organics, then the responses of TOC removal and MCE to current should exhibit similar percentage increases for all four organics. Mass transport is also often an important step in electrooxidation processes, but it cannot be the cause of the significant differences observed here because all of the target molecules have a similar molecular weight and thus diffusion coefficient and are convectively transported at the same experimental flow rate of 3.0 mL min\(^{-1}\). Thus, the different TOC removal and MCE of alcohols, formaldehyde, formate, and oxalate is likely due to their different sorption kinetics onto electrode surface.
4.5 Conclusions

A binder-free, conductive, and stable CNT 3D porous network with a BTO nanoparticle coating was successfully prepared via a sequential electrosorption-hydrothermal method in this study. The high oxygen-evolution potential (1.71 V), improved conductivity, and high porosity of the BTO-CNT network make it a promising anode material for electrooxidative filtration. The BTO coating has a thickness of <10 nm and is composed of nanoparticles of 3.9 ± 1.5 nm in diameter. The surface Bi/Sn atomic ratio is 0.02, as determined by XPS analysis. The BTO-CNT anode displayed the fastest oxalate electrooxidation kinetics, with up to 98% TOC removal of 100 mg L⁻¹ in a single pass of 1.2 s residence time (3 × 10⁻⁸ mol s⁻¹ cm⁻²), which is ~32% faster than the TO-CNT because of Bi doping and ~53% faster than the uncoated CNT anode. The current efficiency of BTO-CNT was over 3-fold higher and consumed 5-fold less energy than the uncoated CNT at a current supply of 40 mA. The energy consumption of the BTO-CNT anode was 25.7 kWh kgCOD⁻¹ at 40 mA with 90% TOC removal, comparable to state-of-the-art electrochemical oxidation (average range of 5–100 kWh kgCOD⁻¹) and near the lower end of energy consumption reported for oxalate oxidation (22.5–81.7 kWh kgCOD⁻¹).

A comparison (uncoated CNT vs BTO-CNT) of the steady-state-current-dependent TOC and CE values for oxalate electrooxidation combined with the anode stability data yielded information on the CNT passivation mechanisms at high steady-state currents. Anode passivation is observed to be due to electrochemical water oxidation, eq 1.5, yielding oxygen bubbles that can (a1) block reactive sites and (a2) mechanically break the CNT network connectivity and conductivity as well as CNT corrosion resulting from (b1) direct CNT oxidation because of increased surface hole concentration and (b2) indirect oxidation via free-radical production. In regards to the corrosion sites, the surface oxy-functional groups oxidation was predominant between 1.4–2.2 V, and rapid CNT bulk corrosion occurs at >2.2 V. In regards to the corrosion reactions, direct corrosion because of electrolyte-stabilized high surface holes concentration is the dominant mechanism at ≥1.4 V (mechanism b1), and free-radical produc-
tion from water and sulfate oxidation also contributes at \( \geq 2.2 \) V (mechanisms b1 and b2). The re-
dox stability of the BTO-CNT anode against corrosion was observed up to 2.2 V, which is >800 mV higher than the uncoated CNT anode. In agreement with the proposed mechanism, the significantly improved TOC removal, CE, and stability of the BTO-CNT anode relative to the CNT anode can be attributed to a high OEP resulting in less oxygen evolution and reduced exposure to surface holes.

The maximum filtration volume of BTO-CNT was estimated to be 2.6 \( \text{m}^3 \text{gCNT}^{-1} \) at 1.4 V and 1.7 \( \text{m}^3 \text{gCNT}^{-1} \) at 2.2 V. The electrooxidative filtration experiments of four types of organic molecules, ethanol, methanol, formaldehyde, and formate, showed that the BTO-CNT anode achieved a significantly higher (2–8-fold) TOC removal and (0.5–11-fold) MCE than the uncoated CNT anode. The BTO-CNT nanocomposite porous electrode has promise for high-potential anode applications, and subsequent research should be on novel composites to extend the anode lifetime further.
Titanium Dioxide-Coated Carbon Nanotube Network Filter for Rapid and Effective Arsenic Sorption
5.1 Abstract

In this study, a TiO$_2$-coated carbon nanotube (CNT) network filter was prepared via a simple filtration-steam hydrolysis method and evaluated with respect to aqueous arsenic removal. The TiO$_2$ coating was 5.5 ± 2.7 nm thick, completely covered the CNT network surface, and had a specific surface area of 196 m$^2$ g$^{-1}$, which was ~2-fold greater than that of the CNT network. The TiO$_2$-CNT As sorption kinetics increased with both increasing flow rate and cell potential, with increasing flow rate having a significantly stronger effect. At 6 mL min$^{-1}$ in the absence of potential and in recirculation mode, the first-order As sorption rate constants were 4.3 and 4.4 s$^{-1}$ for As(III) and As(V), respectively. The TiO$_2$-CNT electro-assisted equilibrium sorption capacities at a cell potential of 2 V for effluent [As] = 10 ppb in single-pass mode were 1.8 and 1.3 mg g$^{-1}$ for As(III) and As(V), respectively. The enhanced TiO$_2$-CNT filter As sorption kinetics and capacity result from increased mass transport due to internal convection and pore radius range, improved sorption site accessibility due to porosity and TiO$_2$ dispersion, and reduced TiO$_2$ negative surface charge due to anodic capacitance. Groundwater samples containing 44 ppb As were treated by single-pass filtration, and 12500 bed volumes (residence time of 4.5 s; 127 L m$^{-2}$ h$^{-1}$; 5.8 mg m$^{-2}$ h$^{-1}$) were filtered prior to the effluent As level reaching >10 ppb. A spent TiO$_2$ filter was successfully regenerated by 5 mM NaOH for both As(III) and As(V).

5.2 Introduction

Arsenic-contaminated groundwater can have severe human health effects,[138] and globally, more than 100 million people are estimated to utilize As-contaminated groundwater as their drinking water source.[139] Various As treatment technologies, including sorption,[140] reverse osmosis,[141] electrocoagulation,[142] and a permeable reactive barrier,[143] are effective in reducing As concentrations below the U.S. Environmental Protection Agency (EPA) drinking water limit of 10 µg L$^{-1}$.[144] Sorption is a promising technique for the removal of low-concentration aqueous contaminants because of
its cost-effectiveness, ease of operation, and consistent performance.[145] To improve sorption performance, large-surface area metal oxide sorbents with As specificity have been developed, such as nano-
TiO$_2$,[146] CuO,[147] CeO$_2$-TiO$_2$,[5] CeO$_2$-ZrO$_2$,[148] and manganese ferroxyhyte.[149] Nanoad-
sorbents such as nano-TiO$_2$[146] and CuO[147] have great performance with respect to As removal. Despite improvements in As sorption capacity, there are two practical limitations: (1) slow kinetics and (2) loss of performance with scale and column format.

With regard to the first limitation, the time required to reach equilibrium is at minimum multiple hours for powdered sorbents[5, 145, 146, 150] and can be more than a week for granules,[151] whereas practical column filtration typically has an empty bed contact time (EBCT) of a few minutes. This leads to fractional utilization of sorption capacity at column breakthrough. Even with good hydraulic mixing, slow near surface and internal diffusion (Figure 5.1a, step 2)[152] can limit overall kinetics.[153, 154] If the sorbent and sorbate have the same charge polarity, electrostatic repulsion may also limit sorption kinetics (Figure 5.1a, step 3).[50] There are solutions to slow sorption kinetics. For example, electromigration enhanced PFOS sorption kinetics with carbon nanotubes (CNTs) 94-fold,[155] and a small pore size (short diffusion length) enhanced As sorption kinetics with ZrO$_2$ embedded in a PVDF membrane.[156]

With regard to the second limitation, powder sorbents are made into granules (>50 µm), coated onto similar sized sands, or blended into membranes to allow filtration without significant hydraulic resistance. These structures result in a loss of performance due to the reduction of the effective surface area, i.e., blocking and burial of surface sorption sites, as a result of particle aggregation and/or binder addition.[5, 156, 157] For example, the ZrO$_2$-PVDF As sorption capacity was 50% of that of the ZrO$_2$ powder due to the additional weight (33%) and blocking of sites by PVDF.[156] Similarly, the granular schwertmannite As(V) sorption capacity was reduced by 70% compared to that of the powder,[158] and granular TiO$_2$ As(V) sorption capacity was reduced by 85% compared to that of the powder.[150]

An electrochemical CNT filter coated with a nanothin TiO$_2$ film may be a potential solution. For
example, increased sorption capacity and kinetics are expected because of the electrochemical reactivity\[^{159, 160}\] as well as the high porosity (>85%) and small pore size (<100 nm)\[^{14}\] of the fibrous filter, resulting in easily and rapidly accessible sorption sites. TiO\(_2\) is a potential sorbent candidate as previous reports have observed excellent sorption performance toward both As(III) and (V)\[^{146}\] and can oxidize As(III) to As(V)\[^{161}\]. TiO\(_2\)-CNT powder composites produced via sol-gel methods on dispersed CNTs have been reported; however, the CNT-CNT contact was lost, and thus, the composite has limited conductivity and suitability for filtration\[^{162–164}\].

Here, we report on the synthesis of a binder-free, TiO\(_2\) nanofilm-coated carbon nanotube (TiO\(_2\)-CNT) network to address the key limitations with respect to the practical application of colloidal sorbents. A simple filtration-steam hydrolysis method was used to coat a nanometer thin TiO\(_2\) film onto a preformed CNT network. The TiO\(_2\)-CNT network was characterized by goniometry, BET specific
surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM),
X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and electrochemical impedance
spectroscopy (EIS). Sorption kinetics and isotherms were evaluated for both arsenate and arsenite.
The effect of operation mode (batch vs flow), flow rate, cell voltage, and pH on the sorption capacity
and kinetics was evaluated. Extended flow experiments with both synthetic water and natural ground-
water containing arsenic as well as regeneration experiments were completed to evaluate the potential
for practical application.

5.3 Experimental Procedures

5.3.1 Chemicals and Materials
Titanium isopropoxide (TTIP, >97%), sodium arsenate dibasic heptahydrate (Na$_2$HAsO$_4$·7H$_2$O,
>98.0%), sodium (meta)arsenite (NaAsO$_2$, >90%), and sodium hydroxide (NaOH, >98%) were pur-
chased from Sigma-Aldrich. Ethanol (200 proof) was purchased from EMD Chemicals. PTFE mem-
branes (pore size of 5 µm, diameter of 47 mm) were purchased from Millipore (Omnipore, JMWP).
CNTs were purchased as preformed circular networks (depth, 80 µm; diameter, 47 mm; mass, 40 ± 2
mg) from NanoTechLabs, Inc. (Yadkinville, NC), with a specific surface area of 88.5 m$^2$ g$^{-1}$.[14]

5.3.2 Titanium Dioxide Coated CNT Filter Preparation
The TiO$_2$-CNT filters were prepared via a filtration-steam hydrolysis method. First, 2.5 mL of TTIP
was dispersed in 10 mL of pure ethanol by bath sonication for 5 min. Next, the CNT filter was placed
on a PTFE membrane support within a vacuum filtration setup (Millipore) with an inner diameter of
35 mm. Then 10 mL of ethanol was filtered to wet the CNTs, followed by the TTIP/ethanol mixture.
Next, water vapor at 65 °C was passed through the CNT filter for 15 min to induce TiO$_2$ hydrolysis.
The product membrane was dried at 105 °C overnight for characterization or preserved in deionized
(DI) water for sorption experiments. The effective filtration area is 7 cm² and consists of 14.7 mg of TiO₂ coated onto 16.3 mg of CNTs (31 mg total) measured by weighing the dry filter before and after coating on an analytical balance.

5.3.3 TiO₂-CNT Filter Characterization

The water contact angle was measured with a goniometer (Rame-Hart Instruments Co.), and reported values are the average of 100 measurements. For the TiO₂-CNT filters, the contact angle was measured after 3 s as the droplet was rapidly absorbed into the network. SEM (Zeiss FESEM Ultra55) and TEM (JEOL 2100TEM) were completed at Harvard’s Center for Nanoscale Systems (CNS). For TEM, the samples were dispersed in ethanol by sonication for 1 h and then loaded and dried on a holey carbon-coated copper grid. TEM was completed with an accelerating voltage of 200 kV. All SEM and TEM images were analyzed with ImageJ (National Institutes of Health, Bethesda, MD) for tube diameter and coating thickness. Reported values were the average of at least 100 measurements from at least two network images. XPS was completed on a Thermo Scientific Kα XPS instrument with a monochromatic Al Kα X-ray source. Survey spectra were scanned from 0 to 1400 eV. Individual element scans were completed for C 1s (278–298 eV), O 1s (524–546 eV), and Ti 2p (448–475 eV). XPS survey and elemental scans are displayed in Figure C.1 of the Appendix. Surface charge density was measured by titration and capacitive charge as a function of anode potential. The electrochemical activity of the TiO₂-CNT filter was probed by CV and EIS, and method details are available in the Appendix.

5.3.4 Sorption Experiments

Three sorption methods (batch, single-pass filtration, and recirculated filtration) were utilized. For the batch method, 31 mg of TiO₂-CNT was ground into flakes (<1 mm) and added to a flask con-
taining 100 mL of 900 ppb aqueous As(III) or As(V) at pH 7. The flasks were sealed and put into a thermostatic shaker at 25 °C and 150 rpm for 8 h. Aliquots of 0.1 mL were taken at specific time intervals to examine sorption kinetics. For single-pass filtration, the arsenic solution was pumped at a rate of 1.5 mL min$^{-1}$ through two TiO$_2$-CNT filters (2 × 31 mg) at pH 7 or 10 and a cell voltage of 0 or 2 V. Five milliliters of effluent was collected at various time points for arsenic analysis. The filtration setup has been previously described in detail, and the schematic and images are given in Figure 1.4 of the Appendix. For recirculated filtration, one TiO$_2$-CNT filter (31 mg) was used in the same setup and aqueous arsenic was pumped from a 100 mL reservoir and then returned.

To examine sorption kinetics, recirculated filtration experiments were conducted at J values of 1.5, 3, and 6 mL min$^{-1}$, $V_{cell}$ values of 0, 1, and 2 V, an $[As]$ of 900 ppb, and pH 7. To examine sorption isotherms, experiments were completed in recirculation mode at a J value of 3 mL min$^{-1}$, a $t_{eq}$ of 12 h, a $V_{cell}$ of 0 or 2 V, $[As]$ of 100–10000 ppb, and pH 7. For the regeneration experiments, single-pass filtration of 240 ppb As(V) or 330 ppb As(III) at pH 7 and a J value of 1.5 mL min$^{-1}$ was completed in 5 h, and then the filter was regenerated by recirculation of 100 mL of 5 mM NaOH at a rate of 1.5 mL min$^{-1}$ for 3 h. The regenerated filter was then rinsed with DI water until the pH of the effluent was 7. For the groundwater experiments, samples contained 44 ppb of arsenic at pH 7.42 (Jackson, WY); groundwater details are given in the Appendix. Aqueous arsenic concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer 6100), and details are given in the Supporting Information.

5.4 Results and Discussion

5.4.1 Filter Characterization

Images of contact angle measurements for the CNT and TiO$_2$-CNT networks are displayed in panels a and b of Figure 5.2, respectively. The CNT network was hydrophobic with an average contact angle of
The TiO$_2$-CNT network was hydrophilic with a contact angle of 35°. Filter images before (left) and after (right) TiO$_2$ coating are displayed in Figure 5.2c. The TiO$_2$ coating is the inner gray circle. The effective TiO$_2$-CNT filter (inner diameter of 30 mm inside the 35 mm diameter coated CNT area) contained 14.7 mg (47%) of TiO$_2$ and 16.3 mg (53%) of CNTs, and the filter thickness was 80 ± 4 µm. SEM images of the CNT and TiO$_2$-CNT are displayed in panels d and e of Figure 5.2, respectively. The CNT network has a smooth surface with $d = 23.4 \pm 7.3$ nm. The TiO$_2$-CNT has a rough surface with $d = 34.4 \pm 12.7$ nm, indicating a $5.5 \pm 2.7$ nm thick TiO$_2$ coating. The TiO$_2$-CNT pore size (SEM) was 83 ± 62 nm. A TEM image of the TiO$_2$-CNT is presented in Figure 5.2f. The white lines signify the boundary between the CNT and the TiO$_2$; the CNT wall spacing is 0.32 nm, and no crystal structure was observed for TiO$_2$, indicating an amorphous state. Additional SEM and TEM images
are available in Figure C.2 of the Appendix. The specific surface area (BET) of the CNT was \(88.5 \text{ m}^2 \text{ g}^{-1}\) and that of the TiO\(_2\)-CNT was \(196.5 \text{ m}^2 \text{ g}^{-1}\), and the increase was due to the outer surface roughness and additional inner surface area introduced by the TiO\(_2\) coating. The superficial elemental ratio (XPS) of the CNT was 98.8% C and 1.2% O and that of the TiO\(_2\)-CNT was 51.4% C, 33.6% O, and 15% Ti. The surface charge density of TiO\(_2\)-CNT as a function of solution pH is displayed in Figure C.3 of the Appendix. The point of zero charge (pH\(_{zpc}\)) was 5.4, between 5.8 for nanocrystalline TiO\(_2\)\([168]\) and 3.2 for CNTs.\([169]\) CV and EIS of the CNT and TiO\(_2\)-CNT are presented in Figure C.6 of the Appendix and indicate that due to the nanometer thin TiO\(_2\) coating only minor electron transfer resistance (1.5 \(\Omega\)) and electron transfer overpotential (0.07 V) were introduced.

### 5.4.2 Arsenic Sorption Kinetics

To examine the effect of the primary sorption steps on overall kinetics (Figure 5.1a), we will discuss (1) the effect of batch versus flow, (2) the effect of flow rate, and (3) the effect of cell voltage. Negligible arsenic sorption was observed with a CNT filter as displayed in Figure C.4 of the Appendix. The TiO\(_2\)-CNT filter arsenic sorption kinetics was examined in both batch (green) and recirculation \(J = 1.5\) (black), 3 (blue), and 6 \(\text{mL min}^{-1}\) (red) modes using 31 mg of TiO\(_2\)-CNT and 100 mL of \([\text{As}]_0 = 900 \text{ ppb}\) as presented in panels a and b of Figure 5.3 for As(V) and (III), respectively. The symbols are experimental data (milligrams of As per gram of TiO\(_2\)-CNT), and the dashed lines are kinetic fittings. For all conditions, the amount sorbed initially increased and eventually reached equilibrium. The kinetics increased with increasing flow rate in recirculation mode. To quantitatively describe sorption kinetics, the data were modeled (dashed lines Figure 5.3) with pseudo-first-order kinetics (eq 5.1)\([170]\) using the rearranged form in eq 5.2.

\[
\ln\left(\frac{q_t}{q_e}\right) = kt
\]  

\[(5.1)\]
where \( q_t \) and \( q_e \) are the amounts sorbed (milligrams of As per gram of TiO\(_2\)-CNT) at time \( t \) and equilibrium, respectively, \( k \) is the pseudo-first-order kinetic rate constant (inverse hours), and \( t \) is the sorption time (hours). Pseudo-first-order kinetics fit the data well \( (R^2 > 0.99) \) and yielded the \( q_e \) and \( k \) values summarized in Table 5.1. For As(V) in Figure 5.3a, for the batch mode, and \( J = 1.5, 3, \text{ and } 6 \text{ mL min}^{-1} \), the equilibrium times were >8, >8, 6, and 3 h with \( k \) values of 0.8, 0.7, 0.9, and 4.4 h\(^{-1} \), respectively. For As(III) in Figure 5.5b, for the batch mode, where \( J = 1.5, 3, \text{ and } 6 \text{ mL min}^{-1} \), the equilibrium times were >8, >8, 2, and 1 h with \( k \) values of 1.2, 0.7, 2.3, and 4.3 h\(^{-1} \), respectively. A flow rate-dependent \( k \) indicates faster kinetics due to increased mass transport (step 1); e.g., increasing \( J \) by 4-fold led to a 6-fold increase in \( k \). The batch \( k \) was 10-40% higher than that at \( J = 1.5 \text{ mL min}^{-1} \) because the batch system had greater external mixing (Figure 5.1, step 1) compared to the slowest flow rate. The highest flow rate of 6 mL min\(^{-1} \) had sorption kinetics 4-6 times faster than that of the batch mode. Note the batch \( q_e \) was <85% of all recirculation conditions, indicating that sorption sites were lost in the batch mode most likely because of particle aggregation, which was visually observed in the batch experiment. The operational kinetic advantage of increased sorbent external (step 1) and internal (step 2) mass transport is exemplified with the representative TiO\(_2\)-CNT filter sorption mechanism depicted in Figure 5.1b. For example, because of the small pore size and internal convection (step 2), As has to diffuse only from the pore center to the sorbent surface (\( \leq 42 \pm 31 \text{ nm} \)) as compared to micrometers in granular batch or column filtration.[60, 64] 

The sorption kinetics of the TiO\(_2\)-CNT filter here is compared to that of granular TiO\(_2\) (0.15–0.6 mm) to gain insight into the structural advantage of a nanometer thin sorbent coating on a nanofiber network, and a detailed description of the calculations utilized here is available in the Appendix. The TiO\(_2\)-CNT filter operated in recirculation mode achieved equilibrium, 2.8 mg g\(^{-1} \), after sorption for 1
Figure 5.3: TiO$_2$-CNT As sorption kinetics. (a) As(V) and (b) As(III) in batch mode (green) and recirculation mode at flow rates (J) of 1.5 (black), 3 (blue), and 6 mL min$^{-1}$ (red). (c) As(V) and (d) As(III) at 0 (black), 1 (blue), and 2 V (red) at 1.5 mL min$^{-1}$. Symbols are amounts sorbed (milligrams of As per gram of TiO$_2$-CNT), and dashed lines are pseudo-first-order kinetic fittings. The black dashed horizontal lines (2.9 mg g$^{-1}$) are the theoretical maximal amounts of As sorbed. The experiments were completed in recirculation mode using a 100 mL reservoir of 900 ppb As at pH 7 and 31 mg of TiO$_2$-CNT (14.7 mg of TiO$_2$) as the sorbent. The batch sorption kinetics was completed in a shaker at 150 rpm with an amount of sorbent and a sorbate concentration identical to those used in recirculation mode.

h at C$_e^{\text{As(III)}} = 30$ ppb and J = 6 mL min$^{-1}$. For comparison, the granular TiO$_2$ batch sorption capacity (an upper bound for granular TiO$_2$ recirculation column kinetics due to improved external mixing) was 0.11 mg g$^{-1}$ after 5 h for C$_e^{\text{As(III)}} = 30$ ppb. Thus, compared to granular TiO$_2$, the TiO$_2$-CNT filter had a 127-fold increase in sorption rate (milligrams per gram per hour) due to the combined advantage of internal convection and morphology improved site accessibility. Given that internal convection accounted for a 4–6-fold increase, the kinetic enhancement due to increased TiO$_2$-CNT filter structure improved site accessibility is 20–30-fold. This estimation is consistent with a granular TiO$_2$ study in which the sorption site accessibility after 4 months was 15-fold greater than after 2 h due to
Table 5.1: Kinetic Parameters of Pseudo-First-Order As Sorption.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>As(V)</th>
<th>As(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>flow rate (mL min(^{-1}))</td>
<td>(k) (s(^{-1}))</td>
</tr>
<tr>
<td>1.5</td>
<td>0.7</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>2.6</td>
</tr>
<tr>
<td>6</td>
<td>4.4</td>
<td>2.6</td>
</tr>
<tr>
<td>batch</td>
<td>0.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>As(V)</th>
<th>As(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>voltage (V)</td>
<td>(k) (s(^{-1}))</td>
</tr>
<tr>
<td>0</td>
<td>0.7</td>
<td>2.4</td>
</tr>
<tr>
<td>1</td>
<td>0.7</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>2.8</td>
</tr>
</tbody>
</table>

\(^a\) From fitting of data in Figure 5.3 to eq 5.2.

pore diffusion limitations.\(^{150}\) In addition, sorption of As(V) onto granular ferric hydroxide (d = 0.6–2 mm) in recirculation mode (J = 650 mL min\(^{-1}\); \(V_{col}\) = 13.6 L; [As]\(_i\) = 97 ppb) required 240 h to reach equilibrium, which is 2 orders of magnitude greater than that of the TiO\(_2\)-CNT filter.\(^{151}\)

TiO\(_2\)-CNT sorption kinetics may be further improved by application of a potential to reduce the negative surface charge. Arsenic redox reactions on the TiO\(_2\)-CNT filter at 2 V are minimal because of the absence of an electrolyte, and a detailed discussion can be found in the Appendix. Sorption kinetics at 0 (black), 1 (blue), and 2 V (red) cell voltages and J = 1.5 mL min\(^{-1}\) for As(V) and As(III) are displayed in panels c and d of Figure 5.3, respectively. Both As sorption kinetics and capacity increased with increasing potential. The data were modeled by pseudo-first-order kinetics (dashed lines; Table 5.1), and the applied potential increased \(k\) from 0.7 h\(^{-1}\) at 0 V to 0.8 h\(^{-1}\) at 2 V for As(V) and from
0.7 h⁻¹ at 0 V to 1.5 h⁻¹ at 2 V for As(III). Also, the applied potential increased \( q_e \) from 2.4 mg g⁻¹ at 0 V to 2.8 mg g⁻¹ at 2 V for As(V) and from 2.6 mg g⁻¹ at 0 V to 2.8 mg g⁻¹ at 2 V for As(III). At pH 7, the As(V) speciation (pKₐ = 6.94) is 50:50 HAsO₄²⁻:H₂AsO₄⁻ and the As(III) speciation (pKₐ = 9.2) is >99% H₃AsO₃. The filter surface charge density as a function of pH is displayed in Figure C.3 of the Appendix, and the surface charge density at pH 7 is -0.057 C m⁻². Cyclic voltammetry (Figure C.5a of the Appendix) was used to evaluate surface charge under an applied potential. At a 2 V cell voltage (1.11 V anode potential), 0.037 C m⁻² was capacitively charged on the TiO₂-CNT, reducing the surface charge to -0.020 C m⁻² (64%). Thus, the increased kinetics under applied potential for As(V) is due to enhanced near surface transport via electromigration (step 2) and improved electrostatic interactions with the sorption sites (step 3). Because As(III) is neutral, the kinetic enhancement cannot originate from increased electromigration and/or electrostatic attraction. An As-TiO₂ sorption mechanism study indicated that sorbed As is deprotonated, i.e., surface complexes of Ti₂>[AsO₄⁻] and Ti₂>[AsO₃⁻].[168] Therefore, anodic capacitive charging of the CNT-TiO₂ surface would stabilize the sorbed As state and suppress desorption, resulting in increased net sorption kinetics for both As(V) and As(III) (step 3). In addition, the higher kinetic sensitivity of As(III) than of As(V) to potential suggests the suppressed desorption mechanism is more important.

A kinetic comparison of the TiO₂-CNT filter and granular TiO₂ in both batch and filtration modes is summarized in Figure 5.1c. The TiO₂-CNT filter performance has three key origins: operational, structural, and electrochemical. First, filtration increases sorption kinetics by 4–6-fold compared to that in batch mode due to increased mass transport. Second, the well-dispersed nanometer thin TiO₂ film on the nanofibrous (>85% porosity; \( r_{\text{pore}} = 41 \pm 31 \) nm) CNT network results in a 20–30-fold increase in sorption kinetics due to easily accessible sorption sites, a short diffusion length, and negligible <10 nm pores. Third, the applied potential (2 V) increases the TiO₂ surface charge and in turn increases sorption kinetics of As by 0.15–2-fold.
5.4.3 Arsenic Sorption Isotherms

Arsenic sorption isotherms on the TiO$_2$-CNT filter were completed in recirculation mode. The results for As(V) and As(III) at 0 (black) and 2 V (red) are presented in panels a and b of Figure 5.4, respectively, where the points are experimental data and the dashed lines are fittings to the Freundlich isotherm (eq 5.3).

\[ q_e = K_f C_e^{1/n} \]  \hspace{1cm} (5.3)

where $q_e$ (milligrams of As per gram of TiO$_2$-CNT) is the amount sorbed at equilibrium, $C_e$ (parts per billion) is the equilibrium concentration, and $K_f$ and $n$ are constants. The Freundlich isotherm fit the data well ($R^2 > 0.99$), in agreement with a previous study of sorption of As to nanocrystalline TiO$_2$ particles,[146] indicating heterogeneous sorption site energies likely due to the coating roughness and the range of CNT properties such as the diameter, number of walls, and level of oxidation. At pH 7, for As(V) the TiO$_2$-CNT maximal experimental $q_e$ was 14.1 mg g$^{-1}$ ($C_e = 4700$ ppb) at 0 V and 18.2 mg g$^{-1}$ ($C_e = 4200$ ppb) at 2 V; for As(III), the $q_e$ was 13.2 mg g$^{-1}$ ($C_e = 740$ ppb) at 0 V and 13.6 mg g$^{-1}$ ($C_e = 550$ ppb) at 2 V. The true maximal sorption capacity will be greater as the $q_e$ values did not reach a plateau. With regard to drinking water applications, the level of effluent As should be <10 ppb and
the TiO$_2$-CNT $q_{10\text{ ppb}}$ under this constraint was 0.8 mg g$^{-1}$ for As(V) and 1.6 mg g$^{-1}$ for As(III) at 0 V and 1.3 mg g$^{-1}$ for As(V) and 1.8 mg g$^{-1}$ for As(III) at 2 V. Again, application of potential had a greater impact on the sorption capacity of As(V) (+63%) than on that of As(III) (+12.5%) because As(V) is negatively charged at neutral pH.

At 0 V, the TiO$_2$-CNT $q_{10\text{ ppb}}$ was 5 and 45% higher for As(V) and As(III), respectively, than that of state-of-the-art TiO$_2$ sorbents such as nanocrystalline TiO$_2$ (0.5–2 µm aggregates of 6 nm particles) where $q_{10\text{ ppb}} = 0.76$ and 1.13 mg g$^{-1}$ for As(V) and As(III), respectively.[146] Application of 2 V (additional energy requirement of 0.03 kWh m$^{-3}$) improved the performance of TiO$_2$-CNT compared to that of suspended nano-TiO$_2$ by >40% [1.3–1.8 mg g$^{-1}$ for As(III)]. Of note is the fact that the TiO$_2$-CNT filter contains ~50% TiO$_2$ yet has performance superior to that of pure TiO$_2$ alternatives. For example, arsenite sorbed on TiO$_2$-CNT has a surface density of 0.11 µmol m$^{-2}$ compared to a value of 0.04 µmol m$^{-2}$ for nanocrystalline TiO$_2$ due to the nanocrystalline TiO$_2$ forming 0.5–2 µm aggregates.[146]

5.4.4 Extended Single-Pass As Filtration Experiments

To examine the practical application potential of the TiO$_2$-CNT filter, we conducted extended time experiments with synthetic and groundwater As. The TiO$_2$-CNT empty bed contact time (EBCT) was 4.5 s at a flow rate of 1.5 mL min$^{-1}$ (127 L m$^{-2}$ h$^{-1}$), 1–2 orders of magnitude lower than the typical column EBCT (1.5–15 min),[5, 145, 150, 158] and half of a ZrO$_2$-PVDF membrane.[156] The breakthrough curves for As(V) and As(III) in synthetic waters at [As]$_{in} = 100$ ppb, pH 7 (blue) and 10 (red), and cell voltages of 0 (circles) and 2 V (squares) are presented in panels a and b of Figure 5.5, respectively. At pH 7 and 0 V, the effluent arsenic concentration remained below 10 ppb for 8000 bed volumes [$q_{10\text{ ppb}} = 1.4$ mg g$^{-1}$ (calculation in the Appendix)] for As(V) and 16000 bed volumes for As(III) (2.8 mg g$^{-1}$). At pH 7 and 2 V, the effluent As concentration remained below 10 ppb for 13500 bed volumes (2.3 mg g$^{-1}$) for As(V) and for 19100 bed volumes (3.3 mg g$^{-1}$) for As(III). The sorp-
Figure 5.5: Extended TiO$_2$-CNT As sorption experiments. (a) As(V) and (b) As(III) with synthetic water at 0 (circles) or 2 V (squares) and pH 7 (blue) or 10 (red) in single-pass filtration mode with [As]$_i$ = 100 ppb. (c) Four adsorption-regeneration cycles where influent was [As(V)]$_i$ = 240 ppb or [As(III)]$_i$ = 330 ppb at 0 V in single-pass filtration mode and the regeneration solution consisted of 100 mL of 5 mM NaOH operated in recirculation mode. (d) As-contaminated groundwater single-pass filtration. The influent for lab water contained 100 ppb arsenic. The influent groundwater solution contained [As]$_i$ = 44 ppb at pH 7.42. Two TiO$_2$-CNT filters (31 mg each) were used for each filtration experiment. In all filtration experiments, the J value was 1.5 mL min$^{-1}$, the filter bed volume was 0.113 mL, and the EBCT was 4.5 s. The upper dashed horizontal line is the influent As concentration and the lower dashed horizontal line the U.S. EPA As drinking water regulation (10 ppb).

The solution rate was 7.8 mg m$^{-2}$ h$^{-1}$ in all experiments. For comparison, a granular TiO$_2$ column sorbed a similar amount ([As]$_i$ = 39 ppb; 1.7 mg of As(V) g$^{-1}$) at breakthrough but had a significantly longer EBCT (3 min). A comparison of reported column studies for a range of As sorbent materials is presented in Table C.1 of the Appendix. The TiO$_2$-CNT filter has a medium to high sorption capacity at breakthrough and requires an EBCT 1–2 orders of magnitude lower than that of granular sorbents. The TiO$_2$-CNT filter has a 0.5–1.5-fold higher sorption capacity and 50% less EBCT compared to a ZrO$_2$-PVDF sorptive membrane.

At pH 10 and 0 V, breakthrough occurred immediately for all experiments and the initial removal
percentage for As(III) at 60–80% was greater than that of As(V) at 20%. The relative arsenic removal at pH 7 and 10 yielded insight into how surface and molecular charge affects sorption (step 3). The filter surface charge density (Figure C.3b of the Appendix) was -0.057 C m$^{-2}$ at pH 7 and became more negative (-0.311 C m$^{-2}$) at pH 10. The As(V) molecular charge also increased from -1.5 at pH 7 to -2 at pH 10. The electric potential near a charged surface is described by eq 5.4,[171] and the electrostatic force between the charged surface and a point charge is described by eq 5.5.

\[
\psi = -\frac{\sigma L}{\varepsilon} e^{-x/L} \tag{5.4}
\]

\[
F = Eq = -\frac{d\psi}{dx} q = -\frac{\sigma q}{\varepsilon} e^{-x/L} \tag{5.5}
\]

where $\psi$ is the electric potential (volts), $\sigma$ is the surface charge density (coulombs per square meter), $L$ is the Debye layer thickness (meters), $x$ is the distance between the charged surface and the point charge (meters), $\varepsilon$ is the permittivity (farads per meter), $F$ is the electrostatic force (newtons), $E$ is the electric field intensity (volts per meter), and $q$ is the molecular charge (coulombs). At pH 10, the electrostatic repulsion between the TiO$_2$-CNT surface and As(V) was increased by 7-fold compared to that at pH 7, resulting in significantly reduced sorption capacity and slower sorption kinetics. As a result, sorption (Figure 5.1, step 3) becomes the rate-limiting step. As(III) sorption is less sensitive to TiO$_2$ surface charge than As(V) sorption because the predominant arsenite species (H$_2$AsO$_3^-$) at pH 10 has a less negative charge. The greater sorption capacity of As(III) compared to that of As(V) between pH 7 and 10 had been observed for many iron oxide minerals.[172] Cyclic voltammetry (Figure C.5 of the Appendix) indicates that at a cell voltage of 2 V (anode potential of 0.86 V) the TiO$_2$ surface charge increased by +0.136 C m$^{-2}$, reducing the negative surface charge to -0.175 C m$^{-2}$ and the electrostatic As-TiO$_2$ repulsion by 44%, thus improving initial As(V) removal (90% at 1 h) and slightly improving As(III) removal. Again, the weaker effect of potential on As(III) is due to its lower charge. Therefore,
the rate-limiting step at high pH is sorption due to As-TiO$_2$ electrostatic repulsion, and the kinetics are improved by anodic capacitive charging of the TiO$_2$-CNT.

Four sorption and regeneration cycles were completed by single-pass filtration at high influent As ([As(V)]$_{in}$ = 240 ppb (black); [As(III)]$_{in}$ = 330 ppb (red)) as displayed in Figure 5.5c and detailed in Table C.2 of the Appendix. The TiO$_2$-CNT was regenerated by recirculation of 100 mL of 5 mM NaOH at a rate of 1.5 mL min$^{-1}$ for 3 h. After regeneration, 70–90% of the sorbed As(V) and 60–70% of the As(III) were desorbed. For As(V), the TiO$_2$-CNT filter was effectively regenerated multiple times as the level of effluent As(V) was initially <10 ppb after three sequential sorption-regeneration cycles. For As(III), the regenerated effluent concentration was <10 ppb after two cycles and 15–25 ppb after the third cycle. The initial As removal percentage decreased slightly from 99% in the first cycle to 97% for As(V) and 94.5% for As(III) in the fourth cycle. Electrochemical regeneration at 2 V with electrodes reversed was also evaluated but was observed to be less effective [10–30% desorbed after 3 h (Figure C.7 of the Appendix)] than the basic solution method (99% desorbed after 3 h). Therefore, the TiO$_2$-CNT membrane can be effectively regenerated with a moderately basic solution.

TiO$_2$-CNT filtration results for As-contaminated groundwater samples (Jackson, WY) are displayed in Figure 5.5d. At safe drinking water breakthrough (10 ppb effluent), the filtered bed volume was 12500 and $q_{\text{breakthrough}} = 0.94$ mg g$^{-1}$. This indicates that 1 m$^3$ of TiO$_2$-CNT membrane can treat 2040 L of groundwater before regeneration is necessary. The amount of As sorbed from the groundwater at breakthrough is between $q_{10 \text{ ppb}} = 0.8$ mg g$^{-1}$ and $q_{44 \text{ ppb}} = 1.5$ mg g$^{-1}$ calculated from the sorption isotherm. For comparison, the amount sorbed at breakthrough for lab synthetic water at [As]$_{in}$ = 100 ppb is 1.4 mg g$^{-1}$, about the average of $q_{10 \text{ ppb}} = 0.8$ mg g$^{-1}$ and $q_{100 \text{ ppb}} = 2.1$ mg g$^{-1}$ from the isotherm, and would be expected to be 1.15 mg g$^{-1}$ for [As]$_{in}$ = 44 ppb if the same relationship holds. Thus, the groundwater breakthrough capacity is 20% lower than expected for lab synthetic water. The less optimal performance in a groundwater matrix can be attributed to the pH of groundwater (pH 7.4) being slightly higher than that of lab water (pH 7), resulting in a 10–20% decrease in BV filtered before break-
through (Figure C.8 of the Appendix). When the pH increases from 7 to 7.4, arsenate (pKₐ = 6.94) speciation would change from 50:50 HAsO₄²⁻:H₂AsO₄⁻ to 75:25 HAsO₄²⁻:H₂AsO₄⁻, increasing the level of As-TiO₂ electrostatic repulsion. There was a minimal effect (As sorption reduced by <1%) of typical groundwater anions such as phosphate, carbonate, sulfate, and silicate (Figure C.9 of the Appendix). The chemical composition of the filtered groundwater was not altered significantly with only the pH (7.4 to 6.9) and total P (19 to 9 ppb) having observed decreases. In summary, the groundwater matrix has a slightly negative impact (20% reduction) on the TiO₂-CNT As sorption capacity compared to DI water.

5.5 Environmental Implications

A nanometer thin TiO₂ sorbent coating on a preformed nanofibrous network has significant kinetic advantages compared to suspended nanoparticle sorbents that may aggregate. The kinetic improvements are due to three factors: flow-through operation increasing mass transport (4–6-fold), small pore size and highly dispersed TiO₂ coating structure reducing diffusion length and increasing sorption site accessibility (20–30-fold), and anodic capacitive charging increasing electromigration and reducing negative surface charge (0.15–2-fold). As a result, the TiO₂-CNT filter requires an EBCT of a few seconds to achieve an efficacy similar to that of a conventional granular column sorbent with an EBCT of a few minutes. In turn, the TiO₂-CNT filter could be made into a significantly smaller filtration device that would save capital and may have potential to be developed into a portable filtration device for point-of-use water treatment applications. For example, assuming the average daily water intake for an adult male is 3.7 L,[173] to treat this water in 10 min the granular column volume required (EBCT = 3 min) is 1.1 L. For the same volume of water, the TiO₂-CNT filter area required is 0.17 m², yielding a total filter volume of 0.028 L or 1/40 of the volume of a conventional granular column. Also, the nanometer thin metal oxide-coated nanofibrous filter material will not be limited to
the sorption of As onto TiO$_2$, as the material synthesis method will be applicable to other metal oxide sorbents if an appropriate organometallic precursor is available, e.g., a CeO$_2$-coated filter for fluoride removal. As the electrochemical capacitance yielded minimal enhancement as compared to the other factors, the material cost could be reduced by utilizing SiO$_2$ or Al$_2$O$_3$ nanofibers as the base sorbent network.
6 Conclusions and Outlook

6.1 CONCLUSIONS

In this dissertation, we dove deep into qualitative and quantitative reaction mechanisms and demonstrated great potential of the recently developed CNT-based electrochemical filter for oxidative and adsorptive pollutant removal. A good spectrum of chemicals were tested to verify the effectiveness of this technology including organics such as oxalate, formaldehyde, ethanol, MO, MB, as well as inor-
ganics such as arsenic and ferrocyanide. These studies, I believe, have made important contributions to solving the critical challenges in water treatment. With both theoretical and experimental work, three significant conclusions should be noted.

First, the combination of membrane filtration and electrochemistry as electrochemical filtration creates significant synergies. Compared with the non-reactive membrane filtration alone, CNT-based electrochemical filtration achieves in-situ chemical oxidation in addition to the conventional separation. Organic dyes including MO and MB (Chapter 1 and 2) were successfully oxidized as well as oxalates and other small organics (Chapter 4). Compared with the conventional electrochemical cell, the electrochemical filtration has significant kinetic advantages due to forced convection and the special dispersed CNT structure that allows access to greater number of reactive sites. Forced convection increased mass transport and the oxidation kinetics by >6 times for MO (Chapter 2) and 4–6 times for arsenic adsorption (Chapter 5). The filter structure works together with forced convection to further improve performance. The CNT-based materials have much higher specific surface area compared to conventional non-porous plate electrodes. The high porosity of the filter network (>90%) also allows forced convection to go through the membrane pores (the interstitial space between CNT). Therefore, all the surface area is on average <90 nm (pore size) away from the target species brought by flow. In contrast, conventional porous materials such as activated carbon have the majority of their surface area buried deep inside inner pores, which are kinetically inaccessible by diffusional mass transport. Convective transport does not happen inside the inner pores but rather goes between the granules. The structural advantage results in 20–30 times faster kinetics and up to 95% more adsorption capacity (Chapter 5).

Second, the CNT network can be coated by a nanolayer of catalysts or adsorbents to further take advantage of the synergy for oxidative and adsorptive pollutant removal. As demonstrated with the 5 nm BTO coating, the electrochemical filtration greatly improved the current efficiency and energy consumption for a series of small organics including oxalate, ethanol, formate and formaldehyde (Chapter
4). For example, the energy consumption for oxalate is 25.7 kWh kgCOD⁻¹ at ~93% TOC removal and 8.6 kWh kgCOD⁻¹ at ~50% TOC removal, comparable to state-of-the-art oxalate oxidation processes (22.5–81.7 kWh kgCOD⁻¹). The anode stability after coating also improved, lifting the upper limit of operation potential to 2.2 V from 1.4 V for bare CNT. For inorganic pollutants, we demonstrated the coating of a TiO₂ adsorbent nanolayer takes advantage of the kinetic and reactive sites synergy and increased the arsenic adsorption kinetics my 1–2 orders of magnitude (Chapter 5). The filter is only 80 µm thick and can remove 44 ppb As in a single pass (in 4.5 s) whereas conventional filtration column is much taller and needs ~10 min to similarly decrease the As concentration.

Third, mechanism studies indicate that the usually rate-limiting mass transport can be improved by enhancing hydraulic convection (Chapter 2) and the subsequent electron transfer through CNT has two types of reactive sites (Chapter 3). The general electrochemical processes consists of mass transport, adsorption and electron transfer. We studied the normal pulse voltametry plots of batch end filtration electrochemical systems for MO oxidation and found that forced convection through the filter pores increased the mass transport limited kinetics by >6-fold. The electron transfer was studied via ferrocyanide oxidation experiments to investigate the relationship of reactive kinetics with CNT properties. We found the electron transfer can go through the sidewall reactive sites and the transfer rate is proportional to surface area starting at 0.15 V. The other type of reactive sites is the the tube end oxy-defect sites which can be activated at higher overpotential (0.3 V) but with faster kinetics (Chapter 3). In addition, microscopic flux simulation indicated the local concentration gradient was almost parallel to the flow streamline, corroborating the previous conclusion that forced convection is critical in maintaining a high concentration gradient and good mass transport.
6.2 OUTLOOK

Moving beyond the scope of this dissertation, we will continue to develop the electrochemical filtration technology. On the engineering side, we have developed a scale-up of the lab-scale prototype discussed in previous chapters. The scale-up device was displayed in Figure 6.1. It operates at 12 L h\(^{-1}\), two orders of magnitude greater than the lab-scale device. The scaled-up filter use CNT as anode and a fine stainless steel mesh as cathode and achieved equal or even better chemical oxidation performance than the lab-scale device likely due to the higher specific surface area of the cathode. In the future, a larger scale up could be designed and build for a water treatment pilot test that would give valuable information potential applications.

On the scientific side, we also tried to combine the electrochemical filtration technology with ozone treatment. The actual oily wastewater from the Boston shipyard was treated by recirculating in an ozone reaction tank and electrochemical filter. Preliminary experiment showed significant synergies
and excellent performance in TOC removal by the combined treatment over individual processes. The TOC removal data was presented in Figure 6.2. The individual electrochemical filtration and ozone treatment removes <20% of TOC as shown in Figure 6.2a but combined treatment can achieve >91% TOC mineralization if using the scaled-up device as shown in Figure 6.2b.

The detailed mechanism of the synergy between electrochemistry and ozonation remains unknown and should be an interesting and important research topic in the future. Moreover, many studies developed catalysts that can generate ozone electrochemically. Another interesting research topic would be developing the ozone generation catalyst coating on the CNT network such that a separate ozonation unit is unnecessary. Our previous experience on coating metal oxide nanolayers onto CNT surface may be of great value in directing such studies.

Figure 6.2: Electrochemical and ozone oxidation of industrial waste water by combined and individual treatment. pH = 7; [NaCl] = 10 mM; [TOC]_{in} = 470 ppm. (A) TOC removal when applying an electrochemical oxidation at 2.5 V with the small lab device; V_{reservoir} = 100 mL and ozone oxidation of industrial waste water as a function of time. (B) TOC removal with a combined electrochemical and ozone oxidation of the industrial waste with the small lab device (black square) and the scaled-up device (red circles) at a potential of 2.5 V; V_{reservoir} = 200 mL.
Supporting Discussion for Quantitative 2D Electrooxidative CNT Filter Model Study

A.1 Determining the contribution of target species migration in mass transport

Mass transfer in solution occurs by diffusion, convection and migration. In the species transport model in this study we claim the contribution of target molecule migration to mass transfer is minimal in the model domain and in the existence of excess electrolytes. This claim can be assessed by estimating contribution (%) of target molecule migration to the overall mass transport process. By the following equation we can calculate the transference number $t_i$, which is defined as the fraction of current carried by ion $i$ in the migration process:[4]

$$ t_i = \frac{|Z_i C_i \lambda_i|}{\sum_j |Z_j C_j \lambda_j|} $$

(A.1)

Where $Z_i$ is the charge of ion $i$, $C_i$ (M) is the ion $i$ concentration and $\lambda_i$ (cm$^2$ Ω$^{-1}$ equiv$^{-1}$) is the ionic conductivity of ion $i$. Ionic conductivities ($\lambda$) values for Na$^+$, 1/2 SO$_4^{2-}$, 1/4 Fe(CN)$_6^{4-}$, and K$^+$ are 50.11, 79.8, 110.5, 73.52 cm$^2$ Ω$^{-1}$ equiv$^{-1}$, respectively. Methyl orange conductivity was not reported but should be close to or a little less than the ionic conductivity of acetate (OAc$^-$), 40.9 cm$^2$ Ω$^{-1}$ equiv$^{-1}$, because both are organic species with the same charge and MO has a larger molecular weight, thus a smaller ionic conductivity. So 40.9 cm$^2$ Ω$^{-1}$ equiv$^{-1}$ is used as an estimation of MO
ionic conductivity for Ti calculations. The transference number calculation was completed for two extreme solution conditions with highest target molecule concentration used in experiment, 0.0055 M MO + 0.1 Na₂SO₄, and 0.035 M K₄Fe(CN)₆ + 1 M Na₂SO₄. Table A.2 listed the transference number of all species in the two extreme solution conditions. The transference number was 0.03 for MO and 0.05 for ferrocyanide. These numbers were the upper bound because they were calculated at the highest concentration of target species used in experiment. Therefore, the current carried by target species migration is at most 5%, indicating electromigration is negligible due to the excess electrolyte used in the experiment.

A.2 Effect of model geometry on electrooxidative filtration kinetics simulation

To validate the major assumptions on the model geometry; the effect of CNT slice shape and diameter are examined here in regards to their effect on the predicted electrooxidation kinetics. The other simulation conditions was based on what described in the text. In the 2D model geometry, the CNTs vertical sections are treated as circles, even though in the actual CNT network they should be ellipses due to CNTs may be tilted at various angles with the paper plane. From the microscopy images in Figures 3.2 and 3.3, the 3D network were constructed by stacking up thin layers of CNTs that are 2D randomly oriented in the x-y direction, with a small tilt to the x-y plane. A representative scheme of the 3D filter structure and a vertical section are displayed in Figure A.5 assuming uniform CNT diameter. The vertical section of the CNT network consisted of randomly located ellipses with large void volume in between, with the eccentricity depending on the angle of CNT to the section plane. For affordable model calculation, all the ellipses were substituted by the right number of circles that provides the same total surface area of the filter. To check the validity of this simplification, a partial ellipse model (only includes top 6% of the A-CNT filter) was created and compared with the circular model of the
same surface area at influent 500 µM and 0.2 V. The concentration simulation results were plotted in Figure A.6. Both model predicted the same effluent concentration of 482.9 µM, indicating the circular model being a good approximation of the ellipse model. Due to the random orientation of CNTs in the x-y plane, the homogeneous average kinetics can be assumed (the same surface normalized reaction rate) in the y direction when considering from the larger scope of the entire 3D filter. Thus, the 2D vertical slice used in the model (Figure 3.3a) kinetically resembles the actual structure of the same total surface area in terms of overall kinetics and offers a close estimation for the effluent concentration in the 3D system.

The second difference between the actual filter and the model geometry is the diameter of CNTs. The model utilizes the average CNT diameter from Table 3.1; however, the CNTs are observed (TEM) to have a wide diameter distribution, histograms are displayed in Figure A.2. A model for the C-CNT sample that included diameter distribution was used to estimate electrooxidation kinetics and compared to the average diameter model. For comparison, the single diameter geometry consisted of 2516 CNT slices with \(d_{CNT} = 71.4\) nm and the multiple diameter geometry consisted of 2499 CNTs distributed with \(25\) nm < \(d_{CNT}\) < \(238\) nm. Both geometries had the same specific surface area to volume ratio. Single diameter and diameter distribution simulations were completed with \(C_{in} = 25\) mM and \(E = 0.2\) V. The concentration (mM) and diffusional flux (mol m\(^{-2}\) s\(^{-1}\)) field results in a short filter section (35 µm to 40 µm) are shown in Figure 3.10 for the single diameter geometry and in Figure A.7a & b for the diameter distribution geometry where red and blue represent the highest and lowest values in the filter section, respectively, and the up and down arrows represent the highest and lowest values in the entire geometry. The effluent ferrocyanide concentration results in Figure 3.10a and Figure A.7a are identical (22.6 mM), indicating the assumed single diameter geometry well represents the true diameter distribution geometry in regards to macroscopic electrooxidation kinetics. This result was further confirmed by modeling C-CNT electrooxidation at \(E = 0.2\) V at various \(C_{in}\) as all the model results are identical for the single and diameter distribution geometries. Kinetic simulation
studies evaluating different geometry suggests surface area is the dominant parameter rather than flow field, in well agreement with the fact that diffusion itself dominates at the short scale within CNT filter (<100 nm) instead of convection. In summary, the two simplifications of single CNT diameter and circular 2D geometry have negligible effect on the macroscopic concentration simulation results.

A.3 Determining the number of CNTs in the model domain

The number of CNTs in the model domain must be carefully calculated so that the model geometry reflects the same surface area as the real CNT anode. First, the apparent density of the CNT filter is given by eq A.2.

\[
\omega = \frac{m}{Ab}
\]  

(A.2)

Where \( \omega \) is the apparent density, \( m \) is the weight of the CNT filter, \( A \) is the cross section area, and \( b \) is the filter thickness. And then it follows that surface area \( SA \) can be expressed as eq A.3.

\[
SA = \frac{TOTA_{\text{filter}}}{m_{\text{filter}}} = \frac{n\pi dl}{\omega V_{\text{filter}}}
\]  

(A.3)

Where the numerator is the total surface area of CNT filter in the model domain and the denominator is the CNT weight in the model domain, \( n \) is the number of CNTs in the domain, \( d \) is the average CNT diameter, \( l \) is the length of the aligned CNTs (the length in the direction perpendicular to the reference paper), and \( V_{\text{filter}} \) is the 3D volume of the filter in the model domain area, given by eq A.4.

\[
V_{\text{filter}} = hlB
\]  

(A.4)

Where \( B \) is the width of the model domain. And then it follows that \( n \) can be solved by combining eqs A.2–A.4, the solution is eq A.5.

\[
n = \frac{mbSA}{\pi dA}
\]  

(A.5)
All the inputs in eq A.5 are directly from experimental measurement and listed in Table 3.1. From above discussions, setting the arbitrary domain width as 0.2, 0.24, 0.6, 0.77, 0.31 µm, the numbers of CNTs in the model domain for A-CNT, B-CNT, C-CNT, D-CNT, and E-CNT are 5,834, 2,973, 2,516, 1,167, 4,164, respectively.

A.4 Details of CNT characterization methods

A.4.1 Electron Microscopy

TEM analysis was completed with a JEOL 2100 TEM at an accelerating voltage of 200 kV at Harvard’s Center for Nanoscale Systems. Before imaging, 10 mg CNTs were dispersed in 20 mL ethanol by bath sonication (Branson 2510) for 1 hour and then a drop of the suspension was placed onto a copper grid with holey carbon support. The CNT diameters and number of walls were analyzed by ImageJ and were the average of at least 100 measurements from at least 2 network images. SEM was completed on a Zeiss FESEM Ultra55 at Harvard’s Center for Nanoscale Systems.

A.4.2 XPS

XPS was completed on a Thermo Scientific K-Alpha XPS with a monochromatic Al-K X-ray source in Harvard’s Center for Nanoscale Systems. Survey spectra were scanned (average of 10 scans) for all samples from 0 to 1,400 eV to determine the CNT surficial elemental composition. Individual elemental scans were also completed for the C-1s (274-294 eV) and the O-1s (522-542 eV) regions. Avantage software was used to determine the integrated peak areas for the individual elements and calculate the sample surficial elemental percentages. The surficial oxygen atomic ratio for each CNT network was the average of four measurements.
A.4.3 BET Surface Area Analysis

The specific surface area (SSA) of the carbon nanotube filters was measured with a Beckman Coulter SA 3100 surface area and pore size analyzer. Prior to analysis, approximately 0.1 g filter sample was outgassed at 120 °C for 1 h and then was placed into a glass tube for analysis.

A.5 COMSOL 4.2a Numerical Simulation Settings and Boundary Conditions

In order to minimize computational time, a simplified 2D model was used for simulation. The simulation geometry is a thin rectangular region, such that there are nanotubes aligned along the horizontal direction (in agreement with the CNT network being composed of randomly-oriented CNT in a 2D plane), while the extended vertical direction is for diffusion boundary layer considerations. The CNT are modelled as random or regular and circular or elliptical voids with electrochemically active surfaces inside the rectangular geometry. The fluid flow and mass transport occur in the space not occupied by the CNT. The bulk properties of water are taken from the COMSOL library.

Two physical COMSOL modules: the Laminar Flow module and Transport of Diluted Species module were applied sequentially. The velocity field of the fluid can be solved via the Laminar Flow module and thus provides the necessary inputs for solving the concentration field from the Transport of Diluted Species module. In terms of the fluid flow boundary conditions, the top edge of domain is defined as the inlet ($U_{\text{inlet}} = 70.8 \mu m \ s^{-1}$) and the bottom edge is an outlet ($p_0 = 0$), while the left and right edges are periodic boundary conditions ($U_{\text{left}} = U_{\text{right}}, P_{\text{left}} = P_{\text{right}}$). The no-slip boundary condition ($U = 0$) is applied to the CNT surfaces. In regard to the target molecule concentration boundary conditions, the top edge is defined as the inlet ($C_{\text{inlet}} = C_{\text{in}}$) and the bottom edge is the outlet ($-\partial C/\partial y = 0$), while the left and right edges are assigned periodic boundary conditions ($C_{\text{left}} = C_{\text{right}}$). The boundary conditions at the CNT surfaces are customized to reflect the potential and concentration dependent electron transfer kinetics; eqs 3.4 and 3.15. As the geometry of
the model is complex, a default free triangular meshing algorithm was used for the COMSOL finite element simulation method. The element size was extra fine. To accurately capture the response near the CNT surfaces, at least 8 boundary layer elements were inserted near the CNT surface. Approximately 256’000 elements were used in total. To numerically solve the coupled differential equations, two stationary steps were solved iteratively: the first step solved the fluid velocity and pressure fields and in turn used as input for the second step that solved the concentration field.

A.6 Effective diffusivity and ordinary diffusivity

Typically, movement of fluid through the solid phase may give rise to mechanical mixing and result in a greater effective diffusivity. However, this study the flow rate is quite low so that ordinary diffusion still dominates and so ordinary diffusion coefficient can be used.

However, we will show the characteristic time for diffusion is 4 orders of magnitude less than for hydraulic flow, thus diffusion is dominating. The characteristic time for pure diffusion process to reach a characteristic length, for example CNT diameter, is estimated as follows:

\[ \delta = d = \sqrt{\pi D t} \]  \hspace{1cm} (A.6)

\[ t = \frac{d^2}{\pi D} = 2 \times 10^{-8} \text{s} \]  \hspace{1cm} (A.7)

where \( d = 23.4 \text{ nm} \), \( D = 8.5 \times 10^{-5} \text{ cm}^2 \text{s}^{-1} \). The characteristic time for flow to reach the same distance is \( 23.4 \times 10^{-9} \text{ m s}^{-1} \) divided by \( 70.8 \times 10^{-6} \text{ m s}^{-1} \), and equals to \( 3.3 \times 10^{-4} \text{ s} \), 4 orders of magnitude longer than diffusion. Therefore, diffusion is definitely dominating over mechanical mixing due to the slow flow velocity used in the study. As a result, ordinary diffusivity was used in this study.
A.7 Hydraulic field simulation

Fluid velocity was solved first to set up basis for convective transport calculation before the concentration and other fields can be solved. The spatial resolved velocity field at flow rate of 3.0 mL min$^{-1}$ is presented in Figure A.8. Although the figure generally shows random patterns, fluid velocity rapidly decreases to zero near the CNT surfaces due to the applied no-slip condition on solids. On the other hand, high fluid velocity is observed in the interstices of two adjacent CNTs due to the substantial decrease of cross-sectional area. The average fluid velocity of 70.8 $\mu$m s$^{-1}$ was set as boundary condition $V_{in}$ at inlet. But the flow accelerates to 334 $\mu$m s$^{-1}$ at the narrowest cross section, over 4 times of the average velocity. This heterogeneous pattern of the fluid velocity field significantly affects the mass transport and thus the overall flux as will be discussed later in text.
Table A.1: Reaction rate fitting parameters summary for five CNT anodes at different anode potentials.

<table>
<thead>
<tr>
<th>CNT anode</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 V</td>
<td>2.04 × 10⁻⁸</td>
<td>2.05 × 10⁻⁸</td>
<td>8.22 × 10⁻⁹</td>
<td>2.18 × 10⁻⁹</td>
<td>6.32 × 10⁻⁹</td>
</tr>
<tr>
<td>k₄ω</td>
<td>0.20 V</td>
<td>3.19 × 10⁻⁸</td>
<td>6.43 × 10⁻⁸</td>
<td>3.39 × 10⁻⁸</td>
<td>6.80 × 10⁻⁸</td>
</tr>
<tr>
<td>(mol m⁻² s⁻¹)</td>
<td>0.30 V</td>
<td>1.05 × 10⁻⁷</td>
<td>1.61 × 10⁻⁷</td>
<td>1.90 × 10⁻⁷</td>
<td>2.05 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>0.40 V</td>
<td>1.18 × 10⁻⁷</td>
<td>2.77 × 10⁻⁷</td>
<td>2.76 × 10⁻⁷</td>
<td>3.58 × 10⁻⁷</td>
</tr>
<tr>
<td></td>
<td>0.15 V</td>
<td>5.00 × 10⁻⁸</td>
<td>4.80 × 10⁻⁸</td>
<td>4.28 × 10⁻⁸</td>
<td>5.31 × 10⁻⁸</td>
</tr>
<tr>
<td>k₅ω</td>
<td>0.20 V</td>
<td>2.90 × 10⁻⁷</td>
<td>2.52 × 10⁻⁷</td>
<td>2.48 × 10⁻⁷</td>
<td>2.48 × 10⁻⁷</td>
</tr>
<tr>
<td>(m s⁻¹)</td>
<td>0.30 V</td>
<td>6.95 × 10⁻⁷</td>
<td>1.30 × 10⁻⁶</td>
<td>1.46 × 10⁻⁶</td>
<td>4.63 × 10⁻⁶</td>
</tr>
<tr>
<td></td>
<td>0.40 V</td>
<td>1.89 × 10⁻⁶</td>
<td>2.89 × 10⁻⁶</td>
<td>2.97 × 10⁻⁶</td>
<td>7.73 × 10⁻⁶</td>
</tr>
<tr>
<td>R²</td>
<td>0.15 V</td>
<td>0.94</td>
<td>0.97</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>0.20 V</td>
<td>0.98</td>
<td>0.99</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>0.30 V</td>
<td>0.94</td>
<td>0.93</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>0.40 V</td>
<td>0.90</td>
<td>0.86</td>
<td>0.91</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table A.2: Transference number calculations for MO and ferrocyanide solutions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na⁺</th>
<th>1/2 SO₄²⁻</th>
<th>1/4 Fe(CN)₆⁴⁻</th>
<th>K⁺</th>
<th>MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ</td>
<td>50.11</td>
<td>79.8</td>
<td>110.5</td>
<td>73.52</td>
<td>40.9</td>
</tr>
<tr>
<td>t_i (5.5 mM MO, 100 mM Na₂SO₄)</td>
<td>0.38</td>
<td>0.59</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>t_i (35 mM K₄Fe(CN)₆, 1 M Na₂SO₄)</td>
<td>0.35</td>
<td>0.56</td>
<td>0.05</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure A.1: Aerial TEM images of B-CNT, C-CNT, D-CNT and E-CNT anode networks.
Figure A.2: Histograms of CNT diameter distribution. a) A-CNT. b) B-CNT. c) C-CNT. d) D-CNT. e) E-CNT.

Figure A.3: Histograms of number of walls per nanotube. a) A-CNT. b) B-CNT. c) C-CNT. d) D-CNT. e) E-CNT.
Figure A.4: XPS survey scans for a) A-CNT. b) B-CNT. c) C-CNT. d) D-CNT. e) E-CNT. Survey spectra were scanned 10 times for all samples from 0 to 1400 eV to determine the elemental composition near the CNT network surface.
Figure A.5: CNT anode 3D structure and a vertical section. The CNT 3D network were constructed by stacking up thin layers of CNTs that are 2D randomly oriented in x-y direction, with a small tilt angle to the x-y plane. The vertical section was parallel to y-z plane.

Figure A.6: Concentration simulation results for a) circular model and b) ellipse model. The model area consists of 5 µm diffusion layer followed by a 5 µm CNT filter. The circular geometry has 351 individual CNTs with 23.4 nm in diameter. The ellipse geometry has 250 ellipses with the same overall surface area. The eccentricity and angle of major axis is determined by the orientation of CNTs. It is assumed CNTs with 23.4 nm in diameter are randomly oriented in x-y direction (Figure A.5) and has a tilt angle to x-y plane that homogeneously distributed between ±30°. The section plane is the z-y plane in Figure A.5. Influent concentration is 500 µM, $E$ is 0.2 V, other conditions are the same as previous ferrocyanide models. The influent/effluent concentrations are noted in the figure with up/down arrows.
Figure A.7: Concentration field and diffusional flux simulation for C-CNT in multiple diameter geometry. a) Concentration field for multiple diameter geometry, concentration ranging from 23.3 mM on top to 23.2 mM at the bottom, and b) diffusional flux field for multiple diameter geometry, ranging from the largest magnitude (red color), $4.2 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ to the smallest magnitude (blue color) $5.3 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$. The representative patterns inside the CNT filter are shown from $y = 35 \mu m$ to $40 \mu m$. Simulation conditions are $C_\text{in} = 25$ mM, $V_\text{in} = 7.08 \times 10^{-5}$ m s$^{-1}$, and $E = 0.2$ V.
Figure A.8: Velocity field simulation at the A-CNT filter inlet. The representative patterns inside the CNT filter are shown from $y = 87.2 \mu m$ to $88.8 \mu m$. Velocity ranges from $334 \mu m s^{-1}$ (red) at the interstice of solids to $0 \mu m s^{-1}$ at the solid surfaces. Influent velocity was $70.8 \mu m s^{-1}$.

Figure A.9: Fitting T-site reaction rates with concentration were complete with eq 3.15 to estimate electron transfer kinetic parameter $k_5\omega$ at a) $0.3 \text{ V}$, b) $0.4 \text{ V}$. The open symbols are T-site reaction rate of A-CNT (black), B-CNT (red), C-CNT (blue), D-CNT (pink), and E-CNT (green), respectively. The solid lines are fittings.
Supporting Discussion for Bismuth-Doped Tin Oxide-Coated Carbon Nanotube Network Study

B.1  Pseudo first order rate coefficient calculation for small organics

The electrochemical filter has a thickness of $h = 40 \mu m$ and geometric area of $A = 7 \text{ cm}^2$. The flow rate $J$ in organic oxidation experiments was $3.0 \text{ ml min}^{-1}$. According to eq B.1 the residence time $t$ can be calculated to be $t = 0.63 \text{ s}$.

$$t = \frac{Ab}{J} \quad (B.1)$$

The first order kinetics can in the electrochemical filter can be modeled by eq B.2, where $C_{in}$ is the influent TOC concentration, $C_{out}$ is the effluent TOC concentration and $k_{obs}$ is the observed first order rate coefficient for given molecules.

$$C_{out} = C_{in}e^{-k_{obs}t} \quad (B.2)$$

Rearranging eq B.2 we obtain eq B.3 which can be used to calculate $k_{obs}$

$$k_{obs} = ln\left(\frac{C_{in}}{C_{out}}\right)/t \quad (B.3)$$
Then normalize \( k_{\text{obs}} \) with respect to ethanol for \( k_{\text{obs}}^0 \) by eq B.4:

\[
k_{\text{obs}}^0 = k_{\text{obs}} / k_{\text{obs}}^{\text{EtOH}}
\]

(B.4)

### B.2 Oxalate oxidation kinetics and energy consumption comparison

A comparison of oxalate oxidation kinetics and energy consumption by various anode materials and methods\cite{118,124–126} is presented in Table B.1. The average oxidation rates and energy consumptions were calculated at 90% TOC removal and the best results for the various studies are presented. The pseudo-first-order kinetic rate coefficients were estimated from oxidation experimental results in the literature and were normalized by electrode surface area. Detailed calculation steps are described in the previous section. The oxalate oxidation method can be categorized into direct anodic oxidation and indirect oxidation processes where during the former the electrons are directly transferred from oxalate to the anode and during the latter oxidation is via dissolved hydroxyl radicals (\( \cdot \text{OH} \)) produced at the anode or during Fenton chemistry. The BDD anode, although well recognized for its high OEP, energy efficiency, and organic oxidation activity via \( \cdot \text{OH} \) production, did not show a particular advantage towards the recalcitrant oxalate oxidation with \( k = 1.4 \times 10^{-7} \ \text{cm}^2 \text{mA}^{-1} \text{s}^{-1} \), even lesser than a Pt anode, where \( 4.3 \times 10^{-7} \ \text{cm}^2 \text{mA}^{-1} \text{s}^{-1} \), due to the relatively slow reaction of oxalate with \( \cdot \text{OH} \) (\( k = 7.7 \times 10^6 \ \text{M}^{-1} \text{s}^{-1} \)).\cite{127} For comparison, the reaction rate constant of the \( \cdot \text{OH} \) with methanol is \( 9.7 \times 10^8 \ \text{M}^{-1} \text{s}^{-1} \) and is typically in the range of \( 10^9–10^{10} \ \text{M}^{-1} \text{s}^{-1} \) for most organics, i.e. diffusion-controlled.\cite{127} Other studies on oxalate oxidation by advanced oxidation processes (AOPs) displayed a slightly higher oxidation rate coefficient, but still on the same order of magnitude as compared to \( \cdot \text{OH} \) production by BDD anode. In contrast, the normalized pseudo-first-order kinetics rate coefficients for ATO-CNT and BTO-CNT are \( 3.9 \times 10^{-6} \) and \( 4.1 \times 10^{-6} \ \text{cm}^2 \text{mA}^{-1} \text{s}^{-1} \), respectively, and 2.5 times greater than the next highest rate coefficient (Ti-IrO\(_2\) anode, \( 1.6 \times 10^{-6} \ \text{cm}^2 \text{mA}^{-1} \text{s}^{-1} \)).
The standard oxidation potential for oxalate/CO$_3^{2-}$ is 1.18 V at pH = 14,

$\text{eqs 4.5 and 4.6,[133]}$ whereas the standard oxidation potential is 1.9 V for -OH/OH and 2.7 V for -OH/H$_2$O.$\text{[134]}$ Thus it is thermodynamically possible to oxidize oxalate directly at the anode surface without producing -OH. The oxalate oxidation rate coefficients of the ATO-CNT and BTO-CNT anodes are an order of magnitude higher than those producing -OH and oxidation of oxalate started at anode potentials of 1.1 V, lesser than required for -OH production. This indicates an alternative electrooxidation mechanism for oxalate via direct electron transfer from oxalate to the anode, in agreement with previous studies on organic oxidation by a CNT electrochemical filter.$\text{[64]}$ The energy consumptions in kWh kgCOD$^{-1}$ of the ATO-CNT and BTO-CNT for oxalate oxidation are 26.6 and 25.7 at 60 mA, respectively, are both at the low end, e.g., slightly higher than a Ti-IrO$_2$ anode (22.5), but lower than Pt (81.7) and BDD (39.7) anodes. Besides oxidation kinetics and energy consumption, material cost and lifespan must also be considered in anode evaluation. Although Ti-IrO$_2$ has the lowest energy consumption, Ir is quite expensive (32 USD g$^{-1}$) as compared to CNT (2 USD g$^{-1}$) and Sn (0.2 USD g$^{-1}$), which may limit its large-scale electrochemical applications. BDD was also limited to laboratory research due to its extremely high cost. For example, a thin coating of BDD on a 3 mm diameter substrate could cost 370 USD (Windsor Scientific, UK). However, BDD anode has a long service time even in aggressive conditions, ranging from 264 h to 804 h. The lifespan of CNT and coated CNT anodes will be discussed in detail later.

B.3 Organic Mineralization Current Efficiencies

In the CNT anode electrooxidation experiments, ethanol had the highest peak MCE of 11.8% at 40 mA, follow by methanol with an MCE peaked of 7.2% at 30 mA. Formate displayed an average MCE of 5.5% from 10 mA to 60 mA. Formaldehyde displayed an MCE of 6% at 10 mA, decreased to 1% at 20 mA, and then at $I \geq 20$ mA the MCE became negative due to CNT corrosion. The organic
electrooxidation MCE of the BTO-CNT anode was substantially improved relative to the uncoated CNT anode. The MCE of ethanol and methanol increased with increasing steady-state current and eventually reached 29% and 18.4% at 60 mA, respectively, both 2.5-fold greater than the MCE of the uncoated CNT anode. The MCE maximum for formaldehyde electrooxidation was 11.3% at 20 mA, an 11-fold increase as compared to uncoated CNT anode under the same conditions. The BTO-CNT MCE for formate averaged 8.2% over the current range of 20 mA to 40 mA, 50% higher than the MCE of formate oxidation on uncoated CNT.
Figure B.1: The effluent concentration change with time during the CNT anode stability test. Flow rate was $J = 1.5 \text{ mL min}^{-1}$, the electrolyte was 10 mM Na$_2$SO$_4$ and the anode potential was 2.0 V.

Table B.1: Comparison of kinetics and energy consumption for oxalate oxidation by various methods.

<table>
<thead>
<tr>
<th>Anode material</th>
<th>Method</th>
<th>Initial I mA cm$^{-2}$</th>
<th>Oxalate mM</th>
<th>Pseudo 1st order rate constant k cm$^2$ mA$^{-1}$ s$^{-1}$</th>
<th>Energy consumption kWh kgCOD$^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATO-CNT</td>
<td></td>
<td>5.7</td>
<td>4.17</td>
<td>$3.9 \times 10^{-6}$</td>
<td>26.6</td>
<td>This study</td>
</tr>
<tr>
<td>BTO-CNT</td>
<td>Anodic</td>
<td>5.7</td>
<td>4.17</td>
<td>$4.1 \times 10^{-6}$</td>
<td>25.7</td>
<td>This study</td>
</tr>
<tr>
<td>Ti-IrO$_2$</td>
<td>Oxidation</td>
<td>25</td>
<td>31.25</td>
<td>$1.6 \times 10^{-6}$</td>
<td>22.5</td>
<td>[124]</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>25</td>
<td>31.25</td>
<td>$4.3 \times 10^{-7}$</td>
<td>81.7</td>
<td>[124]</td>
</tr>
<tr>
<td>BDD</td>
<td>OH radical</td>
<td>60</td>
<td>12.0</td>
<td>$1.4 \times 10^{-7}$</td>
<td>39.7</td>
<td>[125]</td>
</tr>
<tr>
<td>BDD-Fe-UVA</td>
<td>EAOP+UVA</td>
<td>33.3</td>
<td>2.08</td>
<td>$5.6 \times 10^{-7}$</td>
<td>-</td>
<td>[118]</td>
</tr>
<tr>
<td>Ti-RuO$_2$/IrO$_2$</td>
<td>AOP-fenton</td>
<td>160</td>
<td>8</td>
<td>$8.2 \times 10^{-7}$</td>
<td>-</td>
<td>[126]</td>
</tr>
</tbody>
</table>
Figure B.2: XPS survey scans for a) Fresh CNT, b) CNT after 10 min at 1.8 V in 10 mM Na$_2$SO$_4$ electrolyte. c) Fresh BTO-CNT d) BTO-CNT after 10 min at 3.0 V in 10 mM Na$_2$SO$_4$ electrolyte.

Figure B.3: Thermogravimetric analysis of CNT and BTO-CNT. Mass percent and dW/dT (peaks) in % °C$^{-1}$ as a function of temperature for bare CNT and BTO-CNT.
Figure B.4: Correlation between observed electrooxidation rates and known rate constants with the hydroxyl and sulfate radical. Relationships of a) \(k_{\text{obs}}^0\) vs \(k_{\text{OH}^+ + S}^0\), b) \(k_{\text{obs}}^0\) vs \(k_{\text{SO}_4^{2-} + S}^0\). Note the rate constants are relative with respect to those of ethanol (i.e., no units).

Table B.2: Comparison of kinetics and energy consumption for oxalate oxidation by various methods.

<table>
<thead>
<tr>
<th></th>
<th>Heats of Combustion (kCal mol(^{-1}))^a</th>
<th>Redox pairs</th>
<th>Standard electrode potential (V)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>-173.64</td>
<td>HCHO/MeOH</td>
<td>0.237</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>-136.42</td>
<td>HCOOH/HCHO</td>
<td>-0.029</td>
</tr>
<tr>
<td>Formate</td>
<td>-60.86</td>
<td>(\text{H}_2\text{CO}_3/\text{HCOOH})</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-326.68</td>
<td>(\text{H}_2\text{CO}_3/\text{oxalate})</td>
<td>-0.19</td>
</tr>
<tr>
<td>Oxalate</td>
<td>-58.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a See ref [174]

^b See ref [133]
Table B.3: Comparison of observed and theoretical rate coefficients of small organic target molecules.

<table>
<thead>
<tr>
<th></th>
<th>$k_{\text{obs}}$ ($k_{\text{th}}$)</th>
<th>$k_{\text{OH} + S}$ M$^{-1}$s$^{-1}$</th>
<th>$k_{\text{SO}_4^- + S}$ M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mA</td>
<td>20 mA</td>
<td>30 mA</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.019 (1)</td>
<td>0.026 (1)</td>
<td>0.03 (1)</td>
</tr>
<tr>
<td>MeOH</td>
<td>0.024 (1)</td>
<td>0.042 (1)</td>
<td>0.075 (1)</td>
</tr>
<tr>
<td>HCHO</td>
<td>0.024 (1)</td>
<td>0.031 (1)</td>
<td>0.056 (1)</td>
</tr>
<tr>
<td>HCOO$^-$</td>
<td>0.067 (0.67)</td>
<td>0.09 (0.72)</td>
<td>0.15 (0.46)</td>
</tr>
</tbody>
</table>

See ref [175]

$^a$ See ref [176]
Titanium Dioxide-Coated Carbon Nanotube Network Filter for Rapid and Effective Arsenic Sorption

C.1 Arsenic measurement by ICP-MS

Arsenic concentrations were measured by ICP-MS (Perkin Elmer 6100). The ICP-MS was first calibrated by the blank (DI water) and 9 arsenic solutions of known concentration (0, 0.1, 0.5, 1, 2, 5, 10, 50, 100 ppb) prepared by dilution of arsenic standards (1000 ppm; Sigma-Aldrich) with DI water. The mass counts were then linearly fit to the known concentrations for quantitative determination of the calibration curve. Then, samples of unknown concentration were analyzed by the ICP-MS. A standard reference (SR, NIST1640a) and a calibration verification solution of known As concentration were tested after 10 consecutive measurements for quality control purposes.

C.2 Total P measurement

C.2.1 Persulfate Digestion

- Add 0.1 mL strong acid solution to each 5 mL sample.

- Add 50 mg solid K₂S₂O₈ and mix well.
• Heat for 30 minutes at 98 to 137 kPa and 121 °C in autoclave.

• Cool, then add 1 drop phenolphthalein indicator solution and neutralize to faint pink color with 1 N NaOH (may take approximately 1.5 mL of 1 N NaOH or more).

• Make up to 10 mL with distilled-deionized water.

C.2.2 Measurement Process (Stannous Chloride Method)

• To 5 mL sample or standard, add 1 drop phenolphthalein indicator. If sample turns pink, add strong acid solution dropwise to discharge the color. (Typically only 1 drop of acid is required.)

• Add 200 µL of molybdate reagent I to sample; mix thoroughly.

• Dilute stannous chloride reagent I 50–50 (v–v) with DI water. Add 1 drop of diluted stannous chloride reagent I to sample; mix thoroughly.

• Let reaction proceed for 10-12 minutes (all samples should be measured at the same time in the reaction).

• Pour the contents of each tube into a cuvette (1 cm or 10 cm path length)

• Measure absorbance at λ = 690 nm.

• Use a blank DI water sample to set for the zero absorbance (auto zero)

• The 0 mg P/L standard should be measured first.

• Ideally, measure absorbance of samples with increasing concentration.

• Ensure cuvette is adequately rinsed with DI water between measurements
C.3 Ion chromatography

Sulfate concentrations were determined with a Dionex ICS-5000 Ion Chromatography System using a RFIC Ion Pac AS20 column and a KOH eluent.

C.4 Surface charge measurement

The surface charge density and point of zero charge (pHpzc) of the CNT and TiO$_2$-CNT were measured by titration.[166] First, sulfuric acid was used to adjust 5 mL DI water to pH$_i$ 3.69. Then 10 mg of CNT or TiO$_2$-CNT were added to the 5 mL solution and the mixture was bath sonicated for 20 min. The solution pH at the end of sonication was measured (pH$_r$). The initial surface charge density $\sigma_i$ (C m$^{-2}$) at pH$_r$ can be calculated as eq C.1:

$$\sigma_i = \left(10^{-pH_i} - 10^{-pH_r}\right)F/m \times SSA$$ (C.1)

Where F is Faraday’s constant, 96500 C mol$^{-1}$, m is the weight of sample (g), and SSA (m$^2$ g$^{-1}$) is the specific surface area of samples. Next, the 5 mL mixture was titrated using 0.01 M NaOH until pH 10. The pH is recorded as the function of OH-added, n (µmol). The same titration was completed for 5 mL DI water as background. The results were displayed in Figure refestfigs4a. The difference between the OH$^-$ added to the sample solution (ns) and the DI water (nb) at a given pH represents the OH$^-$ reacted with charged surface groups. The surface charge density can then be calculated using eq C.2:

$$\sigma = \sigma_i - (n_s - n_b)/(m \times SSA)$$ (C.2)

The results were displayed in Figure C.3b. The TiO$_2$-CNT pH$_{zpc}$ = 5.1; the charge density at pH 7 is -0.057 C m$^{-2}$; and the charge density at pH 10 is -0.311 C m$^{-2}$.
C.5 Capacitive surface charge measurement

The TiO$_2$-CNT capacitance and capacitive surface charge as a function of anode potential was measured by cyclic voltammetry.\cite{167} The capacitance was first determined using eq C.3.

$$C = \frac{I_a - I_c}{s} \quad \text{(C.3)}$$

where $I_a$ and $I_c$ (A) are the anodic and cathodic current at the open circuit potential and $s$ (V s$^{-1}$) is the potential sweep rate. The charge density $Q$ (C m$^{-2}$) as a function of anode potential $E_a$ (V) and surface area $SA$ can be calculated using eq C.4.

$$Q = \frac{C \times E_a}{SA} \quad \text{(C.4)}$$

The voltammetry of TiO$_2$-CNT as anode at pH 7 (blue) and pH 10 (red) solution w/ 100 ppb As(V) were displayed in Figure C.5a. The open circuit potentials was 0.056 V for pH 7 and 0.079 V for pH 10. The surface area of effective filter is 0.17 m$^2$. The anode potential at 2 V cell voltage was 1.11 V for pH 7 and 0.86 V for pH 10. The scan rate was 0.005 V s$^{-1}$. The anodic capacitive charge density at a cell voltage 2 V was +0.037 C m$^{-2}$ at pH 7 and +0.136 C m$^{-2}$ at pH 10.

C.6 The electrochemical reactivity of TiO$_2$ and the TiO$_2$-CNT filter electrodes

Bulk TiO$_2$ is a semiconductor with large band gap of 3.1 eV with limited conductivity and electrochemical reactivity. However, its electrochemical properties vary with dopants, chemical composition, crystal structure, and particle size. TiO$_2$ can be doped with ions such as Cr$_3^+$ to reduce band gap, thus increasing conductivity and electrochemical reactivity.\cite{166} Other TiO$_2$ dopants including Ru
and Ir have also been demonstrated to make TiO$_2$ effective towards organic electrooxidation.\cite{167, 177} An alternative to doping, calcination will alter TiO$_2$ stoichiometry e.g., transform TiO$_2$ to the more conductive Ti$_4$O$_7$ resulting in greatly enhanced electrochemical performance.\cite{5} The reactivity also varies with polymorphic form. For example, pure anatase is widely studied for its application in Li ion batteries due to the effective lithium insertion while rutile and brookite has minimal lithium capacity.\cite{9} The electrochemistry of lithium insertion to anatase also has a significant size dependence as nanocrystalline anatase showed superior performance over the micron sized alternatives.\cite{178}

To understand how the nano-TiO$_2$ film affected conductivity and electrochemical reactivity as compared to the pristine CNT filter, CV and EIS experiments were completed. CV scans of CNT and TiO$_2$-CNT were completed in 1 mM ferrocyanide and 100 mM Na$_2$SO$_4$ electrolyte solution from -0.3 V to 0.8 V at a scan rate of 5 mV s$^{-1}$ with Ag/AgCl as the reference electrode. The results are presented in Figure C.6. The CNT scan showed a pair of peaks for ferro/ferricyanide redox reactions at 0.15 and 0.22 V. In comparison, the TiO$_2$-CNT scan showed two pairs of peaks, in the same scan range, indicating TiO$_2$ coating is firstly electrochemically reactive, and secondly introducing different reaction pathways for ferro/ferricyanide solutions. The original redox peaks on CNTs shifted 70 mV to the right at 0.21 and 0.3 V indicating the nano-TiO$_2$ film slightly increases the overpotential required for these requires. And a new pair of peaks occurred at -0.13 V and 0.05 V suggesting that there may be a new electron transfer pathway for adsorbed ferrocyanide. Thus, the nano-TiO$_2$ film is conductive and the key driver may be the nanosize of the TiO$_2$ material i.e., the nano-thin coating is expected to introduce minimal resistance since resistance is directly proportional to the distance (~5.5 nm here) an electron is conducted.
C.7 Redox reactions of arsenate/arsenite on the TiO$_2$-CNT electrode

Figure C.5a shows that in the absence of electrolyte, no redox peaks were observed. In the presence of electrolyte, the CV scans were plotted in Figure C.5b and c for As(III) and As(V), respectively. The black lines are scans for pure CNT electrode in 100 ppm As; the red lines and blue lines are for TiO$_2$-CNT in 100 ppb and 100 ppb arsenic, respectively. No redox peaks are observed for the CNT anode. However, redox peaks appeared in the TiO$_2$-CNT scan for all arsenic oxidation states and concentrations, indicating TiO$_2$ but not CNT is electrochemically active for the As(III)/(V) redox pair. For both 100 ppb As(III) and (V), the redox peak positions (Figure C.5; cathodic -0.2 V; anodic 0.1 V) are in agreement with the standard As(III)/(V) couple of 0.0 V vs Ag/AgCl.

Therefore, although thermodynamically, arsenic redox reactions on TiO$_2$-CNT is possible at the voltage used in the experiment, the absence of electrolyte prohibits the reaction from occurring at an observable rate for all the synthetic arsenic solutions w/o electrolyte used in this study. The reaction may occur more readily in the groundwater solution, but is not expected to be significant since the conductivity of the groundwater ($329 \text{ S cm}^{-1}$) is approximately an order of magnitude less than utilized in Figure C.5b/c.

C.8 Groundwater analysis

The groundwater samples were collected in Jackson, WY. On site measurement gave the following results: pH = 7.42, ORP = +221.7 mV, conductivity = 329 S cm$^{-1}$, TOC = 3 ppm, TIC = 21.4 ppm, [As] = 44 ppb, total P = 19 ppb, [SO$_4^{2-}$] = 21 ppm. After filtration, the groundwater has pH = 6.9, [As] <10 ppb, total P = 9 ppb, other components remain unchanged.
C.9 Sorption capacity calculations

C.9.1 Granular TiO$_2$ sorption capacity

The SB (simulated Bangladesh) water and the scenario without phosphate and silicate in the reference was used here such that the chemical composition in the SB water does not affect arsenic sorption. The chemical content of SB water was listed in Table 2 of the reference, which only contains calcium, magnesium, sodium, and chloride at pH 7 which are not competing ions for arsenic. The Langmuir parameters of this scenario is listed in Table 4 of the reference, labeled as “As(III) No PO$_4$$^+$ SiO$_2$”.

The sorption capacity of As(III) after 5 h was calculated from Langmuir isotherm parameters given in Table 4 (As(III) no phosphate and silicate) and the equation below.

\[
\Gamma = \frac{\Gamma_{\text{max}} K c}{1 + K c}
\]

where $\Gamma$ is the sorption capacity, $\Gamma_{\text{max}} = 39.2 \text{ mg g}^{-1}$ is the maximum sorption capacity, $K = 9.66 \times 10^{-5}$ L $\mu$g$^{-1}$ is the sorption coefficient. Plugging in $\Gamma = 30 \text{ ppb}$ gives $\Gamma = 0.11 \text{ mg g}^{-1}$.

C.9.2 Amount sorbed at breakthrough

The amount arsenic sorbed at breakthrough ($C = 10$ ppb) in Figure 5.5 a and b can be calculated as follows:

\[
q = \frac{V_{BV} \int (C_{in} - C(BV)) dBV}{m}
\]

where $q$ is the amount sorbed in $\mu$g $\text{mg}^{-1}$ (or $\text{mg g}^{-1}$), $C_{in}$ is the influent arsenic concentration in ppb, C(BV) is the effluent concentration in ppb, $V_{BV} = 1.13 \times 10^{-4}$ L is the bed volume and $m$ is the adsorbent weight, 62 mg. The integration is the area between the influent line (100 ppb) and the breakthrough curve. The area times $V_{BV}$ gives amount arsenic sorbed in $\mu$g, divided by adsorbent
weight in mg yielding amount sorbed in mg g\(^{-1}\). For example, for the breakthrough curve of As(V), at pH 7 and 0 V in Figure 5.5a, the area is 7.7 \(\times\) 10\(^4\), the calculation gives:

\[
q = \frac{1.13 \times 10^{-4} \times 7.7 \times 10^4}{62} = 1.4 \text{ mg g}^{-1} \tag{C.7}
\]

Similar calculations can be completed for other breakthrough curves. For Figure 5.5d, for example, the area is 5.16 \(\times\) 10\(^5\) and the q is calculated to be 0.94 mg g\(^{-1}\).

**C.10 Electrochemical regeneration**

An electrochemical regeneration experiment was completed to explore the effectiveness of using a cathodic potential on the spent TiO\(_2\)-CNT adsorbent to desorb the As species. The TiO\(_2\)-CNT filter was first challenged with 4000 BV (0.5 L) of 240 ppb arsenate or 330 arsenite solution in the single pass filtration mode. Then the filter was switched to recirculation mode with 100 mL DI water and 2 V was applied to the filter using the TiO\(_2\)-CNT as the cathode for 3 hours. The results are plotted in Figure C.7. During the filtration stage, the arsenic concentration was kept below 10 for 5 hours, the amount adsorbed was 144.5 \(\mu\)g for As(III) and 107.2 \(\mu\)g for As(V). At the end of electrochemical regeneration, the amount desorbed into solution was 45 and 60 \(\mu\)g with the desorption percentage being 11% and 30% for As(III) and As(V), respectively. The electrochemical regeneration was less effective compared with NaOH regeneration (99% desorption over same time period), thus the NaOH method was used for regeneration studies.
Figure C.1: XPS for TiO$_2$-CNT. a) Survey scan for TiO$_2$-CNT. b) Survey scan. c) C1s scan (278–298 eV). d) O1s scan (524–546 eV). e) Ti 2p scan (448–475 eV).
Figure C.2: SEM (a–d) and TEM images (e–f) of the TiO$_2$-CNT network.
Figure C.3: TiO$_2$-CNT surface charge as a function of pH. a) pH as a function of OH added. b) Surface charge density of TiO$_2$-CNT as a function of pH.
Figure C.4: Single pass filtration of arsenic on a pure CNT filter. \([\text{As(V)}]_0 = 100 \text{ ppb}, \text{pH} 7, \text{flow rate} 1.5 \text{ mL min}^{-1}\). The filter is a single preformed CNT network.
Figure C.5: a) Cyclic voltammetry of TiO$_2$-CNT at pH 7 (blue) and pH 10 (red) for an aqueous solution with (solid) and without (dashed) 100 ppb As(V) and no electrolyte. b) CV scans of CNT and TiO$_2$-CNT at different As(III) with electrolyte. c) CV scans of CNT and TiO$_2$-CNT at different As(V) concentrations with electrolyte. Background electrolyte is 10 mM Na$_2$SO$_4$, the scan range from -0.3 to 0.8 V and the scan rate is 0.005 V s$^{-1}$. Ag/AgCl was used as the reference electrode. All experiments are completed in batch mode.
Figure C.6: CV (A) and EIS (B) of CNT and TiO$_2$-CNT. The electrolyte contains 1 mM K$_3$[Fe(CN)$_6$] and 100 mM Na$_2$SO$_4$. The CV scan rate was 5 mV s$^{-1}$. The amplitude and scan range in EIS were 5 mV and 10$^5$–10$^{-2}$ Hz, respectively.
Figure C.7: Sorption and electrochemical regeneration of the TiO$_2$-CNT filter. The flow rate was 3 mL min$^{-1}$, [As(V)]$_{in}$ = 240 ppb in the adsorption stage. The recirculating flow rate was 6 mL min$^{-1}$ for 3 hours, regeneration voltage 2 V in the regeneration stage.
Figure C.8: Effect of solution pH on arsenate breakthrough curve. $[\text{As(V)}]_i = 100$ ppb over a range of pH conditions from 6 to 9. Two TiO$_2$-CNT filters (31 mg each) were used for each filtration experiment. In all filtration experiments, $J = 1.5$ mL min$^{-1}$, the filter bed volume = 0.113 mL, and the EBCT = 4.5 s. The upper dashed horizontal line is the influent As concentration and the lower dashed horizontal line is the USEPA As drinking water regulation (10 ppb).
Figure C.9: Effect of competing ions on arsenate sorption. The initial concentration for arsenate was 200 ppb, phosphate 100 ppb, bicarbonate 100 ppm, sulfate 250 ppm, silicate 100 ppm. The TiO$_2$-CNT filter was ground into a powder before 9 mg was weighed and added into 100 mL solution for batch experiment. The solution was put into a thermostatic shaker at 150 rpm and 25 oC for 12 hours at 25 °C. All competing ions were evaluated individually.
Table C.1: Comparison of arsenic sorbents.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>EBCT (s)</th>
<th>[As(V)]&lt;sub&gt;in&lt;/sub&gt; (ppb)</th>
<th>Breakthrough (BV)</th>
<th>pH</th>
<th>As loading (mg g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt; spheres</td>
<td>150</td>
<td>30</td>
<td>15000</td>
<td>7.6</td>
<td>0.9</td>
<td>[177]</td>
</tr>
<tr>
<td>Ce-Ti Oxide</td>
<td>90</td>
<td>300</td>
<td>9100</td>
<td>7.6</td>
<td>5</td>
<td>[5, 9]</td>
</tr>
<tr>
<td>Zr-loaded resin</td>
<td>360</td>
<td>1000</td>
<td>400</td>
<td>4</td>
<td>2.4</td>
<td>[178]</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>900</td>
<td>200</td>
<td>8100</td>
<td>8</td>
<td>0.9</td>
<td>[158]</td>
</tr>
<tr>
<td>Granular TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>180</td>
<td>39</td>
<td>45000</td>
<td>7.9</td>
<td>1.7</td>
<td>[146, 150]</td>
</tr>
<tr>
<td>PVDF/Zirconia</td>
<td>10</td>
<td>94.5</td>
<td>3000</td>
<td>3–4</td>
<td>0.9</td>
<td>[156]</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;-CNT</td>
<td>4.5</td>
<td>100</td>
<td>8000</td>
<td>7</td>
<td>1.4</td>
<td>This study</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;-CNT+2V</td>
<td>4.5</td>
<td>100</td>
<td>13500</td>
<td>7</td>
<td>2.3</td>
<td>This study</td>
</tr>
</tbody>
</table>
Table C.2: Regeneration and desorption data.

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
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<tbody>
<tr>
<td><strong>As(III)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Influent (ppb)</td>
<td>327.75</td>
<td>327.75</td>
<td>327.75</td>
<td>327.75</td>
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<tr>
<td>1</td>
<td>0.07</td>
<td>6.4</td>
<td>8.2</td>
<td>14.8</td>
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<tr>
<td>Effluent (ppb)</td>
<td>1.5</td>
<td>6.2</td>
<td>10.1</td>
<td>18.2</td>
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<tr>
<td>2</td>
<td>3.7</td>
<td>8.1</td>
<td>15.3</td>
<td>22.0</td>
</tr>
<tr>
<td>vs time (h)</td>
<td>6.2</td>
<td>12.5</td>
<td>19.9</td>
<td>24.3</td>
</tr>
<tr>
<td>4</td>
<td>8.4</td>
<td>17.2</td>
<td>20.1</td>
<td>21.4</td>
</tr>
<tr>
<td>Desorbed (ppb)</td>
<td>882</td>
<td>833</td>
<td>877.5</td>
<td>868</td>
</tr>
<tr>
<td>As Sorbed (µg)</td>
<td>146.1</td>
<td>143.7</td>
<td>141.8</td>
<td>139.4</td>
</tr>
<tr>
<td>Capacity mg g⁻¹</td>
<td>2.36</td>
<td>2.32</td>
<td>2.29</td>
<td>2.25</td>
</tr>
<tr>
<td>% Desorbed</td>
<td>0.60</td>
<td>0.58</td>
<td>0.82</td>
<td>0.62</td>
</tr>
<tr>
<td>Desorbed (µg)</td>
<td>88.2</td>
<td>83.3</td>
<td>87.75</td>
<td>86.8</td>
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<tr>
<td>Total As (µg)</td>
<td>147.4</td>
<td>147.4</td>
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<td>147.4</td>
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<tr>
<td>% removal</td>
<td>0.99</td>
<td>0.974</td>
<td>0.972</td>
<td>0.970</td>
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Bibliography

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