RICE UNIVERSITY

Development of a Predictive and Mechanistic Model for Capacitive Deionization

by

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ABSTRACT

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The objective of this research was to develop a mechanistic and predictive model for capacitive deionization (CDI). The commonly-known Gouy Chapman Stern (GCS) model was modified to account for finite ion size and pore geometry by including the Carnahan-Starling (CS) equation of state and considering boundary conditions resulting from difference in pore shape and size and the subsequent impact on potential and concentration profiles. This GCS-CS model with pore geometry was applied to six model activated carbons (MACs) of uniform pore size to analyze the effect of influent salt concentration, pore size and geometry, and applied voltage on ion removal. The general trends found in modeling results were consistent with data presented in the literature. These findings were then compared with the commonly used CDI models, which could not replicate them. This indicates the complexity present in this new model is necessary for accurate representation of ion adsorption in CDI.
Acknowledgments

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# Table of Contents

Acknowledgments ............................................................................................................. 3  
List of Symbols ................................................................................................................ 3  
1.0 Introduction ............................................................................................................... 5  
2.0 Literature Review ..................................................................................................... 9  
  2.1.1 Parallel Plate Capacitor ....................................................................................... 10  
  2.1.2 Supercapacitors .................................................................................................. 13  
  2.1.3 Capacitive Deionization ..................................................................................... 16  
  2.2 CDI Description ...................................................................................................... 17  
  2.2.1 Different Configurations ................................................................................... 19  
  2.3 CDI Modeling ......................................................................................................... 20  
    2.3.1 Physisorption Model ........................................................................................ 21  
    2.3.2 Gouy-Chapman-Stern Model .......................................................................... 22  
    2.3.3 Corrections to GCS .......................................................................................... 32  
3.0 Model Development .................................................................................................. 47  
  3.1 mD Model Modifications ....................................................................................... 49  
  3.2 GCS Model Modifications ..................................................................................... 55  
    3.2.1 GCS-CS Model with Pore Geometry .............................................................. 60  
4.0 Results and Discussion .............................................................................................. 64  
  4.1 GCS-CS Model with Pore Geometry Validation .................................................... 64  
  4.2 GCS-CS with Pore Geometry Analysis .................................................................. 67  
    4.2.1 Effect of Pore Size ............................................................................................ 70  
    4.2.2 Effect of Influent Salt Concentration .............................................................. 80  
    4.2.3 Effect of Applied Voltage ............................................................................... 86  
    4.2.4 Effect of Salt Ion ............................................................................................ 90  
4.3 Model Comparison ................................................................................................... 93  
  4.3.1 mD-CS Results .................................................................................................. 94  
  4.3.2 GCS-CS Results ............................................................................................... 97
4.3.3 Result Comparison .................................................................103
5.0 Conclusions and Future Research .............................................107
Appendix .......................................................................................112
mD-CS Model Example Spreadsheet .............................................112
GCS-CS Model Example Code ......................................................113
GCS-CS Model with Pore Geometry Code .....................................117
List of Figures

Figure 1: Parallel Plate Capacitor .............................................................................. 13
Figure 2: Thin Capacitor Formed at Electrode-Electrolyte Interface in Supercapacitors/CDI ..................................................................................................................... 15
Figure 3: Typical CDI Configuration ......................................................................... 18
Figure 4: CDI Configurations 1 .................................................................................. 19
Figure 5: CDI Modeling using Adsorption Isotherms 13 .............................................. 22
Figure 6: Evolution of Charged Surface Models 29 .................................................... 24
Figure 7: Theoretical Depiction of the Capacitor-in-Series Model as applied to CDI ................................................................................................................................. 29
Figure 8: Overlapping EDLs in a Micropore, modified 33 .......................................... 34
Figure 9: Pore Overlap Regimes ............................................................................... 48
Figure 10: Coordinate Systems for Slit-Shaped and Cylindrical Pores .......... 62
Figure 11: Model Validation for A) Slit-Shaped Pores at a 1000 nm Pore Width and B). Cylindrical Pores at a 1,000,000 nm Pore Diameter .......... 66
Figure 12: Observed Pore Regimes ........................................................................... 69
Figure 13: Comparison of the Effects of Pore Size ................................................... 71
Figure 14: Pore Regime Transition – Slit-Shaped Pores ........................................... 76
Figure 15: Pore Regime Transition – Cylindrical Pores ............................................ 77
Figure 16: Surface Plots of the Effect of Pore Diameter, Applied Voltage, and Influent Salt Concentration for Slit-Shaped Pores ...................... 78
Figure 17: Surface Plots of the Effect of Pore Diameter, Applied Voltage, and Influent Salt Concentration for Cylindrical Pores ...................... 79
Figure 18: Curves of Excess Salt Concentration as it Changes with Potential for all Influent Salt Concentrations ................................................................. 81
Figure 19: Coulombic Efficiency Comparison through Variation of Influent Concentration, Applied Voltage, and Pore Diameter for Slit-Shaped Pores 84
Figure 20: Coulombic Efficiency Comparison through Variation of Influent Concentration, Applied Voltage, and Pore Diameter for Cylindrical Pores .85
Figure 21: Effect of Concentration at (A) High and (B) Low Voltage for Slit-Shaped Pores at 1 nm Pore Width .............................................................. 87
Figure 22: Effect of Concentration at (A) High and (B) Low Voltage for Cylindrical Pores at 1 nm Pore Diameter ................................................................. 88
Figure 23: Curves of Charge Concentration as it Changes with Potential for an Influent Salt Concentration of 5000 mg/L .................................................. 90
Figure 24: Effect of Hydrated Ionic Diameter and Valence Charge for (A) Lithium ions, (B) Calcium ions, and (C) Sulfate ions

Figure 25: mD-CS Modeling Results at 1.2V for Various Influent Salt Concentrations in Slit-Shaped Pores

Figure 26: mD-CS Modeling Results for an Influent Salt Concentration of 500 mg/L at Various Applied Voltages in Slit-Shaped Pores

Figure 27: mD-CS Modeling Results at 1.2V for Various Influent Salt Concentrations in Cylindrical Pores

Figure 28: mD-CS Modeling Results for an Influent Salt Concentration of 500 mg/L at Various Applied Voltages in Cylindrical Pores

Figure 29: GCS-CS Interpore Profile Approximation Method

Figure 30: GCS-CS Modeling Results at 1.2 V and Various Influent Salt Concentrations in Slit-Shaped Pores

Figure 31: GCS-CS Modeling Results for an Influent Salt Concentration of 500 mg/L NaCl at Various Applied Voltages in Slit-Shaped Pores

Figure 32: GCS-CS Modeling Results at 1.2 V and Various Influent Salt Concentrations in Cylindrical Pores

Figure 33: GCS-CS Modeling Results for an Influent Salt Concentration of 500 mg/L NaCl at Various Applied Voltages in Cylindrical Pores

Figure 34: Comparison of mD-CS and GCS-CS Modeling Results with the GCS-CS Model with Pore Geometry for Slit-Shaped Pores

Figure 35: Comparison of mD-CS Results with the GCS-CS Model with Pore Geometry for Cylindrical Pores
List of Symbols

$C$ ................................................................. Capacitance (F)
$C_{St}$ ......................................................... Capacitance of the Stern layer (F/m$^2$)
$C_{St,vol}$ ................................................. Volumetric capacitance of the Stern layer (F/m$^3$)
$F$ ............................................................... Faraday’s constant (C/mol)
$q$ ................................................................. Total charge (mol)
$\gamma$ .......................................................... Charge density (mol/m$^2$)
$\sigma_{mi}$ ..................................................... Microporous charge concentration (mol/m$^3$)
$\sigma_p$ ........................................................ Porous charge concentration (mol/m$^3$)
$\rho$ .............................................................. Charge concentration (C/m$^3$)
$\sigma_x$ ....................................................... Local charge concentration (mol/m$^3$)
$V$ .................................................................. Voltage (V)
$\varepsilon_S\varepsilon_0$ ......................................... Dielectric permittivity (C/Vm)
$A$ ................................................................. Specific surface area (m$^2$/g)
$SA$ .................................................................. Surface area (m$^2$)
$d$ ................................................................. Inter-electrode distance (m)
$\Lambda$ ............................................................. Charge efficiency (-)
$\Gamma_{salt}$ ..................................................... Specific salt adsorption (mg/g)
$c_i$ ............................................................... Local concentration of ion, i (mol/m$^3$)
$\varphi$ ............................................................. Local ion density (mol/m$^2$)
$c_b$ ............................................................... Bulk salt concentration (mol/m$^3$)
$c_{mi}$ ........................................................... Microporous concentration (mol/m$^3$)
$c_p$ ............................................................... Porous concentration (mol/m$^3$)
$c_{salt}$ ........................................................ Local salt concentration (mol/m$^3$)
$c_{mA}$ ........................................................ Macroporous concentration (mol/m$^3$)
$c_{solv}$ ......................................................... Solvent molecule concentration (mol/m$^3$)
$z_i$ .............................................................. Valence number and charge of ion, i (-)
$z$ ................................................................. Magnitude of valence number (-)
$\psi$ .............................................................. Dimensionless potential (-)
$\psi_{St}$ ....................................................... Dimensionless potential at the Stern plane (-)
$\psi_0$ .......................................................... Applied dimensionless potential (-)
$\psi_0$ ........................................................ Dimensionless potential of the bulk solution (-)
$T$ ................................................................. Absolute temperature (K)
$\varphi_{ex}$ ..................................................... Excess salt concentration (mol/m$^2$)
$\lambda_p$ ......................................................... Debye length (m)
$\Sigma$ .......................................................... Total charge transferred per unit electrode mass in Coulombs (C/g)
$\Sigma_F$ ....................................................... Charge transferred per unit electrode mass in moles (mol/g)
$V_T$ .............................................................. Thermal voltage (V)
$V_{cell}$ .......................................................... Applied voltage (V)
$\mu_{att}$ ..... Electrochemical potential which causes salt adsorption on uncharged carbon (-)
$c^0_{ions,mi}$ .... Microporous ion concentration on uncharged carbon (mol/m$^3$)
$p_{mi}$ .......................................................... Fraction of microporous electrode volume (-)
$\chi$ ....................................................... Electrode mass per unit pore volume (g/m$^3$)
$a$ .......................................................... GMSA compressibility parameter (-)
$g$ .......................................................... GMSA energy parameter (-)
$e$ .......................................................... Elementary charge (C)
$d_{ion}$ .......................................................... Hydrated ionic diameter (m)
$H$ ............. GMSA function related to compressibility and energy parameters
$\lambda$ ...................................................... GMSA dimensionless atmospheric thickness (-)
$K$ .......................................................... Reciprocal Debye length (1/m)
$\eta$ .......................................................... Volume fraction (-)
$n$ .......................................................... Number density of ions (ions/m$^3$)
$k_B$ .......................................................... Boltzmann constant (J/K)
$\mu_{ex}$ .............. CS correction excess electrochemical potential (-)
$v$ .......................................................... Single ion volume (m$^3$)
$\delta$ ......................... Stern layer thickness and hydrated ionic radius (m)
1.0 Introduction

The related issues of water and energy supply are two of the most pressing problems of today and are inextricably linked. Energy generation requires water as thermoelectric cooling fluid or as the driving force behind hydraulic fracturing for the extraction of oil and gas. Likewise, the utilization of water resources requires energy through powering pumps to transport water and through fueling desalination of brackish water and seawater, just to name a few examples. The absolute necessity and interconnected nature of these resources make it important to use both responsibly.

Desalination is one of the most energy intensive water treatment process. Currently, the most common methods of desalination are reverse osmosis (RO) for brackish and seawater and thermal processes, like multi-effect distillation (MED) or mechanical vapor compression (MVC), for waters more saline than the upper limit of RO. These technologies are currently the most economical desalination methods for the given influent conditions; however both have the same inefficiency: almost complete removal of all non-water constituents. In many situations this is over-treatment of the water and constitutes a waste of energy, as certain components of the feed water are unnecessarily removed.
For example, the Wilcox-Carrizo aquifer in southern Bexar County near San Antonio, Texas is currently being assessed for a RO desalination treatment facility to allow the brackish groundwater found there to be used for the municipal drinking water supply. The treatment required for this water is minor desalination to remove general inorganic ions and disinfection. In this situation, RO will be over treating the water by removing almost all non-water constituents, even if it is the most economical solution at the moment.

Likewise, in hydraulic fracturing, the water used to create fractures in the subsurface subsequently returns, contaminated with inorganic ions, organic matter, and many of the chemical additives used to optimize the fracturing process. For reuse in future fractures, the water must be treated to remove inorganic ions in order to reduce scaling and interference with chemical additives in the case of gel fractures. Both RO and thermal processes will remove all of the previously mentioned constituents, which can be unnecessary in the case of organic matter or wasteful in the case of the expensive chemical additives that must subsequently be replaced. The ideal technology in this case would remove the charged ions from solution, leaving behind the constituents that are unharmed or beneficial.

One such technology that can accomplish this is capacitive deionization (CDI), which uses electrosorption to attract and remove ions from solution.
While CDI currently is not as energy efficient or cost effective as RO, it does have a thermodynamic advantage over RO in many real-world cases. While all ion removal technologies have the same theoretical thermodynamic minimum required energy when the influent solution only includes salt ions, for more realistic solutions that may include organic or uncharged components, CDI has an advantage. While RO will remove these uncharged components, it will likewise incur the energy costs related to the removal of these non-ion constituents. CDI, however, will not remove any non-charged species or incur these additional energy requirements. Therefore, in many real-world scenarios, CDI will have a lower thermodynamic minimum than RO. This possibility warrants further research to reduce the energy consumption of this technology closer to this limit.

The objective of this work is to help direct future research by developing a predictive model that can operate across a broad range of operating conditions, including variable influent salt concentration, applied voltage, and electrode morphology. This will help determine more specific information in areas such as pore geometry tuning and operational voltage adjustment.

To accomplish this objective, previous modeling attempts are analyzed and their strengths and weaknesses determined. From this information, top
contenders were identified and additional modifications made to allow models
to more accurately and mechanistically predict behavior of CDI.
2.0 Literature Review

In this section, the past literature regarding CDI will be presented including its history and origins in electrochemical demineralization during the 1960s and the more recent concurrent innovations in CDI and supercapacitors. Next, the structure, materials, and mechanism of operation of CDI will be examined, including a brief look at different configurations with their drawbacks and advantages versus the basic parallel plate set up. Finally, previous attempts at modeling the behavior of CDI will be presented, their strengths and weaknesses analyzed, and modifications for improvement introduced.

2.1 CDI Development

The development of CDI can be classified into two phases: the early phase, which is followed by a 30 year gap, and the active phase. In 1960, the initial concept that would develop into CDI was conceived by Blair and Murphy. It was first called electrochemical demineralization (ECD) and the mechanism of ion removal was thought to be through ionic bonding with surface functional groups on the electrode assisted by the applied voltage. It was not until 10 years after the inception of ECD that Johnson et al. introduced.
proposed the currently accepted theory that the dominant ion removal mechanism is storage within the electric double layer (EDL).

Meanwhile, in the late 1950s, modifications were made to the basic, parallel plate capacitor to include an electrolyte solution in place of the typically used dry dielectric. Because the ions in this electrolyte solution are free to move, opposing ions will move to the oppositely charged plate, forming the opposing “plate” at a distance equal to the hydrated radius of the ion. This substantially decreased the plate separation distance and, thus, increased the capacitance. Due to this dramatic increase they were termed “supercapacitors” \(^\text{10}\).

Advances in both CDI and supercapacitors were slow until the almost concurrent application of high surface area carbon materials as electrodes, carbon aerogels in CDI and activated carbon in supercapacitors, caused a spike in performance and interest in the two technologies. This has led into the present day work which focuses on development of more advanced materials and models to guide this development \(^1, 10-13\).

2.1.1 Parallel Plate Capacitor

Since parallel plate capacitors lay the foundation of CDI, a brief discussion is warranted. A parallel plate capacitor is comprised of two
conductive plates separated by a thin insulator. When a potential is applied across the capacitor, electrons flow from the anode to the cathode causing a positive charge on the anode and a negative charge on the cathode. Subsequently the voltage can be removed and the system is short-circuited, causing release of the stored charge. Both processes are shown in Figure 1. The degree to which charge, \( q \) (mol), is able to be stored on the electrodes increases proportionally with the applied voltage, \( V_{cell} \), according to Equation 1, where \( C \) is the characteristic capacitance of the capacitor in farads and \( F \) is the Faraday constant.

\[
C = \frac{qF}{V_{cell}} \tag{1}
\]

The primary properties of the capacitor that determine its capacitance are the surface area, \( SA \), the distance between electrodes, \( d \), and the permittivity of the dielectric separating them, \( \varepsilon_r \varepsilon_0 \). This is according to Equation 2.

\[
C = \frac{\varepsilon_r \varepsilon_0 SA}{d} \tag{2}
\]

From this it is apparent that to increase the capacitance of a device, any combination of the following may be done:

1. Decrease the separation distance between plates,

2. Increase the surface area, and/or
(3) Increase the dielectric permittivity of the insulator between the plates.

As will be shown in later sections, CDI and supercapacitors make use of all three of these modifications to increase storage capacity.

Charging and discharging a parallel plate capacitor is accomplished by applying or removing the voltage source, respectively. During charging, the voltage imposed by a DC power source causes a flow of electrons, or current. The magnitude of this current begins at a maximum value and quickly decreases asymptotically to zero, as shown in the bottom left of Figure 1. Concurrently, due to the accumulation of charge from the flowing electrons, a voltage difference is generated across the capacitor plates. Since this potential is due to the current, it increases rapidly at first and then slows to asymptotically approach a maximum value approximately equal to the applied voltage.

During discharging, the external voltage holding the electrons in place is removed by short-circuiting the device. This causes the potential between the plates to be released, inducing a current in the opposite direction of the charging current. As electrons are transported away from the plates, the potential force decreases. This subsequently causes a decrease in the discharging current, leading to the patterns shown in the bottom right of Figure 1.
2.1.2 Supercapacitors

The two major differences between a parallel plate capacitor and a supercapacitor are the electrode material, which increases the electrode surface area, and the addition of an electrolyte solution to the inter-electrode space, which increases the inter-plate permittivity and modifies the separation distance to be at the surface-electrolyte interface instead of the plate-plate distance.

In contrast to the typical flat plate electrodes used in basic capacitors, supercapacitors employ morphologically complex carbonaceous materials to increase the available surface area by up to 4 orders of magnitude over flat
silicon electrodes \textsuperscript{14}. While flat silicon has a specific surface area of less than 1 square meter per gram, activated carbon, carbon nanotubes (CNTs), and graphene electrodes used for supercapacitors have specific surface areas of up to 3500, 450, and 250 square meters per gram, respectively \textsuperscript{1,14}.

In addition, the replacement of the dry dielectric with an electrolyte solution increases the dielectric constant in Equation 2 by an order of magnitude \textsuperscript{15}. Less obviously, this also significantly decreases the separation distance between charged plates in the same equation. This is achieved because the charged ions within the solution are mobile and attracted to the oppositely-charged plate, forming a layer of charge separated from the electrode only by the hydrated radius of the ions in solution. This accumulation of charge on the surface of the electrode forms a charged “plate” and acts as the opposite electrode in the capacitor, as shown in Figure 2. The thickness of the dielectric in traditional capacitors depends on the materials and applied voltage, causing a typical inter-electrode distance of approximately 140 nm\textsuperscript{16}. With the addition of the electrolyte dielectric, this distance is decreased to about 0.35 nm for a NaCl solution, a decrease of 3 orders of magnitude \textsuperscript{17}. 

The combination of these modifications creates a further complication. Since the charge layer will curve with the surface of the morphologically complex electrode material, in areas of concavity, the charge density increases above that which would exist on a flat surface and vice versa on a convex surface. In addition, due to the structure of the pores in carbonaceous materials used as electrodes, in some very small pores, or micropores, there is not enough space for each side of the pore to have a layer of ions as a counterplate. These effects do not allow the typical flat-plate capacitor equations to be applied to supercapacitors because the assumption of a flat
surface is violated. This effect is verified by the non-linear relationship observed between surface area of supercapacitors and total capacitance, counter to the implication in Equation 2

2.1.3 Capacitive Deionization

CDI functions very similarly to a supercapacitor with similar electrode materials and dielectrics; however, it operates with a very different purpose. While supercapacitors operate to maximize charge storage, CDI’s main purpose is to remove ions from the dielectric solution. In an ideal situation, each unit of charge, or electron, transferred to or from an electrode would cause the attraction and removal of an oppositely charged ion, but this is not the case. Since, in the discharged state, the bulk solution is allowed to occupy the electrode pore space, there are equally as many coions, or ions of the same charge as the electrode, and counterions, or ions with an opposing charge from the electrode, in these locations. When the electrode is being charged, some of the energy from the electrons transferred will be used to expel coions already present in the pores and what is left can be used to attract additional counterions into the electrode pore space. Because of this, the number of ions removed will always be less than the number of electrons transferred to or from the electrode. The term representing this concept is called Coulombic efficiency and is given in Equation 3 where $I_{salt}$ is the salt removal capacity
in moles salt removed per unit electrode mass and $q$ is the total charge
delivered to the electrode in moles of electrons, also per unit electrode mass,
and $z$ is the magnitude of the ion valence charge. This term is used to show
the equivalent number of counterions attracted per electron of charge
delivered to the electrode.

$$\Lambda = \frac{2zF_{salt}}{q} \quad (3)$$

In addition, since the dielectric solution used in CDI is always water,
the maximum voltage that should be applied to CDI is 1.23 V, which
corresponds to the voltage of breakdown of the dielectric. Under this electric
field, water molecules will begin to undergo Faradic reactions that are parasitic to the process and further decrease the charge efficiency.

### 2.2 CDI Description

The most common setup for CDI today is shown in Figure 3. It consists of five layers held together by a framing material. The outer layer consists of a current collector that provides support for the electrode material. Typically the material for the current collector is either graphite or titanium, but any material that is both conductive and corrosion resistant is appropriate, and in some cases where the electrode material is rigid, the current collector can be omitted $^{19}$. The next layer is the electrode, which is where the double layer is
formed and ions are stored. The material of the electrode should have a large surface area and internal pore volume and must also be conductive. The most commonly used material is a composite of activated carbon and a binder material, such as PVDF. Research into this area is very active and many materials show promise, including CNTs, carbon aerogels, composite carbon electrodes with an ion exchange resin, and graphene, amongst others.

The middle layer between the electrodes is a non-conductive, porous material. Filter papers or large pore-sized membranes are typically used, although filter paper is more economical. The purpose of the spacer is to separate the electrodes to preserve the capacitor-like nature of the device and
also to serve as a flow channel to facilitate the delivery of water to the electrode material. Large porosity materials are ideal for this purpose 19.

2.2.1 Different Configurations

While the previous is the most common configuration used in the literature, many variations have been developed. Figure 4 first shows the previously mentioned configuration, also called flow-by mode, in the upper, left corner. In the upper right corner is the flow-through configuration. In this setup, no current collectors are used and water flows directly through the porous electrodes. This allows the transfer of ions into the carbon matrix to occur more quickly and improve system kinetics; however, this configuration increases the likelihood of electrode fouling versus the flow-by mode 1, 23.
The approach used in the bottom left of the figure is electrostatic ion pumping and is similar to the flow-by configuration in that water flows parallel to the electrodes, but the electrodes are placed perpendicular to the direction of flow. Valves are located at each side of the flow channel and are opened or closed depending on if a voltage is being applied (adsorption) or not (desorption). This allows for a semicontinuous flow of both streams when many electrode pairs are used $^{1,24}$.

Finally, the bottom right image depicts water desalination with wires. Carbon rod wires are used in this setup and are first placed in the influent stream and a voltage is applied. Once adsorption is complete, the wires are moved from the diluate stream to the concentrate stream and the voltage is released. This method has the advantage of having diluate and concentrate streams separated throughout the process so that no special valves or pumping methods are required and a continuous stream of each is produced; however, this will also require mechanization to move the wires back and forth between the streams, likely causing higher maintenance costs $^{1,25}$.

2.3 CDI Modeling

Ideally, a CDI model should be built upon the underlying principles of the occurring process, be able to predict the performance of any given system
based upon its measurable characteristics, and, of course, do all of this accurately across a range of operating conditions. While attempts have been made to do this, as of this time all have fallen short either through not being predictive, as in the case of the modified Donnan model, or being neither predictive nor mechanistic, as in the case of adsorption isotherms. A more thorough discussion of previous attempts in CDI modeling follows.

### 2.3.1 Physisorption Model

Under the assumption of an adsorption-based model, salt ions would adsorb onto receptor sites on the surface of the carbon electrodes. The fraction of occupied receptor sites occupied by ions is dependent on the bulk concentration of the respective ion, with the fraction of receptor sites increasing as the respective bulk ion concentration increases.

While the Langmuir model provides a very good fit to the data presented in the literature, as shown in Figure 5, there are many issues with assuming that the Langmuir model adequately describes the process of ion removal through CDI. The Langmuir model does not account for the potential driving force of ion transport or the current present in CDI. In addition, the example of the Langmuir model used is only over a very small range of salinity concentrations. For these reasons, physisorption was not considered as a viable modeling approach for this application.
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Langmuir parameters</th>
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<tr>
<td></td>
<td>$q_m$ (μmol/g)</td>
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<tr>
<td>SWCNTs</td>
<td>42.82</td>
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</tbody>
</table>

Figure 5: CDI Modeling using Adsorption Isotherms

2.3.2 Gouy-Chapman-Stern Model

In contrast to the adsorption model, the double layer theory assumes that the salt ions are held close to the surface of the activated carbon structure, trapped within the EDL created by the potential applied to the electrode instead of being held directly to the electrode surface. Within the EDL, ions with a charge counter to the electrode in question, or counterions, can be held
while ions with the same charge as the electrode in question, or coions, will be expelled to balance the charge on the electrode.

The first attempt to model this effect was done by Helmholtz in 1853. Helmholtz proposed a model of a rigid layer of ions held closely to the charged surface in question at a distance equal to the ionic radius of the counterions, as shown in Figure 6A. He assumed, first, that the system was at equilibrium, that the number of ions present in the adsorbed layer would exactly counter the charge on the surface in question, there would be a linear voltage drop from the charged surface to the counterion nucleus, and that the ions have no finite size\textsuperscript{28}. While revolutionary for its day, there are a number of issues with this simplistic model. Firstly, it has been shown that ions do not behave like this in nature and instead form a much looser layer at charged surfaces. Also, for highly charged surfaces or large ions, the number of ions required to exactly neutralize the surface charge could be physically impossible to fit directly on the charged surface due to the finite size of ions.
To correct these inaccuracies, in the early 20th century Gouy (1910) and Chapman (1913) independently developed a model that corrected Helmholtz’s assumption that the ions formed an organized, single layer on the surface of the charged solid by modifying the Poisson-Boltzmann equation to describe the electric potential drop and ion distribution across the new diffuse layer, as shown in Figure 6B, and account for the thermal motion of ions in solution. This model still assumes that the system is at equilibrium, ions are point charges, and that these ions can come infinitely close to the charged surface. The derivation of this model begins with the Poisson equation for rectangular coordinates, which relates the local voltage, $V$, gradient to the local charge, $\rho$, in C/m$^3$ divided by the dielectric permittivity, $\varepsilon_r\varepsilon_0$, and is
given in Equation 4. Here, $x$, $y$, and $z$ denote the usual Cartesian coordinate components.

$$\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{\rho(x,y,z)}{\varepsilon_r\varepsilon_0} \tag{4}$$

Assuming that the flat plate is infinite in the $y$ and $z$ direction and, thus, the voltage gradient in those directions will be negligible, dividing through by the thermal voltage, $V_T$ ($V_T = \frac{k_B T}{e}$), to make the gradient given describe the dimensionless potential, $\psi$, and multiplying by Faraday’s constant, $F$, to convert the charge density term used previously to $\sigma$, the charge density in units of mol/m$^3$, gives the simplified relation shown in Equation 5.

$$\frac{d^2 \psi}{dx^2} = -\frac{\sigma(x)\cdot F}{\varepsilon_r\varepsilon_0\cdot V_T} \tag{5}$$

Now, according to the Boltzmann equation, local ion concentration in the presence of an applied potential can be given by Equation 6, where $c_i$ is the local ion concentration in mol/m$^3$, $c_b$ is the bulk ion concentration in similar units, $z_i$ is the sign and magnitude of valence charge on the ion, $i$, and $\psi(x)$ is the local dimensionless potential, and $\psi_b$ is the dimensionless potential of the bulk solution, which is usually zero.

$$c_i(x) = z c_b \cdot \exp(-z_i(\psi(x) - \psi_b)) \tag{6}$$
This description of ion concentration can be used to determine local charge, \( \sigma \), when the sign of ions is included. In a simple system with a symmetric electrolyte and assuming a negatively-charged electrode, this can be described by the subtraction of the local anion concentration, \( c_- \), from that of the cation, \( c_+ \), as shown in Equation 7, where \( z \) is the magnitude of ion valence charge and is used to account for multivalent ions.

\[
\sigma = zc_+ - zc_- = zc_b \cdot \exp(-z(\psi(x) - \psi_b)) - zc_b \cdot \exp(z(\psi(x) - \psi_b))
\]

Incorporating the Poisson equation describing potential distribution with the concentration profile given by the Boltzmann equation, gives a description of both with relation to a charged flat plate, shown in Equation 8.

\[
\frac{d^2\psi(x)}{dx^2} = \frac{F}{\varepsilon_r \varepsilon_0 \nu_T} \cdot 2zc_b \sinh(z(\psi(x) - \psi_b))
\]

However, this approximation allowed ions to come infinitely close to the charged surface. Due to the finite size of ions and their hydration shell, the charged center cannot reach the oppositely charged surface as is described in this model, leading to large inaccuracies when modeling systems with high bulk concentrations or applied voltages higher than the thermal voltage (approximately 25.7 mV at room temperature). This led to Stern combining
the Helmholtz and Gouy-Chapman models such that ions are not allowed to approach the surface closer than the hydrated radius of the counterion, as shown in Figure 6C. The potential drops linearly across the Stern layer as shown in Equation 9 where \( V \) is local voltage, \( V_{St} \) is the voltage drop across the Stern layer in volts, \( x \) is distance from the charged surface, and \( \delta \) is the thickness of the Stern layer. This model behaves similar to the Helmholtz model in the Stern layer, but then will vary according to the Poisson-Boltzmann equation, as in the Gouy-Chapman model. The voltage profile in the Stern layer is given in Equation 8.

\[
\left. \frac{dV}{dx} \right|_{St} = -\frac{V_{St}}{\delta} \tag{9}
\]

The potential drop across the Stern layer decreases the potential at which the assumption of point charges begins, helping to justify the simplification \(^{30}\).

Mathematically, this is often described using the capacitor-in-series model \(^{31}\). In this model, both the Stern and the diffuse layers are modeled as capacitors. For the Stern layer, this is more intuitive. The charged surface is taken as one of the capacitor plates and the Stern layer as the opposing capacitor plate. The charge of the capacitor is taken as the total charge held on the Stern plane and in the diffuse layer. The diffuse layer portion of the
model is less intuitive. This theoretical capacitor has a plate separation distance equal to the distance between the charged surface and the location at which the potential reaches zero and the local concentration is equal to the bulk concentration. The charge on this capacitor is also equal to the charge held on the Stern plane and in the diffuse layer. A depiction of the theoretical model is given in Figure 7. In the capacitor-in-series model, the total capacitance of the circuit is determined by Equation 10 where \( C \) is capacitance and the subscript 'St' indicates the Stern layer modeled as a capacitor and 'd' indicates the capacitor formed from the charged surface to the end of the diffuse layer.

\[
\frac{1}{C_{\text{tot}}} = \frac{1}{C_{\text{St}}} + \frac{1}{C_{d}} \quad (10)
\]

Using the relation given in Equation 1, where \( q \) is charge held on the capacitor in mol, \( F \) is Faraday’s constant, \( C_{\text{St}} \) is capacitance in farads, \( V \), the voltage across each capacitor, \( V_{\text{St}} \) and \( V_{d} \), can be determined in relation to the total voltage across both capacitors (\( V_{\text{cell}} \)), given by Equation 11. These assumptions will be used to calculate the voltage at the Stern plane so that current EDL theory can be applied to the specific case of CDI.

\[
V_{\text{St}} = \frac{qF}{C_{\text{St}}} \quad (1)\]
\[ V_{cell} = V_{St} + V_d \]  \hspace{1cm} (11)

Figure 7: Theoretical Depiction of the Capacitor-in-Series Model as applied to CDI

The GCS model was adapted to CDI in Biesheuvel et al.\textsuperscript{32} for the case of a monovalent, symmetric salt with the surface concentration of ions, \( \varphi_i \), in mol/m\(^2\) at distance, \( x \), given by the Gouy Chapman Stern (GCS) model. This is governed by the Boltzmann equation, Equation 6, with \( \varphi_b \), the bulk ion surface concentration in mol/m\(^2\), \( z_i \), the valence number and sign of the ion, and \( \psi(x) \), the dimensionless voltage parameter given by the voltage divided by the thermal voltage, \( V_T \) (\( V_T = \frac{k_B T}{e} \)), where \( k_B \) is the Boltzmann constant, \( T \) is the temperature in kelvin, and \( e \) is the elementary charge.

\[ \varphi_i(x) = \varphi_b e^{-z_i(\psi(x) - \psi_b)} \]  \hspace{1cm} (6)
Integrated over the diffuse layer, the excess surface concentration in mol/m², \( \varphi_{ex} \), of the two ions is given by Equation 12 where \( \lambda_D \) is the Debye length in meters, \( \psi_{St} \) is the dimensionless potential at the Stern layer, and \( \psi_b \) is the dimensionless potential of the bulk solution, although this term is usually zero.

\[
\varphi_{ex} = 8\lambda_D c_b sinh^2 \left( \frac{1}{4} (\psi_{St} - \psi_b) \right) \tag{12}
\]

This excess concentration can then be used to find the salt adsorption capacity, \( \Gamma_{salt} \), in mol salt/g electrode in accordance with Equation 13, with \( A \) being the specific electrode surface area in units of m²/g.

\[
\Gamma_{salt} = \varphi_{ex} \cdot A \tag{13}
\]

Likewise, the difference of Equation 6 solved for both cations and anions can also be integrated to determine the surface charge density in mol/m², \( \gamma \), as given by Equation 14 with the total charge transferred to the electrodes in mol/g, \( \Sigma \), given by Equation 15.

\[
\gamma = 4z\lambda_d \varphi_b sinh \left( \frac{1}{2} z(\psi_{St} - \psi_b) \right) \tag{14}
\]

\[
\Sigma = \gamma \cdot A \tag{15}
\]

From these values, the charge efficiency, \( \Lambda \), of the system can be determined using Equation 16.
\[ \Lambda = z \frac{r_{salt}}{\Sigma} = z \cdot \tanh \left( \frac{(\psi_{St} - \psi_b)}{4} \right) \]  \hfill (16)

The potential difference between the applied potential, \( \psi_0 \), and the potential at the Stern plane, \( \psi_{St} \), is related to the applied voltage, \( V_{cell} \), and the potential difference between the Stern plane and the bulk solution, \( \psi_b \), as shown in Equation 17. This potential drop can be determined by utilizing the capacitor-in-series model as presented previously and treating the Stern layer as a capacitor. For this model, the Stern layer capacitance can be determined as in Equation 2, modified for the Stern layer, \( A \) is the surface area is the specific surface area of the porous electrode and the interpolate distance is the hydrated ionic radius, \( \delta \). To determine the charge held on the electrode surface it is assumed to be equal to the charge held on the Stern layer surface and the diffuse layer through the principle of charge neutrality. This assumption is shown in the left hand side of Equation 18:

\[ \frac{V_{cell}}{2V_T} = |(\psi_{St} - \psi_b) + (\psi_0 - \psi_{St})| \]  \hfill (17)

\[ \gamma F = C_{St}(\psi_0 - \psi_{St})V_T \]  \hfill (18)

\[ C_{St} = \frac{\varepsilon_r \varepsilon_0 A}{\delta} \]  \hfill (2)

While these modifications are significant improvements to the original Helmholtz model, there are still model assumptions that do not allow for direct
application of the GCS model to CDI. The assumption of ions as point charges will allow predicted concentrations to exceed the solubility of the salt. Also, the assumption of the charged surface being flat would only be valid in the case of an infinitely wide and long slit-shaped pore. In reality, electrode materials are much more morphologically complex than this and can contain pores of many geometries, although they are most often modeled as either slit-shaped or cylindrical. GCS, however, can serve a good base model and has the added advantage of being able to be modified to show a detailed concentration profile across the diffuse layer. It can also still be directly applied in the special cases of thin double layers or very large pore size since overlapping or interferences from surface curvature in this case will be minimal.

2.3.3 Corrections to GCS

Although the GCS model for the double layer is considered to be robust and is used as a valid approximation even in cases where the underlying assumptions of low salt concentration and applied voltage are violated, the case of CDI appears too complex for this. The porous surface morphology of carbon materials used as electrodes leads to significant overlap of the diffuse layer. Since GCS assumes a flat, isolated surface, the overlapping present will cause GCS to overestimate the amount of salt removed. This is because as
the diffuse layers begin to overlap, the potential, and thus, concentration will be overestimated in those locations.

Second, GCS assumes that ions are point charges. This assumption is valid for applied voltages less than the thermal voltage, or approximately 25.7 mV. Due to the addition of the Stern layer, this limit can be surpassed, but CDI typically operates at 1.2V so the potential applied across each electrode’s EDL will be 0.6 V in a symmetrical cell, or over 20 times the thermal voltage. This is a significantly higher voltage than allowed by GCS, above which it will begin to predict higher concentrations than are physically possible, so modifications must be made to account for the finite ion size.

2.3.3.1 Surface Morphology - Modified Donnan Model

The modified Donnan (mD) model addresses the issue of complex pore geometry and overlapping double layers by assuming that the EDL in the micropores of the carbon structure is so overlapped that the potential within these pores remains unchanged throughout the entire pore, such that the total salt removed is a function of total pore volume instead of surface area 32. The model also assumes that the system is at equilibrium and that ions are point charges. The assumption of constant pore concentration and potential is valid when the Debye length is much longer than the effective diameter or width of the pore, indicating the entire pore volume is available for ion removal. This
concept is illustrated in Figure 8, where the solid line represents the actual voltage profile of the system, while the dotted line represents the approximation by the mD model. The model generated from this assumption is presented in the following equations.

![Figure 8: Overlapping EDLs in a Micropore, modified](image)

Similar to the GCS model, the concentration in the micropores in the mD model, assuming a monovalent, symmetric salt, is described by the Boltzmann equation but with two modifications in Equation 19, where $c_{i,mi}$ is the concentration of ion, $i$, in the micropore and $c_{salt,ma}$ is the concentration of salt ions in the macropores, which is also equal to the bulk ion concentration. In the first modification, the voltage in the pore is taken to be constant, so there is no variation of concentration with distance from the charged surface. Second, an attraction term, $\mu_{att}$, was added by Porada et al.
1 to account for the nonelectrostatic attraction energy which causes salt adsorption onto carbon in the absence of an applied potential. Also, as in the GCS model, $z_i$ is the ion valence and charge, $\psi_{St}$ is the dimensionless Stern plane potential, and $\psi_b$ is the dimensionless potential of the bulk solution, which is usually zero.

$$c_{i,mi} = c_{salt, mA}e^{(-z_i(\psi_{St}-\psi_b)+\mu_{att})}$$ (19)

Similar to the GCS model, the total concentration of ions in the pores, $c_{ions,mi}$, is given by the addition of the concentration terms for the anion, $c_{-,mi}$, and the cation, $c_{+,mi}$, while the total charge held in the pores, $\sigma_{mi}$, is given by the concentration term for the anion subtracted from that of the cation. The values are given by Equations 20 and 21, which assume a symmetric salt. The use of $z$ as the magnitude of the valence charge is to allow this model to be applied to multivalent ions.

$$c_{ions,mi} = c_{+,mi} + c_{-,mi} = 2c_b e^{\mu_{att}} \cosh\left(z(\psi_{St}-\psi_b)\right)$$ (20)

$$\sigma_{mi} = zc_{+,mi} - zc_{-,mi} = -2zc_b e^{\mu_{att}} \sinh\left(z(\psi_{St}-\psi_b)\right)$$ (21)

However, since this method does not account for the initial concentration that would be present in the pores, an additional term, $c_{ions,mi}^0$, which is the ion concentration that occurs in the pore volume when the potential at the Stern plane is equal to the bulk potential, must be subtracted
from the microporous ion concentration to separate the additional ions attracted into the micropores by the applied voltage from the ions held in the pore before potential is applied. Once this is done, the Coulombic efficiency, $\Lambda$, can be determined through Equation 22, where $z$ is the magnitude of the charge on the ions.

$$
\Lambda = \frac{z(c_{ions,mi} - c_{ions,mi}^0)}{|\sigma_{mi}|} = z \cdot \tanh \left( \frac{(\psi_{St} - \psi_b)}{2} \right)
$$

(22)

In order to model the salt adsorption capacity in Equation 23, the excess salt concentration held in the micropores, given by the difference between $c_{ions,mi}$ and $c_{ions,mi}^0$, is multiplied by $\frac{p_{mi}}{\chi}$, which is the fraction of microporous volume in the electrode divided by the electrode mass per unit pore volume. Additionally, since the ion concentrations are a total of both cations and anions, the term is divided by 2 to allow for representation of the entire salt molecule in the specific salt adsorption term, $\Gamma_{salt}$, in mol/g.

$$
\Gamma_{salt} = \frac{1}{2} \cdot \frac{p_{mi}}{\chi} (c_{ions,mi} - c_{ions,mi}^0)
$$

(23)

However, since the carbon pore space can be assumed to be neutrally charged when no potential is being applied, it is unnecessary to include the same correction term at zero applied voltage when calculating the total charge transferred to the system in moles per unit mass, $\Sigma$, as given by Equation 24.
This term is also divided by 2 so that a simple comparison between specific salt adsorption and total charge transferred can give the Coulombic efficiency, as in Equation 16.

\[
\Sigma = -\frac{1}{2} \frac{p_{mi}}{\rho_e} \sigma_{mi} \quad (24)
\]

\[
\Lambda = \frac{r_{salt}}{\Sigma} \quad (16)
\]

Finally, as with the GCS model, the potential at the Stern plane, \( \psi_{St} \), can be incorporated through Equations 17 and 25, where \( C_{St,vol} \) is a Stern layer capacitance given per unit volume basis. Here again, \( V_{cell} \) is the applied voltage and \( V_T \) is the thermal voltage, both in units of volts, \( F \) is the Faraday constant, \( \psi_b \) is the bulk dimensionless potential, again usually zero, and \( \psi_0 \) is the applied dimensionless potential.

\[
\frac{V_{cell}}{2V_T} = |(\psi_{St} - \psi_b) + (\psi_0 - \psi_{St})| \quad (17)
\]

\[
\sigma_{mi} F = -C_{St,vol}(\psi_0 - \psi_{St})V_T \quad (25)
\]

The mD model concept theoretically works well in the case of strongly overlapped diffuse layers; however in a carbon with a small percentage of micropores or high salinity, this assumption will not hold because the Debye length will not be large enough to cause significant overlap and a constant
voltage within the pore. The $\mu_{att}$ term is also troubling in that it seems to have been added as a fitting parameter to ensure the model can better represent the data. In addition, due to the number of fitting parameters present in this model, namely $\mu_{att}$ and $\psi_{St}$, this model is not yet predictive of the function an electrode given its physical parameters.

### 2.3.3.2 Finite Ion Size - Generalized Mean Spherical Approximation

While the GCS model is valid in large pores where there is not significant overlap of the double layer, it is not valid in the case of high concentration as ions are modeled as point charges and this will result in higher than possible predicted concentrations. For this reason, the general mean spherical approximation (GMSA) is considered. The GMSA is based upon the hypernetted-chain closure of the Ornstein-Zernike equation, which describes the interaction of spherical molecules/atoms in solution.

Like both previous models, the GMSA is based upon the Boltzmann equation with the concentration of ions given by Equation 26, where $\psi(x)$ is the dimensionless potential within the diffuse layer, given by dividing the voltage drop across the diffuse layer by the thermal voltage, $V_T$. Continuing, $\alpha$ is the compressibility parameter, and $H$ is a function related to the energy parameter, $q$, where $\alpha$ and $q$ together account for finite ion volume.
Furthermore, $c_b$ is the bulk concentration in mol/m$^3$, $z_i$ is the ion valence number and charge, and $\psi_{St,GC}$ is the dimensionless Stern plane potential predicted by the GC model, and $\psi_b$ is the bulk potential, which is usually zero.

$$c_i(x) = a \cdot c_b e^{-z_i(\psi_{GC}(x) - \psi_b) + H}$$  \hspace{1cm} (26)

$$H = \frac{q \lambda (\psi_{GC}(x) - \psi_b)}{(1 + \lambda)^n}$$  \hspace{1cm} (27)

$$g = \frac{e^2}{4\pi \varepsilon_r \varepsilon_0 d_{ion} kT}$$  \hspace{1cm} (28)

In Equations 27 and 28, $\lambda$ is the dimensionless atmosphere thickness, $n$ is 4.6 for a 1-1 electrolyte, $k_B$ as the Boltzmann constant, and $d_{ion}$ is the average of the ionic hydrated diameters, $\varepsilon_r \varepsilon_0$ is the dielectric permittivity, and $T$ is the absolute temperature in kelvin. The dimensionless atmosphere thickness is a function of the reciprocal Debye length, $K$, and the ionic hydrated diameter, as in Equation 29.

$$\lambda = \left(\frac{1 + 2d_{ion} K}{2}\right)^{1/2} - \frac{1}{2}$$  \hspace{1cm} (29)

In order to find the compressibility parameter, $a$, first the volume fraction of ions, $\eta$, must be found using Equations 30 and 31, where $n$ is the average number density of both ions. The ionic diameter, $d_{ion}$, is approximated as the arithmetic mean of the diameters of the cation and anion.
\[
\eta = \frac{\pi nd_{ion}^3}{6} \tag{30}
\]
\[
a = \frac{(1+2\eta)}{(1-\eta)^2} \tag{31}
\]

Next, to find the total excess concentration, \(c_d\), and charge in the diffuse layer, \(\sigma_d\), the sum and difference of the Equation 26 must be integrated, respectively for each ion, giving Equations 32 and 33, where \(b\) is given by Equation 34.

\[
c_d = ac_b \cosh(H + (\psi(x) - \psi_b)) = c_b \frac{a+b^2}{2} \tag{32}
\]
\[
\sigma_d = ac_b \sinh(H + (\psi(x) - \psi_b)) = c_b b \left(\frac{a+b^2}{4}\right)^{1/2} \tag{33}
\]
\[
b = 2\sinh \left(\frac{(\psi_{GC(x)}-\psi_b)}{2}\right) \tag{34}
\]

The corrections for the dielectric permittivity of the solvent in the diffuse layer and the corrected potential at the Stern plane are given by Equations 35 and 36 with the dielectric decrement parameter, \(\delta_r = 16.1 \, M^{-1}\) for NaCl, a curvature fitting parameter, \(b_r = 3.0\), and \(\epsilon_{r0}\) is the relative permittivity of pure water, and \(\psi_0\) is the dimensionless applied potential. The dielectric detriment parameter is determined through measurement of decreasing dielectric permittivity as concentration increases for bromine and chlorine salts with cations of varying size. Linear regression was performed on the data to determine the equation relating the cation ion size with the
dielectric detriment in units of $M^{-1}$ for chlorine and bromine salts. However, this line is not perfectly linear, so a curvature parameter, $b_r$, was added to account for this \(^{36}\).

\[
\varepsilon_r = \varepsilon_{r0} - \delta_r c_d + b_r c_d^{2/3} \quad (35)
\]

\[
\psi_{St} = \psi_0 - \frac{RT}{F} \sinh^{-1} \left[ \frac{b}{a} \left( a + \frac{b^2}{4} \right)^{1/2} \right] - H \quad (36)
\]

Now, in order to determine the salt adsorption per unit electrode mass, a parameter akin to the Debye length must be determined using the GMSA. Varela et al. gives an approximation of the GMSA equivalent to the Debye-Hückle inverse length, $K_{GMSA}$, as in Equation 37, which would make the GMSA length, $\lambda_{GMSA}$, equivalent to what is shown in Equation 38 \(^{36}\).

\[
K_{GMSA} = \frac{K_{GC}}{\left( 1 + \frac{\eta}{(K_{GC} \sigma)^2} \right)^{1/2}} \quad (37)
\]

\[
\lambda_{GMSA} = 1 / K_{GMSA} \quad (38)
\]

Finally, the salt adsorption capacity, $\Gamma_{salt}$, in mol/g can be found similarly to the GCS model with Equation 39, with $A$ being the specific surface area in $m^2/g$.

\[
\Gamma_{salt} = c_d \cdot A \cdot \lambda_{GMSA} \quad (39)
\]
The GMSA model has a number of drawbacks. In order to correct for
the finite ion size it uses empirical parameters, namely $\delta_r$ and $b_r$, and
nonmechanistic equations, which are not ideal. In addition, the model does
not account for the excess concentration across the entire diffuse layer, but
only through the GMSA length and does not allow a method of determining
the concentration profile through the diffuse layer in order to correct this.

2.3.3.3 Finite Ion Size – Carnahan-Starling Equation of State

A competing theory of how to incorporate finite ion effects is the
Carnahan-Starling (CS) equation of state. Developed by Norman Carnahan
and Kenneth Starling in 1969, the CS equation uses a dimensionless excess
electrochemical potential term to account for finite ion volume by
approximating the additional electrochemical potential required to
concentrate ions based on a volume fraction term $^{37-38}$. Based on previous
attempts by Bikermann and Sparnaay to correct the prediction of impossibly
high ion concentrations close to charged surfaces, the CS excess term was
derived when Carnahan and Starling discovered that the known virial
coefficients for hard spheres could be closely approximated by an algebraic
expression. In fact, the CS equation fits the virial expansion almost exactly
$^{39}$. Since then, it has been determined that the CS equation is extremely
accurate for packing coefficients less than 0.55, but becomes less accurate
after this and does not diverge until a packing coefficient of 1 is reached, despite the maximum packing fraction for spheres being approximately 0.74. Therefore, this modification will need to be used carefully to ensure the packing coefficient does not exceed 0.55.

In order to apply this modification to CDI, the basic framework must be set up, as is done by Biesheuvel et al. First, it is known that the total cell voltage is divided evenly between the two electrode’s EDLs in a symmetrical cell and subsequently split between the Stern and diffuse layers in the EDL, as in Equation 17, where $\psi_{St}$ is the dimensionless potential at the Stern plane, $\psi_0$ is the dimensionless applied potential, and $\psi_b$ is the bulk dimensionless potential, which is usually zero for the case of CDI.

$$\frac{V_{cell}}{2V_T} = |(\psi_{St} - \psi_b) + (\psi_0 - \psi_{St})| \quad (17)$$

The surface charge density on the Stern plane, according to the GCS model is given by Equation 14, where $c_b$ is the bulk ion concentration, and $\lambda_D$ is the Debye length

$$\sigma = 4c_b\lambda_D sinh\left(\frac{(\psi_{St}-\psi_b)}{2}\right) \quad (14)$$

The Stern layer is modeled as a capacitor in order to determine the dimensionless potential at the Stern plane, $\psi_{St}$. To do this, charge neutrality
is used to equate the charge held on the Stern layer surface and the diffuse layer with the charge held on the electrode surface, which is not in accordance with the capacitor-in-series model. This is explained in more detail in Section 2.3.2 and the result is Equation 18, where $C_{St}$ is the capacitance of the Stern layer, $\sigma$ is the charge density in mol/m$^2$, $F$ is the Faraday constant, and $\psi_0$ is the dimensionless applied potential.

$$C_{St}(\psi_0 - \psi_{St})V_T = \sigma F$$  \hfill (18)

The Poisson equation, is given in Equation 40 and describes the curvature of dimensionless potential with respect to distance, $\frac{d^2\psi}{dx^2}$, by relating it to the charge density, $\sigma$, where $\sigma = zc_+ - zc_-$, and the dielectric permittivity is $\varepsilon_r\varepsilon_0$. In the equation for charge density, $c_+$ and $c_-$ are the surface concentrations of cations and anions, respectively and $z$ is the magnitude of the valence charge. The Poisson equation is then solved along with Equation 41, assuming that $x$ is in the direction perpendicular to the charged surface. Equation 41 governs the chemical equilibrium of the ions.

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{F}{\varepsilon_r\varepsilon_0 V_T}(c_+ - c_-)$$  \hfill (40)

$$ln c_i(x) + z_i \psi(x) + \mu_{ex,x} = ln c_b + \mu_{ex,b} + \psi_b$$  \hfill (41)
In Equation 41, is the chemical equilibrium equation relating the local ion concentration, \( c_i \), to the bulk ion concentration, \( c_b \), through a balance between the supplied voltage and the electrochemical potential excesses in the local, \( \mu_{ex,x} \), and bulk, \( \mu_{ex,b} \) cases. This excess electrochemical potential term is determined by from the volume fraction of ions with a higher volume fraction of ions has a higher excess electrochemical potential. This term accounts for the difficulty in packing ions and utilizes a portion of the applied potential for this purpose. These excess electrochemical potential values are dimensionless and are determined through the CS equation of state, explained below. The excess electrochemical potential at a given location is shown in Equation 42, which is the Carnahan-Starling equation of state.

\[
\mu_{ex} = \eta \frac{8 - 9\eta + 3\eta^2}{(1 - \eta)^3} \tag{42}
\]

In Equation 43, \( \eta \) is the local ion fraction in which \( v \) represents the volume of one ion and \( n_+ \) and \( n_- \) are the number concentrations of the cations and anions, respectively. The volumes for cations and anions are the same under the initial assumptions of a monovalent, symmetric salt. The volume of a single ion is determined from the ion’s hydrated diameter, \( d_{ion} \), and geometry as given in Equation 44.
\[ \eta = v(n_+ + n_-) \]  

(43)

\[ v = \frac{\pi d_{\text{ion}}^3}{6} \]  

(44)

Finally, Equation 9 describes the linear reduction of potential across the length of the Stern layer, \( \delta \), given by the hydrated ionic radius. Along with the boundary conditions of \( V = 0 \) as \( x \) approaches infinity and \( V = V_d \) at the Stern plane \(^{40}\). Here \( V_{St} \) is the voltage drop across the Stern layer in volts.

\[ \left. \frac{dV}{dx} \right|_{St} = -\frac{V_{St}}{\delta} \]  

(9)

Providing the volume fraction is never predicted to be above 0.55, the CS equation will provide a very accurate adjustment for the finite ion volume effects experienced in CDI once incorporated into the GCS model for CDI.


3.0 Model Development

Accurately modeling salt adsorption in CDI operation presents a unique challenge due to the complex morphology of the activated carbon composite electrodes commonly used. These electrodes can have wide pore size distributions that include sub 1 nm pores, pores >100 nm as well as varying pore geometries, usually modeled as slit-shaped and cylindrical. When a potential is applied to the carbon surface, these pores will form very different potential distributions. In accordance with GCS theory, if the pore size is large enough to accommodate full, non-overlapping double layers and the charged surface is flat, as shown in Figure 9A, the potential profile will be accurately represented by separate GCS double layers.

In the case of very small pore size, or large surface curvature, the diffuse layers will experience EDL overlapping. In order to model this, Biesheuvel et al. proposed the mD model, as presented in previous sections 32. This model assumes that in micropores (< 2 nm) the double layer will be
overlapped so strongly that the potential profile in the diffuse layer can be approximated by a constant value, as shown in Figure 9C.

These pore regimes could be easily modeled by determining the applicable fraction of pore volume and applying each model respectively; however, neither model can conceptually represent the intermediate case of moderate diffuse layer overlap, as shown in Figure 9B.
In order to create a truly predictive CDI model, all pore regimes must be able to be represented by a model or combination of models that use only measurable electrode characteristics and operating conditions for prediction. In order to do this, the relevant literature was examined and the mD and GCS models were selected for modification due to their well-established theoretical basis and their use of many measurable characteristics. Modifications will focus on strengthening the logical basis for each model as well as removing or replacing arbitrary or fitting parameters.

**3.1 mD Model Modifications**

The mD model has strengths in that it is mathematically simple and has a theoretical basis in the well-established GCS theory. However, the model as presented by Biesheuvel et al.\textsuperscript{32}, relies on a fitting parameter, $\mu_{att}$, assumes a constant value for the capacitance of the Stern layer, $C_{St}$, and does not account for finite ion size\textsuperscript{32, 40}. In order correct these faults, the fitting parameter will be removed, the Stern layer calculation will be revised and the CS correction for finite ion size will be included, all while accounting for both cylindrical and slit-shaped pore geometries.

The $\mu_{att}$ term is explained as the attractive force between the ion and uncharged carbon surface, but in practice is a set value that is established for
a specific carbon material through fitting as this value would be difficult to
determine through measurement because it would be different for each unique
carbon/ion pairing\textsuperscript{32}. For complex influent solutions, this would take
considerable effort. This is incompatible with a truly predictive model so it
was removed. Since this term accounts for the ions removed through
physisorption, the model generated will only predict the quantity of salt ions
removed through electrosorption, which is equivalent to the total number of
ions removed minus the ions removed through physisorption.

The original mD model is assumed to apply only to the microporous
volume. For the purposes of this thesis, the mD model will be considered as
applicable to the total porous volume in order to later be able to determine the
ture pore size cutoff of mD applicability.

Additionally, the potential at the Stern plane in the mD model is
assumed to be a constant value for the entire surface area of the carbon,
regardless of pore structure. Since the Stern layer is treated as a capacitor,
surface charge density must be determined in order to find the voltage drop
across it. In order to determine this surface charge density, the charge will be
integrated across the Stern plane and diffuse layer.
Furthermore, the mD model in its current state has very limited applicability. The assumptions made in the GCS model, the framework on which the mD model is built, require low concentrations and low voltages be present due to the assumption of ions as point charges. Since neither of these conditions is met in typical CDI operation as higher concentrations and applied voltages are present, an additional modification is necessary. To prevent the impossibly high concentrations predicted by GCS-based models in these conditions, the Carnahan-Starling correction will be added in the form of a detractive, dimensionless electrochemical potential, representing the energy required for ions to become closely packed due to decreased solvent volume.

Since the CS correction is based upon decreased solvent volume, first the single ion volume must be calculated, as in Equation 44, were \( d_{ion} \) is the arithmetic mean hydrated ionic diameter of the cation and anion, and then the total volume fraction of ions in solution can be determined as in Equation 43, where \( n_+ \) and \( n_- \) are the cation and anion concentration, respectively, when values are in number concentration per cubic meter and \( \nu \) is in units of cubic meter such that \( \eta \) is dimensionless 40.

\[
\nu = \frac{\pi d_{ion}^3}{6}
\]  

(44)
\[ \eta = v(n_+ + n_-) \quad (43) \]

This volume fraction is then used to calculate the dimensionless electrochemical potential corrections for the bulk and microporous concentrations, \( \mu_{\text{ex},b} \) and \( \mu_{\text{ex},p} \), respectively, in accordance with the CS equation as shown in Equation 42\(^{40}\).

\[ \mu_{\text{ex}} = \eta \frac{8-9\eta+3\eta^2}{(1-\eta)^3} \quad (42) \]

These dimensionless electrochemical potential correction terms for the bulk and microporous concentrations are then used to adjust the applied potential in accordance with the chemical equilibrium given in Equation 45, where \( c_i \) is the local concentration in either the bulk, \( c_b \), or the micropore, \( c_p \), \( z_i \) is the sign of the charge of the ion in question, \( \psi_{\text{St}} \) is the dimensionless potential at the Stern plane and \( \psi_b \) is the dimensionless potential in the bulk solution, usually taken to be zero. Both of the last two terms have been normalized by the thermal voltage (i.e. \( \psi = \frac{V}{V_T} \))\(^{40}\).

\[ \ln c_{i,p} + z_i \psi_{\text{St}} + \mu_{\text{ex},p} = \ln c_{i,b} + \mu_{\text{ex},b} + z_i \psi_b \quad (45) \]

Therefore, solving for the concentration of ion \( i \) in the micropore gives Equation 46, while either adding the concentrations of the ions for a total micropore concentration (i.e. \( c_p = c_{+,p} + c_{-,p} \)) or subtracting the
microporous anion concentration from the microporous cation concentration for the microporous charge (i.e. $\sigma_p = zc_{+,p} - zc_{-,p}$) gives Equations 47 and 48, respectively, where $z$ is the magnitude of the valence charge of the ion.

$$c_{i,p} = c_b \exp \left( \mu_{ex,b} - \mu_{ex,p} - z_i(\psi_{St} - \psi_b) \right) \quad (46)$$

$$c_p = 2c_b \exp(\mu_{ex,b} - \mu_{ex,p}) \cosh(z(\psi_{St} - \psi_b)) \quad (47)$$

$$\sigma_p = -2zc_b \exp(\mu_{ex,b} - \mu_{ex,p}) \sinh[z(\psi_{St} - \psi_b)] \quad (48)$$

The dimensionless potential at the Stern plane, $\psi_{St}$, can be determined by treating the Stern layer as a capacitor as is originally discussed in Section 2.3.2 and modified from the original mD model as described earlier in this section. The dimensionless potential at the Stern plane is given in Equation 49, where $r_{ion}$ is the radius of the hydrated ion, taken as the thickness of the Stern layer, $\varepsilon_r \varepsilon_0$ is the dielectric permittivity, $V_T$ is the thermal voltage, $C_{St}$ is the capacitance of the Stern layer, given in Equation 50 for slit-shaped pores and in Equation 51 for cylindrical pores, $F$ is the Faraday constant, and $\sigma$ is the charge in mol/m$^3$.

$$\psi_{St} = \psi_0 - \frac{\sigma r_{ion} FA}{C_{St} V_T} \quad (49)$$

$$C_{St} = \varepsilon_r \varepsilon_0 \frac{A}{r_{ion}} \quad (50)$$
\[ C_{St} = 2\varepsilon_r\varepsilon_0 \frac{v}{(d/2)^2 \ln \left( \frac{(d/2)}{(d/2-r_{ion})} \right)} \] (51)

Finally, the voltage drop across the diffuse layer can be determined from its relation to the applied cell voltage and the voltage drop across the Stern layer via Equation 17.

\[ \frac{V_{cell}}{2v_T} = |(\psi_{St} - \psi_b) + (\psi_0 - \psi_{St})| \] (17)

Equations 42-44, 46-51, and 17 make up the model that will be subsequently referred to as the mD-CS model. This can easily be worked iteratively using a Microsoft Excel spreadsheet and the basic Solver application.

Specifically, Equations 42-44, 49-51 were calculated in the spreadsheet with an assumed porous ionic and charge concentration term. Equations 47 and 48 were then used to calculate the porous ionic and charge concentrations based upon these values. Finally, Solver was used to make the assumed and calculated values equal to each other, making the model self-consistent. An example spreadsheet is included in the appendix.
3.2 GCS Model Modifications

The GCS theory has been well-established as a robust framework for describing the potential and ion distribution near weakly charged surfaces in dilute solutions. It describes an exponential decrease in both as distance from the charged surface increases. In order to apply this theory to CDI well, a few adjustments were made.

First, it was noted that the previously presented GCS model developed by Biesheuvel et al.\textsuperscript{32} aims to predict the potential and concentration distributions in cylindrical pores while using the PB equation applicable only to flat, charged surfaces. To correct this, the GCS model will be made into two models: one for slit-shaped pores which utilizes the PB equation derived for flat surfaces, shown in Equation 52, and one for cylindrical pores based on the radial PB equation, shown in Equation 53.\textsuperscript{42}

\[
\nabla^2 V = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{\rho(x,y,z)}{\varepsilon_r \varepsilon_0} \tag{52}
\]

\[
\nabla^2 V = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial V}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 V}{\partial \theta^2} + \frac{\partial^2 V}{\partial z^2} = -\frac{\rho(r,\theta,z)}{\varepsilon_r \varepsilon_0} \tag{53}
\]

This is where \( V \) is the local potential in volts, \( x, y, \) and \( z \) are the dimensions perpendicular to the charged plate, parallel and vertical to the charged plate, and parallel and horizontal to the charged plate, \( \sigma_c \) is the local
charge concentration in C/m³, \( \varepsilon_r \varepsilon_0 \) is the dielectric permittivity in C/Vm, and \( r, \theta, \) and \( z \) are the radial, angular, and length axes of the cylindrical pore.

Assuming a slit-shaped pore that is infinitely large in either of its dimensions parallel to the charged plate, there should be no variation in these directions and the equation can be reduced to the 1-D planar Poisson equation in the x direction, as shown in Equation 54.

\[
\frac{\partial^2 V}{\partial x^2} = -\frac{\sigma_c(x)}{\varepsilon_r \varepsilon_0}
\]  

(54)

Also, for an infinitely long cylindrical pore, there will be no variation with angle, \( \theta \), or length, \( z \). This, along with dividing through by the thermal voltage, \( V_T \), to make this equation a description of the dimensionless voltage and replacing charge density in C/m³ to a density in mol/m³, \( \sigma \), converted by \( F \), Faraday’s constant, yields the simplified relation given in Equation 55.

\[
\frac{\partial^2 V}{\partial r^2} = -\frac{\sigma_c(r)}{\varepsilon_r \varepsilon_0} - \frac{\partial V}{\partial r} \frac{1}{r}
\]  

(55)

As with the mD model, the CS correction was incorporated into each GCS model. Quantification of this electrochemical potential is done as in the mD model by first calculating the single ion volume, \( v \), from the average hydrated diameter of the cation and anion, \( d_{ion} \), in Equation 44 then the volume fraction of ions, \( \eta \), from the number concentration of cations and
anions \((n_+ \text{ and } n_-\text{, respectively})\) in Equation 43 and finally the electrochemical potential in accordance with the CS correction in Equation 42\(^{40}\). This correction term is again applied to the chemical equilibrium shown in Equation 41, where \(c_i\) is the local ion concentration of ion \(i\), \(z_i\) is the valence number and charge of the ion, \(\mu_{ex,b}\) and \(\mu_{ex,x}\) are the dimensionless excess electrochemical potential terms for the bulk and local ion concentrations, and \(c_b\) is the bulk ion concentration. This equation differs from the chemical equilibrium given in the mD-CS model only in that the concentration can be determined for any given distance, \(x\), from the charge surface instead of only in the microporous volume \(^{40}\).

\[
\ln c_i(x) + z_i \psi(x) + \mu_{ex,x} = \ln c_b + \mu_{ex,b} + z_i \psi_b
\]  

(41)

\[
v = \frac{\pi d_{ion}^3}{6}
\]  

(44)

\[
\eta = v(n_+ + n_-)
\]  

(43)

\[
\mu_{ex} = \frac{8 - 9\eta + 3\eta^2}{(1-\eta)^3}
\]  

(42)

By solving the chemical equilibrium for the local ionic concentration and then summing the cation and anion concentrations and finding the difference between them, the total ionic concentration, \(c_d\), and local charge
concentration, $\sigma_x$, respectively, can be calculated, each in mol/m$^3$, where $z$ is the magnitude of the valence number on the ion. This is an identical process as was presented to determine Equations 46-48 and was used to determine the slightly modified versions shown in Equations 56-58 that differ only in their ability to determine their values for a given distance, $x$, from the charged surface.

$$c_{i,x} = c_b \exp\left(\mu_{e,x,b} - \mu_{e,x} - z_i(\psi(x) - \psi_b)\right)$$  \hspace{1cm} (56)

$$c_d = 2c_b \exp\left(\mu_{e,x,b} - \mu_{e,x}\right) \cosh(\psi(x) - \psi_b)$$  \hspace{1cm} (57)

$$\sigma_x = -2zc_b \exp\left(\mu_{e,x,b} - \mu_{e,x}\right) \sinh z(\psi(x) - \psi_b)$$  \hspace{1cm} (58)

Incorporation of Equation 58 into the complete Poisson Boltzmann (PB) equations can be determined for each pore geometry, with that for slit-shaped pores given by the planar PB equation in Equation 59 and that for cylindrical pores given by the radial PB equation in Equation 60.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{F}{\varepsilon_r \varepsilon_0 V_T} \left(2zc_b \exp\left(\mu_{e,x,b} - \mu_{e,x}(x)\right) \cdot \sinh(z\psi(x))\right)$$  \hspace{1cm} (59)

$$\frac{\partial^2 \psi}{\partial r^2} = \frac{F}{\varepsilon_r \varepsilon_0 V_T} \left(2zc_b \exp\left(\mu_{e,x,b} - \mu_{e,x}(r)\right) \cdot \sinh(z\psi(r))\right) - \frac{\partial \psi}{\partial r} \frac{1}{r}$$  \hspace{1cm} (60)
Additionally, as with the mD-CS model, the calculation of $\psi_{St}$, in Equation 49, is based on the capacitor-in-series model, taking the Stern layer as a capacitor with the charge held on the Stern plane and within the entire diffuse layer taken as the charge on the capacitor as in the original GCS model developed by Biesheuvel et al.32 This charge value, $\sigma_{St}$, is then used as the charge term when calculating $\psi_{St}$ from both the planar (Equation 50) and cylindrical (Equation 51) capacitance equations.

$$\psi_{St} = \psi_0 - \frac{\sigma_{St} r_{ion} F \cdot SA}{C_{St} V_T} \quad (49)$$

$$C_{St} = \varepsilon_r \varepsilon_0 \frac{SA}{r_{ion}} \quad (50)$$

$$C_{St} = 2 \varepsilon_r \varepsilon_0 \frac{V}{(d/2)^2 \ln \frac{(d/2)}{(d/2-r_{ion})}} \quad (51)$$

The resulting modeling equations will be referred to subsequently as the GCS-CS model and have no analytical solution, so they must be solved numerically. In this work, Matlab’s bvp4c structure was used to solve the second-order, non-linear ordinary differential equations given in Equations 59 and 60 with boundary conditions of the potential at the Stern plane being equal to $\psi_{St}$ calculated from the charge distribution, and the potential at a large distance from the charged plate, $\psi_b$, being equal to zero, as shown in
Equations 61 and 62. In order to determine the correct value of $\psi_{St}$, the bvp4c structure was run iteratively.

\begin{align*}
\text{BC 1: } & \psi(0) = \psi_{St} \quad \quad (61) \\
\text{BC 2: } & \psi(\infty) = 0 \quad \quad (62)
\end{align*}

Concentration profiles and specific adsorption values were calculated once this process concluded in accordance with the appropriate equations presented previously. An example of the code used for this purpose is shown in the appendix.

3.2.1 GCS-CS Model with Pore Geometry

While the previous model approximately replicates the concept of a double layer within very large pores in CDI applications, neither the mD-CS model nor the GCS-CS model can accurately represent the theoretical potential or concentration profile in pores with moderate diffuse layer overlap. In order to replicate this case, the GCS-CS model was modified to account for overlapping EDLs.

To do this, a simple modification of boundary conditions was implemented, as shown in Equations 63 and 64. The overlapping EDL case requires the potential at the Stern plane to be equal to the calculated value of $\psi_{St}$, as in the non-overlapping GCS-CS model; however, for the overlapping
case, the first derivative of potential at the pore center is required to be zero, assuming a symmetric potential profile across the pore, which forces the slope of potential in the center of the pore to be zero. These boundary conditions apply to either slit-shaped or cylindrical pores.

\[ \text{BC 1: } \frac{d\psi}{dr}(0) = 0 \]  \hspace{1cm} (63)

\[ \text{BC 2: } \psi(R') = \psi_{St} \]  \hspace{1cm} (64)

For slit-shaped pores, the \( x \)-coordinate is taken to be the coordinate perpendicular to the charged plates. The zero value for this coordinate will be located in the center of the pore, equidistant from each charged plate. The two charged plates will then be located at \( x \)-values of \( R \) and \(-R\), where \( R \) is the pore radius, and the Stern plane will be located at \( x \)-values of \( R' \) and \(-R'\), where \( R' \) is the pore radius less the thickness of one Stern layer. A depiction of this show in Figure 10.
Figure 10: Coordinate Systems for Slit-Shaped and Cylindrical Pores
For cylindrical pores, the $r$-coordinate is the radial coordinate and will be taken as zero at the center of the pore. The charged outer wall will then be located at an $r$-value of $R$ and the Stern plane at $R'$. Note that this means the entire circular Stern plane exists at the $r$-value $R'$ and there are no negative values in this coordinate system. Because of this, the profile generated for $r$-values $0$ to $R'$ will be mirrored onto values from $0$ to $-R'$ in order for the profiles generated to be more easily compared to profiles generated from the modeling of slit-shaped pores.

Matlab code was written to solve Equations 59 and 60 very similarly to what is described for the GCS-Cs model, only with the above mentioned boundary conditions that apply to the overlapped EDL case. Example code is shown in the appendix.
4.0 Results and Discussion

4.1 GCS-CS Model with Pore Geometry Validation

In order to validate the GCS-CS model with pore geometry, a simplified version of the model previously presented in Section 3.2.1 is compared to a known approximation of the PB equation, the Gouy-Chapman (GC) model. Since the GC model assumes ions are point charges, the ion diameter term in the full, GCS-CS model with pore geometry was reduced to zero, effectively eliminating the Stern layer and the Carnahan-Starling electrochemical potential correction. In addition, the pore width/diameter was increased to minimize the effect of EDL overlap. If the model has been developed correctly, the GCS-CS model with pore geometry with these conditions should agree with the GC approximation, given by Equation 66.

The GC model is governed by Equation 65\textsuperscript{43}, given below.

\[
\psi(x) = 2 \cdot \ln \left( \frac{\exp\left(\frac{z\psi_0}{2} \right) + 1 + \left(\exp\left(\frac{z\psi_0}{2} \right) - 1\right) \exp(-\kappa x)}{\exp\left(\frac{z\psi_0}{2} \right) + 1 - \left(\exp\left(\frac{z\psi_0}{2} \right) - 1\right) \exp(-\kappa x)} \right) \tag{65}
\]

Where \(\psi(x)\) is the local, dimensionless potential, \(\psi_0\) is the applied potential, \(x\) is the distance variable, \(\kappa\) is the inverse Debye length, and \(z\) is the magnitude of the valence charge on the ions.
\[
\kappa = \frac{2zc_b e^2 N_Av}{\varepsilon_r \varepsilon_0 k_B T}
\] (66)

Where \( c_b \) is the bulk salt concentration in mol/m\(^3\), \( e \) is the elementary charge, \( N_Av \) is Avogadro’s number, \( \varepsilon_r \varepsilon_0 \) is the dielectric permittivity, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature.

When the GCS-CS model with pore geometry for slit-shaped pores is compared with the GC approximation when the applied voltage is 1.2 volts, the influent concentration is 10 mg/L (0.1711 mol/m\(^3\)), and the pore width is 1000 nm (1 \( \mu m \)), the results are approximately identical, as shown in Figure 11A. However, when the same conditions are applied to a cylindrical pore the results are not as precise. This is because the curvature present in the cylindrical pore is still significant enough to cause a small deviation from the GC approximation, which is based on the assumption of a flat surface.

However, if the pore diameter is increased further to 1,000,000 nm (1 mm) to reduce overlapping due to surface curvature, the results are much closer, as in Figure 11B. Because these results are extremely similar in value, it is determined that the GCS-CS model with pore geometry is valid and has been developed correctly.
Figure 11: Model Validation for A) Slit-Shaped Pores at a 1000 nm Pore Width and B) Cylindrical Pores at a 1,000,000 nm Pore Diameter
4.2 GCS-CS with Pore Geometry Analysis

Model activated carbons (MACs) with uniform pore size distributions were mathematically constructed for both slit-shaped and cylindrical pores in order to facilitate comparable results. Each MAC construct was given the same bulk density (450 kg/m$^3$), porosity (0.78), and the total pore volume was also kept constant at 1.73 cm$^3$/g to ensure relevant intermodel comparisons.

MACs were assumed to have either completely uniform cylindrical pores whose volume and surface area could be modeled as a single, long cylinder with no ends, or completely uniform slit-shaped pores whose volume and surface area could be modeled as two large parallel plates with no sides. As such, the surface area could be calculated for each through simple geometry. Values used are typical activated carbon values. Six MACs were generated with uniform pore widths/diameters of 1, 2, 3, 4, 5, and 10 nm.

Influent concentrations were varied from 500 mg/L to 50,000 mg/L (500, 1000, 5000, 10,000, 25,000, and 50,000 mg/L) and applied voltages between 0.2 and 1.2 V (0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 V). In each case, the influent salt compound used is sodium chloride. Hydrated ionic diameters of 850 pm and 600 pm were assumed for Na$^+$ and Cl$^-$, respectively, giving an average ionic diameter of 725 pm $^{44}$. This was assumed for both ions for simplicity.
Modeling results indicated that nonoverlapped, moderately overlapped, and strongly overlapped pore regimes were all indeed present for both pore geometries in the operational conditions typical of CDI. Below are samples of each type of pore regime found during modeling including the strongly overlapped (Figure 12A), moderately overlapped (Figure 12B), and nonoverlapped (Figure 12C) pore regimes.
Figure 12: Observed Pore Regimes

A) strongly overlapped, B) moderately overlapped, and C) nonoverlapped
Along with the potential profile, the concentration profile was also generated and was integrated over the pore volume to give a specific salt adsorption term. These results will be used to determine the effect of pore size and geometry, applied voltage, and influent salt concentration on CDI performance in subsequent sections.

4.2.1 Effect of Pore Size

Interestingly, the pattern of specific salt adsorption of NaCl for each pore geometry remained generally constant across all applied voltages and salt concentrations. For slit-shaped pores the pattern starts with low adsorption values in 1 nm pores, due to the large volume occupied by the Stern layer, after which adsorption increases rapidly with increasing pore size until an optimal value is reached at approximately a 2 nm pore diameter. The adsorption values then decrease at a slower, but steady rate with increasing pore size until the maximum modeled pore size of 10 nm is reached. The consistency of this pattern can be seen in in the comparison of adsorption plots for 500 mg/L at 1.2 V (Figure 13A) and 0.2 V (Figure 13B). The large difference in specific adsorption observed between the presented data is due to the significant difference in applied voltage.
Figure 13: Comparison of the Effects of Pore Size
At A) 1.2 V, B) 0.2 V both at 500 mg/L influent concentration
This pattern is largely due to the structure of the concentration profile given by the GCS-CS model with pore geometry. In the 1 nm pores, the Stern layer encompasses about 73% of the pore volume such that very small amounts of salt adsorption are accomplished in them. The percentage of the pore that is inaccessible to ions can be determined through simple geometry. If the sides of the pore are separated by the pore width and the Stern layer extends for a distance equal to the hydrated ionic radius, twice this value should be subtracted from the original pore width to account for both Stern layers and give the width of pore available for ion removal. This can then be divided by the original pore width to determine the percentage of pore volume available for ions. As the pore diameter increases up to the optimal pore diameter of approximately 2 nm, the effect of the increase in pore proportion that is available for salt adsorption is dominant. This is due to the combination of decreased percentage of volume occupied by the Stern layer (now only about 35%) and sustained constant potential profile. After this point, the additional diameter decreases salt adsorption ability due to the low potential values that are reached in the pore center.

This trend can be better visualized by viewing the series of concentration profiles in pores of varying sizes at an applied voltage of 1.2 V and influent salt concentration of 10,000 mg/L, shown in Figure 14. This data
set was chosen for its ability to depict the transition from strongly overlapped pores to nonoverlapped pores only by varying pore diameter. Changes in influent concentration and applied voltage can also contribute to changes in pore regime. These effects will be discussed in subsequent sections.

For cylindrical pores, salt adsorption is very low for 1 nm pores and gradually increases to a broad peak of maximum salt adsorption between 3 and 4 nm. As pore size continues to increase, salt adsorption gradually decreases, but more slowly than for slit-shaped pores.

This trend can also be explained by imagining the pore geometry in combination with the Stern layer and any portion of the pore in the center where the potential is low and there is no significant ion removal, with the help of the concentration profiles in Figure 15. In cylindrical pores with a diameter of 1 nm, the Stern layer for an NaCl electrolyte would occupy approximately 92% of the pore volume as compared to only 73% for slit-shaped pores. Again, with this percentage figure determined by basic geometry, but here the ratio of pore area not occupied by the Stern layer to total pore cross-sectional area is important. As the pore diameter increases, the cylindrical pores maintain higher salt adsorption values for a larger range of pore diameters than for slit-shaped pores. This is due to the stronger EDL overlapping caused by the surface curvature present. Also, when the potential
does decrease in the center of the pore when the pore diameter becomes large enough for this, the center of the pore is a smaller portion of the pore volume that in a slit-shaped pore with an identical cross-sectional potential profile.

The influent salt concentration also influences the optimum pore size and geometry for carbon materials used as CDI electrodes. Figure 16 and Figure 17 show the relationship between influent salt concentration, applied voltage, and pore diameter for each salt concentration with regard to both slit-shaped and cylindrical pores. The model shown in these figures is assuming a negatively charged electrode and the bulk concentration shown in the plots is the influent ion concentration, which is twice the influent salt concentration. These series of graphs are valuable tools for determining the optimal operating conditions for a waste stream with a given salinity. In the case of slit-shaped pores, the optimal pore width was consistently 2 nm and seemed to be independent of either applied voltage or influent salt concentration. Similarly, cylindrical pores present optimal salt adsorption values between 3 and 4 nm. This again does not vary significantly with either influent salt concentration or applied voltage.

While it is likely these optimal pore diameters are only valid for NaCl or ions with similar charge and hydrated radii, it is useful to know that the
optimal pore width/diameter is only dependent on the salt ions present and the pore geometry, not the applied voltage and influent salt concentration as well.
Figure 14: Pore Regime Transition – Slit-Shaped Pores
Concentration profiles at 10,000 mg/L, 1.2 volts, and A) 1 nm wide pores, B) 2 nm wide pores, C) 3 nm wide pores, D) 4 nm wide pores, E) 5 nm wide pores, and F) 10 nm wide pores
Figure 15: Pore Regime Transition – Cylindrical Pores
Concentration profiles at 10,000 mg/L, 1.2 volts, and A) 1 nm diameter pores, B) 2 nm diameter pores, C) 3 nm diameter pores, D) 4 nm diameter pores, E) 5 nm diameter pores, and F) 10 nm diameter pores
Figure 16: Surface Plots of the Effect of Pore Diameter, Applied Voltage, and Influent Salt Concentration for Slit-Shaped Pores at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L
Figure 17: Surface Plots of the Effect of Pore Diameter, Applied Voltage, and Influent Salt Concentration for Cylindrical Pores

at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L
4.2.2 Effect of Influent Salt Concentration

Influent salt concentration impacts the ultimate amount of salt adsorbed by CDI because the local ion concentration is a function of the bulk salt concentration, among other variable, as shown in Equation 57. In this equation $c_{ex}(x)$ is the local excess ion concentration found by subtracting the bulk ion concentration from the local ion concentration to separate the additional ions removed, $c_b$ is the bulk salt concentration, $\mu_{ex,b}$ and $\mu_{ex,x}$ are the bulk and local dimensionless electrochemical potential correction terms derived from the CS correction, and $\psi(x)$ and $\psi_b$ are the local dimensionless potential and the bulk dimensionless potential, respectively. From this equation it can be hypothesized that a higher bulk concentration will result in a higher amount of salt removed as long as the ions do not become too crowded and cause a large CS correction term and/or the bulk ion concentration does not become so high that subtracting it from the local ion concentration becomes significantly detrimental to the excess ion concentration. The balancing of these factors is shown in Figure 18.

$$c_{ex}(x) = 2c_b \left[ \exp(\mu_{ex,b} - \mu_{ex,x}) \cosh(\psi(x) - \psi_b) - 1 \right]$$  \hspace{1cm} (57)

In this figure it can be seen that the optimal influent salt concentration at the applied dimensionless potential of 23.353 is at or below 10,000 mg/L,
which is a situation that would be present in many smaller pores of approximately 1 nm for slit-shaped pores and 1-2 nm for cylindrical pores. However for lower potentials, this optimal influent salt concentration range becomes narrower. For example, at a local dimensionless potential of 10, which is more common in larger pores, the optimal influent salt concentration range is between 5000 and 10,000 mg/L.

![Figure 18: Curves of Excess Salt Concentration as it Changes with Potential for all Influent Salt Concentrations](image)

This analysis indicates that the optimal influent salt concentration can be different for each pore size and geometry and is a lower concentration in
larger size pores. For example, in the case of 10 nm pores in both slit and cylindrical geometries, the optimal influent salt concentration is 1000 mg/L, but for pores size 5 nm and less, this shift occurs at 5000 mg/L. This shift in optimal salt concentration is due to increased importance of the CS correction term of Equation 57.

These results can also explain the literature data indicating that the optimal influent salt concentration is much less than 5000 mg/L \(^1\). Since many composite AC electrodes are comprised of particles of powdered activated carbon (PAC), there are often larger macropores present between particles which can sum to a significant portion of total pore volume \(^{45}\). As is seen from the modeling results, increasing pore diameter leads to a decrease in optimal influent salt concentration which could influence the optimal value for the composite electrode as a whole. This result is promising for the technology because it indicates that if materials are generated that have a very tunable pore size, as with vertically-aligned carbon nanotubes (CNTs), the applicable salinity range of CDI could be increased.

Furthermore, an analysis of Coulombic efficiency was conducted across all conditions and for both pore geometries, the results of which are shown in
Figure 19 and Figure 20. To determine these values, the excess concentration and charge were integrated through the volume of the pore to give the total amount of excess ions and charge per unit pore volume. These were then compared in accordance with Equation 22 to give the charge efficiency, or the number of salt ions removed per electron transferred to the electrode, where $c_{d,tot}$ is the total amount of ions in the pore, integrated across the diffuse layer, $c_b$ is the bulk concentration, $q$ is the charge present in moles, integrated across the diffuse layer, and $z$ is the magnitude of the charge on the cation and anion.

$$\Lambda = \frac{z(c_{d,tot}-c_b)}{q}$$ \hspace{1cm} (22)

This data is useful in cases where energy efficiency is valued either over specific salt adsorption capacity or in conjunction with it. For slit-shaped pores, results indicate that Coulombic efficiency decreases with increasing pore width. Additionally, it is observed that decreasing applied voltage is associated with decreasing Coulombic efficiency as is increased influent salt concentration, as can be seen in Figure 19.
Patterns for cylindrical pores show very similar overall trends, but with a decreased negative effect when increasing pore diameter, as can be seen in Figure 20.
Figure 19: Coulombic Efficiency Comparison through Variation of Influent Concentration, Applied Voltage, and Pore Diameter for Slit-Shaped Pores at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L
Figure 20: Coulombic Efficiency Comparison through Variation of Influent Concentration, Applied Voltage, and Pore Diameter for Cylindrical Pores at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L.
The decrease of applied dimensionless potential and increase in pore size both have a negative impact on Coulombic efficiency, and really for the same reason. The ultimate cause is the presence of low dimensionless local potential values within the pore. At these lower potential values, a lower local ion concentration is predicted. When this happens, the detrimental bulk concentration term in Equation 20 becomes increasingly significant. This effect is only magnified by the already larger bulk salt concentration term present for higher influent salt concentrations, all of which is reflected in the graphs of Coulombic efficiency above.

4.2.3 Effect of Applied Voltage

As is logical, the modeling results indicate that in all cases at a fixed combination of influent concentration and pore size and geometry, increasing the applied voltage up to a value of 1.2V also increases predicted specific salt adsorption.

More interestingly, the effect of concentration was found to be magnified at lower applied voltages, as shown in Figure 21 for slit-shaped pores and Figure 22 for cylindrical pores. The changes in the potential profile across the Stern layer are more pronounced in the case of 0.6 V applied than for 1.2 V.
Figure 21: Effect of Concentration at (A) High and (B) Low Voltage for Slit-Shaped Pores at 1 nm Pore Width
Figure 22: Effect of Concentration at (A) High and (B) Low Voltage for Cylindrical Pores at 1 nm Pore Diameter

This can be explained through the non-linearity in the relation between the predicted local ion concentrations and local dimensionless potential, as
shown in Figure 23 and Equation 58. At lower local potentials, which would be more likely to be present at a lower applied potential, the magnitude of the change in charge for a given change in potential is much greater than the corresponding change in charge that would occur for the same magnitude of change in potential at a higher potential, as is shown by the relative slopes shown in Figure 23. This trend along with the dependence of the potential at the Stern plane on the charge held in the diffuse layer, leads to higher variability of the potential at the Stern plane at lower voltages and at similar influent salt concentrations, as is evidenced in Figures 21 and 22. In addition, referring back to the Poisson Boltzmann equations given in Equations 59 and 60, the curvature of the potential profile is dependent in both geometries on the local charge concentration with a higher charge leading to a higher magnitude of curvature in the potential profile. This, again, supports the findings in Figure 21 and Figure 22 where the curvatures observed are increased at lower applied voltages for the same influent concentration.

\[
\sigma(x) = -2zc_b \exp(\mu_{ex,b} - \mu_{ex,x}) \sinh(\psi(x) - \psi_b)
\]  

\[
\frac{\partial^2 \psi}{\partial x^2} = -\frac{F}{\varepsilon_r \varepsilon_0 V_T} \cdot \sigma
\]  

\[
\frac{\partial^2 \psi}{\partial r^2} = -\frac{F}{\varepsilon_r \varepsilon_0 V_T} \cdot \sigma - \frac{\partial \psi}{\partial r} \frac{1}{r}
\]
Figure 23: Curves of Charge Concentration as it Changes with Potential for an Influent Salt Concentration of 5000 mg/L

4.2.4 Effect of Salt Ion

To analyze the effect of the influent salt ion, ions of different hydrated radii and valence charge were chosen. Namely, Li$^+$ and Ca$^{2+}$ were chosen because they each have a hydrated ionic diameter of 1.2 nm, but differ in valence charge \(^{44}\). Finally, SO$_4^{2-}$ was chosen because of its similar valence charge magnitude to Ca$^{2+}$ but has a smaller hydrated ionic diameter of 0.8 nm \(^{44}\). In each case, ions are assumed to have a counterion of equal size and
charge. This allows for easier comparison and determination of the effect of ion size and valence charge.

From the comparison between lithium (1.2 nm diameter, +1 charge) and calcium (1.2 nm diameter, +2 charge), shown in Figure 24, it is apparent that higher magnitude valence charge causes both a higher optimal adsorption capacity and a more compact diffuse layer. The higher optimal salt adsorption value is due to the stronger attraction between the ion and electrode, but is hindered by the inclusion of ion volume effects. The more compact diffuse layer, which results in a slightly smaller optimal pore width/diameter, depending on the pore geometry, causes an increased detrimental effect of increasing pore size.

Next, when comparing the graphs of calcium (1.2 nm diameter, +2 charge) and sulfate (0.8 nm diameter, -2 charge), it is obvious that a smaller hydrated ionic diameter has a much more dramatic effect of increasing the optimal salt adsorption value, with approximately three times more ions removed than at the optimal value for Ca$^{2+}$. This is due to the ability of more ions to fit into the same space. Ion size is also responsible for the even more compact diffuse layer and dramatic increase in the detrimental effect of increasing pore size. Also, the optimal pore diameter for sulfate is smaller, which is logical for its smaller size.
Figure 24: Effect of Hydrated Ionic Diameter and Valence Charge for (A) Lithium ions, (B) Calcium ions, and (C) Sulfate ions

4.3 Model Comparison

It is hypothesized by Biesheuvel et al.\textsuperscript{32} that the mD model proposed therein only accurately models the salt adsorbed in the micropores (<2 nm), but this is still an adequate model because, due to this overlapping effect, the majority of salt adsorption occurs in these micropores and the salt adsorbed in the meso- and macropores is insignificant. Likewise, it is hypothesized that the GCS model will be valid for large pores and/or high influent salt concentrations, but the resulting salt adsorption will be small in comparison to the mD prediction for microporous salt adsorption\textsuperscript{1,40}. These assumptions were made to allow for a mathematically simple model to be used to represent a complicated reality. While the views expressed in this thesis are not in agreement with the previously stated hypothesis, the value of representing a complex phenomenon with a simple construct is not lost as long as the simple construct can approximate the phenomenon relatively accurately.

Therefore, comparisons will be made between the GCS-CS model with pore geometry that has been validated through GC theory and the GCS-CS and mD-CS models described in previous sections to determine if these simpler models can, either alone or in combination, can approximate the GCS-CS model with pore geometry for both slit-shaped and cylindrical pores.
4.3.1 mD-CS Results

While the mD-CS model is only hypothesized to be applicable in the microporous range, it was applied to all MACs of varying pore sizes and geometries only in order to attempt to find the point for each geometry at which transition occurs between the mD-CS model and the GCS-CS model with pore geometry.

For slit-shaped pores, it was found that all three variables (influent salt concentration, applied voltage, and pore diameter) had a significant impact on specific salt adsorption for the mD-CS model. First, the effect of influent salt concentration can be seen below in Figure 25. The prediction for each concentration remains approximately unchanged for concentrations up to 10,000 mg/L, but is reduced dramatically from this concentration to 25,000 mg/L and again when the concentration is raised to 50,000 mg/L, as shown in Figure 25. This is hypothesized to be due to the combined effects of nonlinearity of the CS correction and the increased charge that must be used to expel the higher concentrations of coions initially in the pore space.

The effect of voltage is also significant, as shown in Figure 26, with consistently higher specific salt adsorption predicted for similar pore size and influent salt concentration at higher applied voltages, as would be expected.
Patterns seen for cylindrical pores are extremely similar. When analyzing the effect of influent salt concentration, it was also found that increasing the influent salt concentration has little effect through a value of 10,000 mg/L, as is seen in Figure 27. The same effect of voltage and pore size is also observed in Figure 28 as well.

Figure 25: mD-CS Modeling Results at 1.2V for Various Influent Salt Concentrations in Slit-Shaped Pores
Figure 26: mD-CS Modeling Results for an Influent Salt Concentration of 500 mg/L at Various Applied Voltages in Slit-Shaped Pores

Figure 27: mD-CS Modeling Results at 1.2V for Various Influent Salt Concentrations in Cylindrical Pores
As can be seen from the above figures, pore size also has a significant effect on the predicted specific salt adsorption. In the hypothesized applicable pore sizes of 1 and 2 nm, in each case the 2 nm pores have significantly higher specific adsorption that the 1 nm pores. This is due to the significant amount of space occupied by the Stern layer in the smaller pores.

4.3.2 GCS-CS Results

While the most common method of accounting for EDL overlap is through superposition, this method is only valid for slightly overlapping EDLs and would result in predicted potentials higher than the applied potential when
utilized for very small pores. For this reason, superposition was not used in the GCS-CS model. Instead, potential and concentration profiles were generated in accordance with the GCS-CS model previously proposed, assuming the potential falls to zero by a distance of 1000 nm from the charged surface. Once these profiles are generated, they are then truncated at a distance equal to the pore half-width or radius, as depicted in Figure 29. Subsequent to this, this truncated profile will be mirrored and the two profiles will be unified to create a complete potential profile for each pore geometry and pore size.
Figure 29: GCS-CS Interpore Profile Approximation Method
As with the mD-CS model, there is very little effect of influent concentration experienced at concentrations below 10,000 mg/L for slit-shaped pores. For cylindrical pores, at 10,000 mg/L the trend of decreasing salt adsorption is visible. For both pore geometries, between influent concentrations of 10,000 mg/L and 25,000 mg/L, there is a significant decrease in specific salt adsorption and again for the influent concentration increase to 50,000 mg/L, which can all be seen in Figure 30 and Figure 32. Like the mD-CS model, this is due to the nonlinear relationship between the local dimensionless potential and the local ion concentrations.

Again, as in the mD-CS model, applied voltage has a very predictable effect on specific salt adsorption, as shown in Figure 31 and Figure 33. As the applied voltage decreases for similar pore diameter/influend salt concentration pair, the specific salt adsorption predicted increases steadily with increasing applied voltage up to 1.2 V.
**Figure 30**: GCS-CS Modeling Results at 1.2 V and Various Influent Salt Concentrations in Slit-Shaped Pores

**Figure 31**: GCS-CS Modeling Results for an Influent Salt Concentration of 500 mg/L NaCl at Various Applied Voltages in Slit-Shaped Pores
Figure 32: GCS-CS Modeling Results at 1.2 V and Various Influent Salt Concentrations in Cylindrical Pores

Figure 33: GCS-CS Modeling Results for an Influent Salt Concentration of 500 mg/L NaCl at Various Applied Voltages in Cylindrical Pores
4.3.3 Result Comparison

Beginning with the mD-CS model, the original hypothesis is that it will accurately represent pores of diameter less than 2 nm. From the modeling results shown in Figure 34 and Figure 35, it is clear that this assumption was incorrect for slit-shaped pores. For the most common CDI operating voltage of 1.2 V, the mD-CS model is within 11-19 % of the GCS-CS model with pore geometry for slit-shaped pores with a 1 nm pore width and between ~0-1% of the GCS-CS with pore geometry for cylindrical pores under the same conditions. For 2 nm pores, the error becomes significantly larger with slit-shaped pores at 1.2 V ranging from 18 to 25% difference between the mD-CS and GCS-CS models with and without pore geometry. However, this error remains less than 3% for cylindrical pores with 2 nm diameters at 1.2 V.

At lower applied voltages, divergence from the GCS-CS model with pore geometry is larger. At 0.6 V and 500 mg/L, the mD-CS prediction for 2 nm cylindrical pores is already 4% and this same figure for 0.2 V is 5%. For slit-shaped pores, error reaches 30% at 0.6, but begins to decrease at 0.2 V with a deviation of only 20 % for 500 mg/L and 2 nm pores.

These results indicate that the assumption that the mD model can accurately model micropores of 2 nm in width/diameter or less is an adequate assumption for cylindrical pores, but extremely inadequate for slit-shaped
pores. In addition, in almost every case, regardless of pore geometry, optimal pore width/diameter is between 2 and 3 nm with cylindrical pores of up to 5 nm showing more adsorption potential than 2 nm pores, limiting the usefulness of the mD model even further.

This explains the required use of the fitting parameter, $\mu_{att}$, in the mD model as presented by Biesheuvel et al.\textsuperscript{32}. In all observed cases. This term is relatively large and positive, which would result in a larger predicted salt adsorption value. This would be necessary in order to make up for all the salt adsorption happening in pores sized greater than 2 nm, which is not considered in the mD model.

The GCS-CS model’s simplifying assumptions are reflected in its inaccuracy in predicting the GCS-CS model with pore geometry. Its inability to predict for cylindrical pores, its similar level of mathematical complexity to the GCS-CS model with pore geometry, and its weaker theoretical basis compared to the GCS-CS model with pore geometry make this a poor option for predictive modeling of CDI.
Figure 34: Comparison of mD-CS and GCS-CS Modeling Results with the GCS-CS Model with Pore Geometry for Slit-Shaped Pores

at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L
Figure 35: Comparison of mD-CS Results with the GCS-CS Model with Pore Geometry for Cylindrical Pores

at A) 500 mg/L, B) 1000 mg/L, C) 5000 mg/L, D) 10,000 mg/L, E) 25,000 mg/L, and F) 50,000 mg/L
5.0 Conclusions and Future Research

The intent of this thesis was to explore and evaluate existing CDI models and select promising candidates for modification in order to develop a predictive, mechanistic model to describe the salt adsorption capacity and Coulombic efficiency of a given CDI setup from only measurable electrode characteristics and known operating conditions. This was accomplished through the evaluation and modification of the mD and GCS models to develop the GCS-CS model with pore geometry. The GCS-CS model with pore geometry allows for inclusion of ion volume effects through the use of a CS equation of state correction term as well as development of interpore profiles of potential and concentration specific to a given pore size. Through comprehensive analysis of the effect of CDI operating conditions and electrode characteristics, a useful decision making tool was generated. This tool is immediately useful for selecting an optimal carbon electrode based on waste stream characteristics and treatment goals, with the ability to optimize specific salt adsorption capacity, Coulombic efficiency or a balance of the two. Furthermore, the model provides direction for future research into capacitive deionization electrode materials, ensuring that these efforts can be guided and effective.
Further modification of the proposed GCS-CS model with pore geometry should be done in future work. It would be beneficial to be able to consider electrolytes that are nonsymmetric in both valence charge and size. Additionally, consideration of ion competition in the case of a mixed influent solution should be included in future models.

For use in supercapacitors, nonspherical ions would need to be considered as models for the organic ions that are used in that application.
References


Known Calculated

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<td>Volkov et al.</td>
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GCS-CS Model Example Code

clear; %remove all variables previously stored in the workspace
clc; %clear the command window

global MW z c_bulk dion rion del d Vcell vion Av eta_bulk mu_bulk e ereo Vt F y_0 y_St y %Make all variables usable in all functions
MW=58.44; %MW of NaCl is 58.44 g/mol
z=1; %Magnitude of valence charge on Na and Cl is 1

c_bulk=input('Enter the bulk salt concentration in mg/L ') / MW;
%Retrieve the bulk concentration from user and convert to mol/m3

dion=725*10^-12; %The average ion diameter with NaCl is 725 pm
rion=dion/2; %Calculate the hydrated ionic radius

del=rion; %Set the Stern layer thickness
d=100/10^9; %Set pore diameter to 100 nm
Vcell=input('Enter the applied voltage in volts '); %Retrieve the applied voltage
vion=pi/6*dion^3; %Calculate the volume of one ion from its diameter
Av=6.022*10^23; %Set Avogardo’s number

eta_bulk=vion*c_bulk*2*Av; %Calculate the volume fraction of ions
mu_bulk=eta_bulk*(8-9*eta_bulk+3*eta_bulk^2)/((1-eta_bulk)^3); %Calculate the bulk electrochemical potential correction in accordance with the CS correction

e=-1.60218*10^-19; %Set the charge of an electron
ereo=78.64*8.854*10^-12; %Set the dielectric permittivity of water
Vt=0.025692577; %Set the thermal voltage
F=96485; %Set the Faraday constant

y_0=Vcell/2/Vt; %Input the equation for the potential at the charged surface

y_St=Vcell/2/Vt; %Set the applied d’less potential as the initial Stern plane potential

n=0; %Counter, n, for running bvp4c
g=0; %Dummy variable, g, used to compare previous and current Stern plane potentials
b=0; %Counter, b, for determining structure of distance variable, x
tol=.001; %The acceptable error between subsequent calculations of Stern plane potential

while abs(g-y_St)>tol %Continue running slit-shaped bvp4c routine until two subsequent calculations of the Stern plane potential are less than 0.001 apart

while n<1 %Only run bvp4c routine with mybvpin1 initial values the first time through

x(1:1000)=linspace(d/2-rion, 10^-12, 1000);

solinit = bvpinit(linspace(10^-12, (d/2-rion), 2000), @mybvpin1); %Create the initial structure of the potential variable, y
options=bvpset('NMax', 100000); %Increase the largest possible mesh size allowed for solving
sol = bvp4c(@mybvp_rect500,@mybvpbc,solinit,options); %Run the bvp4c routine for the appropriate boundary conditions and equations for slit-shaped pores

y=deval(sol,x); %Evaluate solution of y at each value of x
n=n+1; %Increase the counter by 1 so that the mybvpin1 initial values are only used for the first run

q_x=-2*z*c_bulk*exp(mu_bulk-(-0.00000077623795508020*y(1,:).^6 + 0.00005770456607974150*y(1,:).^5 - 0.00157146618778795000*y(1,:).^4 + 0.01741408203686370000*y(1,:).^3 - 0.02083727222689190000*y(1,:).^2 - 0.04017233713740710000*y(1,:) + 0.06547185566376560000).*sinh(z*(y(1,:)))); %Calculate the charge present at each x value using an empirical relationship between y(1) and the local electrochemical potential

q_tot=sum((q_x(1:999).*(x(2:1000)-x(1:999)))); %Integrate charge over pore volume

y_St=y_0-abs(q_tot*rion*F/ereo/Vt); %Calculate the Stern plane potential

end

g=y_St; %Set the dummy variable, g, to the previous value of the Stern plane potential

solinit = bvpinit(linspace(10^-12,(d/2-rion),2000),@mybvpin2); %Create the initial structure of the potential variable, y

options=bvpset('NMax', 100000); %Increase the largest possible mesh size allowed for solving

sol = bvp4c(@mybvp_rect500,@mybvpbc,solinit,options); %Run the bvp4c routine for the appropriate boundary conditions and equations for slit-shaped pores

y=deval(sol,x); %Evaluate solution of y at each value of x
n=n+1; %Increase the counter by 1 so that the mybvpin1 initial values are only used for the first run

q_x=-2*z*c_bulk*exp(mu_bulk-(-0.00000077623795508020*y(1,:).^6 + 0.00005770456607974150*y(1,:).^5 - 0.00157146618778795000*y(1,:).^4 + 0.01741408203686370000*y(1,:).^3 - 0.02083727222689190000*y(1,:).^2 - 0.04017233713740710000*y(1,:) + 0.06547185566376560000).*sinh(z*(y(1,:)))); %Calculate the charge present at each x value using an empirical relationship between y(1) and the local electrochemical potential

q_tot=sum((q_x(1:999).*(x(2:1000)-x(1:999)))); %Integrate charge over pore volume

y_St=y_0-abs(q_tot*rion*F/ereo/Vt); %Calculate the Stern plane potential

end

%Calculate the concentration profiles for total conc, anions, and cations
c=2*z*c_bulk*exp(mu_bulk-(0.000007762379550820*y(1,:).^6 + 0.00005770456607974150*y(1,:).^5 - 0.00157146618778795000*y(1,:).^4 + 0.01741408203686370000*y(1,:).^3 - 0.02083727222689190000*y(1,:).^2 - 0.4017233713740710000*y(1,:)) + 0.06547185566376560000).*cosh(z*(y(1,:))));
c_an=z*c_bulk*exp(mu_bulk-(0.000007762379550820*y(1,:).^6 + 0.00005770456607974150*y(1,:).^5 - 0.00157146618778795000*y(1,:).^4 + 0.01741408203686370000*y(1,:).^3 - 0.02083727222689190000*y(1,:).^2 - 0.4017233713740710000*y(1,:)) + 0.06547185566376560000)+(z*(y(1,:))));
c_ca=z*c_bulk*exp(mu_bulk-(0.000007762379550820*y(1,:).^6 + 0.00005770456607974150*y(1,:).^5 - 0.00157146618778795000*y(1,:).^4 + 0.01741408203686370000*y(1,:).^3 - 0.02083727222689190000*y(1,:).^2 - 0.4017233713740710000*y(1,:)) + 0.06547185566376560000)-(z*(y(1,:))));
c_bulk(1:2000)=2*c_bulk; %Multiply bulk concentration by 2 to convert
it into an ion concentration instead of a salt molecule
concentration

%Calculate specific adsorption for each pore diameter
d6=10/10^9;
dc6=(x(1:1266)-x(2:1267)).*(c_an(1:1266)+c_ca(1:1266)-c_bulk(1));
ions6=sum(dc6);
gamma6=sum(dc6)*.78*2.2222*10^-6/d6*58.44*1000;
d5=5/10^9;
dc5=(x(1:781)-x(2:782)).*(c_an(1:781)+c_ca(1:781)-c_bulk(1));
ions5=sum(dc5);
gamma5=sum(dc5)*.78*2.2222*10^-6/d5*58.44*1000;
d4=4/10^9;
dc4=(x(1:684)-x(2:685)).*(c_an(1:684)+c_ca(1:684)-c_bulk(1));
ions4=sum(dc4);
gamma4=sum(dc4)*.78*2.2222*10^-6/d4*58.44*1000;
d3=3/10^9;
dc3=(x(1:587)-x(2:588)).*(c_an(1:587)+c_ca(1:587)-c_bulk(1));
ions3=sum(dc3);
gamma3=sum(dc3)*.78*2.2222*10^-6/d3*58.44*1000;
d2=2/10^9;
dc2=(x(1:464)-x(2:465)).*(c_an(1:464)+c_ca(1:464)-c_bulk(1));
ions2=sum(dc2);
gamma2=sum(dc2)*.78*2.2222*10^-6/d2*58.44*1000;
d1=1/10^9;
dc1=(x(1:108)-x(2:109)).*(c_an(1:108)+c_ca(1:108)-c_bulk(1));
ions1=sum(dc1);
gamma1=sum(dc1)*.78*2.2222*10^-6/d1*58.44*1000;
%Generate figure
figure
plot(x,y(1,:),'-r');
xlabel('Distance (m)');
ylabel('Potential (-)');
axis([-d/2+rion,d/2-rion,0,23.35]);
beep

function dydx = mybvp_rect500(x,y)

global F z ereo Vt c_bulk mu_bulk
dydx = [ y(2,:); 2*z*F*c_bulk/ereo/Vt*exp(mu_bulk-
0.00000077623795508020*y(1,:).^6 +
0.00005770456607974150*y(1,:).^5 -
0.00157146618778795000*y(1,:).^4 +
0.01741408203686370000*y(1,:).^3 -
0.02083727222689190000*y(1,:).^2 - 0.04017233713740710000*y(1,:)+
0.06547185566376560000)).*sinh(y(1,:))];
end

function res = mybvpbc(yl,yr)

global y_d
res = [yr(1)-y_d; yl(1)];
end

function in = mybvpin1 (x)

global Vcell Vt
in=[Vcell/2/Vt 0];
end

function in = mybvpin2 (x)

global y
in=[y(1) y(2)];
end
GCS-CS Model with Pore Geometry Code

clear; % remove all variables previously stored in the workspace
clc; % clear the command window

global MW z c_bulk dion rion del d Vcell vion Av eta_bulk mu_bulk e

MW=58.44; % MW of NaCl is 58.44 g/mol
z=1; % Magnitude of valence charge on Na and Cl is 1

c_bulk=input('Enter the bulk salt concentration in mg/L ')/MW;
% Retrieve the bulk concentration from user and convert to mol/m^3

dion=725*10^-12; % The average ion diameter with NaCl is 725 pm
rion=dion/2; % Calculate the hydrated ionic radius

del=rion; % Set the Stern layer thickness

d=input('Enter the pore diameter in nm ') / 10^9; % Retrieve the pore
% diameter and store it as d in units of m

Vcell=input('Enter the applied voltage in volts '); % Retrieve the
% applied voltage

vion=pi/6*dion^3; % Calculate the volume of one ion from its diameter

Av=6.022*10^23; % Set Avogadro's number

eta_bulk=vion*c_bulk*2*Av; % Calculate the volume fraction of ions

mu_bulk=eta_bulk*(8-9*eta_bulk+3*eta_bulk^2)/((1-eta_bulk)^3); %
% Calculate the bulk electrochemical potential correction in
% accordance with the CS correction

e=-1.60218*10^-19; % Set the charge of an electron

ereor=78.64*8.854*10^-12; % Set the dielectric permittivity of water

Vt=0.025692577; % Set the thermal voltage

F=96485; % Set the Faraday constant

y_0=Vcell/2/Vt; % Input the equation for the potential at the charged
% surface

y_St=Vcell/2/Vt; % Set the applied d'less potential as the initial Stern
% plane potential

n=0; % Counter, n, for running bvp4c

g=0; % Dummy variable, g, used to compare previous and current Stern
% plane potentials

b=0; % Counter, b, for determining structure of distance variable, x
	tol=.001; % The acceptable error between subsequent calculations of
% Stern plane potential

while abs(g-y_St)>tol % Continue running slit-shaped bvp4c routine until
% two subsequent calculations of the Stern plane potential are less
% than 0.001 apart

while n<1 % Only run bvp4c routine with mybvpin1 initial values the
% first time through

g=y_St; % Set the dummy variable, g, to the previous run's Stern
% plane potential

x(1:1000)=linspace(d/2-rion, 10^-12, 1000);

solinit = bvpinit(linspace(10^-12, (d/2-rion), 2000), @mybvpin1);
% Create the initial structure of the potential variable, y
options=bvpset('NMax', 100000); %Increase the largest possible mesh size allowed for solving
sol = bvp4c(@(mybvp_rect500, mybvpbc, solinit, options); %Run the bvp4c routine for the appropriate boundary conditions and equations for slit-shaped pores
y=deval(sol,x); %Evaluate solution of y at each value of x
n=n+1; %Increase the counter by 1 so that the mybvpin1 initial values are only used for the first run

q_x=-2*z*c_bulk*exp(mu_bulk-(-0.0000077623795508020*y(1,:).^6 + 0.0005770456607974150*y(1,:).^5 - 0.0015714661877879500*y(1,:).^4 + 0.0174140820368637000*y(1,:).^3 - 0.0208372722268919000*y(1,:).^2 + 0.0401723371374071000*y(1,:)+ 0.0654718556637656000).*sinh(z*(y(1,:)))); %Calculate the charge present at each x value using an empirical relationship between y(1) and the local electrochemical potential
q_tot=sum((q_x(1:999).*(x(2:1000)-x(1:999)))); %Integrate charge over pore volume
y_St=y_0-abs(q_tot*rion*F/ereo/Vt); %Calculate the Stern plane potential

end

%Set the dummy variable, g, to the previous value of the Stern plane potential

solinit = bvpinit(linspace(10^-12, (d/2-rion), 2000), @mybvpin2); %Create the initial structure of the potential variable, y
options=bvpset('NMax', 100000); %Increase the largest possible mesh size allowed for solving
sol = bvp4c(@(mybvp_rect500, mybvpbc, solinit, options); %Run the bvp4c routine for the appropriate boundary conditions and equations for slit-shaped pores
y=deval(sol,x); %Evaluate solution of y at each value of x
n=n+1; %Increase the counter by 1 so that the mybvpin1 initial values are only used for the first run

q_x=-2*z*c_bulk*exp(mu_bulk-(-0.0000077623795508020*y(1,:).^6 + 0.0005770456607974150*y(1,:).^5 - 0.0015714661877879500*y(1,:).^4 + 0.0174140820368637000*y(1,:).^3 - 0.0208372722268919000*y(1,:).^2 + 0.0401723371374071000*y(1,:)+ 0.0654718556637656000).*sinh(z*(y(1,:)))); %Calculate the charge present at each x value using an empirical relationship between y(1) and the local electrochemical potential
q_tot=sum((q_x(1:999).*(x(2:1000)-x(1:999)))); %Integrate charge over pore volume
y_St=y_0-abs(q_tot*rion*F/ereo/Vt); %Calculate the Stern plane potential

end
y_St1 = Vcell/2/Vt; % Set the applied d’les potential as the initial Stern plane potential
m=0; % Counter, m, for running bvp4c
h=0; % Counter, m, for determining structure of distance variable, x1
i=0; % Dummy variable, i, used to compare previous and current Stern plant potentials
tol=0.01; % The acceptable error between subsequent calculations of Stern plant potential

while abs(i-y_St1)>tol % Continue running cylindrical bvp4c routine until two subsequent calculations of the Stern plane potential
    while m<1 % Only run bvp4c routine with mybvpin1 initial values the first time through
        x1(1:1000) = linspace((d/2)-rion, 10^-12, 1000);
        solinit = bvpinit(linspace(10^-12,(d/2-rion),2000),@mybvpin1);
        options=bvpset('NMax',100000); % Increase the largest possible mesh size allowed for solving
        sol = bvp4c(@mybvp_cyl500,@mybvpbc1,solinit,options); % Run the bvp4c routine for the appropriate boundary conditions and equations for cylindrical pores
        y1=deval(sol,x1); % Evaluate solution of y1 at each value of x1
        m=m+1; % Increase the counter by 1 so that the mybvpinl initial values are only used for the first run
        q_x1=-2*z*c_bulk*exp(mu_bulk-(0.00000077623795508020*y1(1,:).^6 + 0.00005770456607974150*y1(1,:).^5 - 0.00157146618778950000*y1(1,:).^4 + 0.01741408203686370000*y1(1,:).^3 - 0.02083727222689190000*y1(1,:).^2 - 0.04017233713740710000*y1(1,:)) + 0.06547185566376560000).*sinh(z*(y1(1,:)))); % Calculate the charge present at each x1 value using an empirical relationship between y1(1) and the local electrochemical potential
        dq1=sum(q_x1(1:999)*pi.*(x1(1:999)).^2-(x1(2:1000)).^2)); % Integrate charge over pore volume
        y_St1=y_0-abs(q_tot1*log((d/2)/(d/2-rion)))*F/2/pi/ereo/Vt)); % Calculate the Stern plane potential
    end

i=y_St1; % Set the dummy variable, i, to the previous value of the Stern plane potential
solinit = bvpinit(linspace(10^-12,(d/2-rion),2000),@mybvpin3);
options=bvpset('NMax',100000); % Increase the largest possible mesh size allowed for solving
sol = bvp4c(@mybvp_cyl500,@mybvpbc1,solinit,options); % Run the bvp4c routine for the appropriate boundary conditions and equations for cylindrical pores
\[ y_1 = \text{deval(sol, } x_1) \]; \% Evaluate solution of \( y_1 \) at each value of \( x_1 \)
\[ m = m + 1 \]; \% the counter, \( n \), is increased
\[ q_{x_1} = -2z^c_{\text{bulk}}^\text{exp}(mu_{\text{bulk}} - (0.00000077623795508020y_1(1,:))^6 + 0.00005770456607974150y_1(1,:)^5 - 0.00157146618778795000y_1(1,:)^4 + 0.01741408203686370000y_1(1,:)^3 - 0.02083727222689190000y_1(1,:)^2 - 0.04017233713740710000y_1(1,:)) + 0.06547185566376560000)\cdot \sinh(z^*(y_1(1,:))) \]; \% Calculate the charge present at each \( x \) value using an empirical relationship between \( y(1) \) and the local electrochemical potential
\[ dq_1 = \text{sum}(q_{x_1}(1:999)\cdot pi^*(x_1(1:999)).^2 - (x_1(2:1000)).^2))); \% Integrate charge over pore volume
\[ y_{\text{St1}} = y_0 - \text{abs}(q_{\text{tot1}}*\text{log}(d/2)/(d/2 - rion))*F/2/pi/\text{ero}/Vt) \]; \% Calculate the Stern plane potential
end

\% Mirror all \( x \) and \( y \) variables to account for the opposite side of the pore.
\% Note: for cylindrical pores this is purely for graphic purposes since all \( \% sides of the pore should have positive distance values. \\
xt(1:1000) = -x; 
xt(1001:2000) = \text{fliplr}(x); 
xt(1:1000) = -x1; 
xt(1001:2000) = \text{fliplr}(x1); 
yt(1:1000) = y(1,:); 
yt(1001:2000) = \text{fliplr}(y(1,:)); 
yt(1:1000) = y1(1,:); 
yt(1001:2000) = \text{fliplr}(y1(1,:));

\% Calculate the concentration profiles for total conc, anions, and cations
\[ c = 2z^c_{\text{bulk}}^\text{exp}(mu_{\text{bulk}} - (0.00000077623795508020y1(1,:))^6 + 0.00005770456607974150y1(1,:)^5 - 0.00157146618778795000y1(1,:)^4 + 0.01741408203686370000y1(1,:)^3 - 0.02083727222689190000y1(1,:)^2 - 0.04017233713740710000y1(1,:)) + 0.06547185566376560000)\cdot \cosh(z^*(y1(1,:))));
\[ c1 = 2z^c_{\text{bulk}}^\text{exp}(mu_{\text{bulk}} - (0.00000077623795508020y1(1,:))^6 + 0.00005770456607974150y1(1,:)^5 - 0.00157146618778795000y1(1,:)^4 + 0.01741408203686370000y1(1,:)^3 - 0.02083727222689190000y1(1,:)^2 - 0.04017233713740710000y1(1,:)) + 0.06547185566376560000)\cdot \cosh(z^*(y1(1,:))));
\[ c_{\text{an}} = z^c_{\text{bulk}}^\text{exp}(mu_{\text{bulk}} - (0.00000077623795508020y1(1,:))^6 + 0.00005770456607974150y1(1,:)^5 - 0.00157146618778795000y1(1,:)^4 + 0.01741408203686370000y1(1,:)^3 - 0.02083727222689190000y1(1,:)^2 - 0.04017233713740710000y1(1,:) - 0.06547185566376560000)\cdot \cosh(z^*(y1(1,:))));
0.0401723713740710000*yt(1,:) +
0.0654718566376560000+(z*(yt(1,:))));
c_an1=z*c_bulk*exp(mu_bulk -
- 0.00000077623795508020*yt1(1,:).^6 +
0.00005770456607974150*yt1(1,:).^5 -
0.0174140820366370000*yt1(1,:).^4 +
0.0174140820366370000*yt1(1,:).^3 -
0.0083727222689190000*yt1(1,:).^2 -
0.0401723713740710000*yt1(1,:) +
0.0654718566376560000)+(z*(yt1(1,:))));
c_ca=z*c_bulk*exp(mu_bulk -
- 0.00000077623795508020*yt(1,:).^6 +
0.00005770456607974150*yt(1,:).^5 -
0.0174140820366370000*yt(1,:).^4 +
0.0174140820366370000*yt(1,:).^3 -
0.0083727222689190000*yt(1,:).^2 -
0.0401723713740710000*yt(1,:) + 0.0654718566376560000) -
(z*(yt(1,:))));
c_ca1=z*c_bulk*exp(mu_bulk -
- 0.00000077623795508020*yt1(1,:).^6 +
0.00005770456607974150*yt1(1,:).^5 -
0.0174140820366370000*yt1(1,:).^4 +
0.0174140820366370000*yt1(1,:).^3 -
0.0083727222689190000*yt1(1,:).^2 -
0.0401723713740710000*yt1(1,:) + 0.0654718566376560000) -
(z*(yt1(1,:))));
c_bulk(1:2000)=2*c_bulk; %Multiply bulk concentration by 2 to convert
it into an ion concentration instead of a salt molecule
concentration
ions=sum((x(1:999)-x(2:1000)).*(c_an(1:999)+c_ca(1:999)-c_bulk(1))); %Integrate the total #mol of ions in slit-shaped pores
gamma=ions*2*.78*2.2222*10^-6/d*58.44*1000; %Calculate the mg/g of salt
removed based on MAC construct
ionsl=sum((c_anl(1:999)+c_cal(1:999)-(c_bulk(1)))^2-
(xl(1:999)).^2)); %Integrate the total #mol of ions in
cylindrical pores
gammal=ionsl*(1.733*10^-6)/pi/((d/2)^2)*58.44*1000; %Calculate the mg/g
of salt removed based on MAC construct
q_tot=sum((q_x(1:999).*x(2:1000)-x(1:999))); %Integrate the total
#mol of charge in slit-shaped pores
q_totl=sum(q_xl(1:999).*xl(2:1000)-xl(1:999)); %Integrate the total #mol of charge in cylindrical pores
eff=(ions/q_tot); %Calculate the Coulombic efficiency for slit-shaped
pores
eff1=(ionsl/q_totl); %Calculate the Coulombic efficiency for
cylindrical pores
%Generate figures
figure
plot(x,y(1,:),'-r',xl,yt1(1,:),'-b');
xlabel('Distance (m)');
ylabel('Potential (\text{-})');
legend('slit-shaped', 'cylindrical');
axis([-d/2+rion, d/2-rion, 0, 23.35]);
figure
plot(xt, c, '-r', xt, c_an, '--g', xt, c_ca, '-m', xt, c_bulk, '--k');
xlabel('Distance (m)');
ylabel('Concentration (mol/m3)');
legend('total', 'anion', 'cation', 'bulk');
axis([-d/2+rion, d/2-rion, 0, 5000]);
figure
plot(xt1, c1, '-r', xt1, c_an1, '--g', xt1, c_ca1, '-m', xt1, c_bulk, '--k');
xlabel('Distance (m)');
ylabel('Concentration (mol/m3)');
legend('total', 'anion', 'cation', 'bulk');
axis([-d/2+rion, d/2-rion, 0, 5000]);
beep

%--------------------------------------------------------
function dydx = mybvp_rect500(x,y)

global F z ereo Vt c_bulk mu_bulk
dydx = [ y(2,:); 2*z*F*c_bulk/ereo/Vt*exp(mu_bulk-
  0.00000077623795508020*y(1,:).^6 +
  0.00005770456607974150*y(1,:).^5 -
  0.00157146618778795000*y(1,:).^4 +
  0.01741408203686370000*y(1,:).^3 -
  0.02083727222689190000*y(1,:).^2 - 0.0401723713740710000*y(1,:) +
  0.06547185563765600000).*sinh(y(1,:));];
end

%--------------------------------------------------------
function dydx = mybvp_cyl500(x1,y1)

global F z c_bulk ereo Vt mu_bulk
dydx = [ y(2,:); 2*z*F*c_bulk/ereo/Vt*exp(mu_bulk-
  0.00000077623795508020*y1(1,:).^6 +
  0.00005770456607974150*y1(1,:).^5 -
  0.00157146618778795000*y1(1,:).^4 +
  0.01741408203686370000*y1(1,:).^3 -
  0.02083727222689190000*y1(1,:).^2 - 0.0401723713740710000*y1(1,:) +
  0.06547185563765600000).*sinh(y1(1,:))-(y1(2,:)/(x1))];
end

%--------------------------------------------------------
function res = mybvpbc(yl,yr)

global y_d
res = [yr(1)-y_d; yl(2)];
function res = mybvpbc1(yl, yr)

global y_d1
res = [yr(1) - y_d1; yl(2)];
end

function in = mybvpin1 (x)

global Vcell Vt
in=[Vcell/2/Vt 0];
end

function in = mybvpin2 (x)

global y
in=[y(1) y(2)];
end

function in = mybvpin3 (x)

global y1
in=[y1(1) y1(2)];
end