
Design and optimisation of electrocoagulation for use in wastewater treatment.

Master's Thesis
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Titel:

Design and optimisation of electro-coagulation for use in wastewater treatment

Semester:

3rd and 4th semester

Semestertema:

Coagulation of wastewater

Project period:

02.09.19 - 4.06.20

ECTS:

60

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Project gruppe

Separationsgruppen

Master student:

Silas Alf Christian Duus

Oplag: 1

Antal sider: XXX sider

Appendix: XXX

Bilag: Zip file

Abstract:

This project investigates the build of an electrocoagulation cell, using a fixed current density, concentration, electrode sets and flow rate. The cell was generated in COMSOL multiphysics 5.5, to simulate the fluid dynamics through the cell to investigate the turbulent velocities encountered by the array of electrodes. Further more the influence of the potential needed to run an electrocoagulation process will be investigated using Nernst equation and the standard reduction potentials for iron electrodes.

Preface 1

The project 'Design and optimisation of electrocoagulation for use in wastewater treatment' was written by Silas A. C. Duus at the Department of Chemistry and Bioscience at Aalborg University during the 3rd and 4th semester (M.Sc) in Chemical engineering.

I would like to thank Mads Koustrup Jørgensen for supervising the project, interesting collaboration, valuable inputs and guidance through the project.

References are listed as [number] after order of appearance at the end of the report. The report is split into 8 chapters. Additional pictures, schematics, calculations and data can be found in the enclosed additional folder.



Silas Alf Christian Duus

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Abbreviations list

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| Abbreviation | Unit | Explanation |
|-----------------|---------------------------|---------------------------------|
| EC | - | Electro coagulation |
| CC | - | Chemical coagulation |
| d | [cm] | diameter of electrodes |
| r | [cm] | radius of electrodes |
| Res | [Ohm] | Resistance |
| U | [V] | potential |
| I | [Amp] | Current |
| S.H.E | - | Standard hydrogen electrode |
| G | [kJ] | Gibbs free energy |
| E° | [V] | Standard reduction potential |
| F | [C/mol] | Faraday's constant |
| E | [V] | Cell potential |
| R | $[\frac{J}{mol \cdot K}]$ | Gas constant |
| T | [K] | Temperature |
| z | - | Electrons |
| V _{ov} | [V] | overpotential |
| V _{Ea} | [V] | Activation energy overpotential |
| V _c | [V] | Concentration overpotential |
| ρ | $[\frac{m}{S}]$ | resistivity |
| κ | $[\frac{S}{m}]$ | Conductivity |
| n | [mol] | Moles |
| t | [s] | time in seconds |
| Q | $[\frac{L}{min}]$ | Flow rate |
| M | $[\frac{g}{mol}]$ | molar mass |
| AC | - | Alternating current |
| DC | - | Direct current |
| γ | - | Activity coefficient |

Introduction 3

Current method for water treatment involve filtering, coagulation and sedimentation and biological degradation. This is done to reduce and remove waste products, organic matter, such as nitrogen and phosphor and other residue ions such as heavy metals.[1]

Recent research have been looking into new ways to treat surface water, ground water and waste water, for drinking and sanitary uses. Denmark have large reservoirs of ground water, which are pumped up and filtered before being used in households and industries. After use all water exiting from household and industries, is considered waste water, which are transported using tilted sewage pipes and pumps to treatment plants. The waste water contain residue organic material, waste paper, sand, gravel and rags once it reaches the treatment plant.

3.0.1 Treatment of waste water

The sewage works in Denmark have two prominent features; one is to lead waste water to treatment plants, done by tilted pipes angled in a downwards position and pumps. The other feature is to transport rainfall back to lakes, sea or ponds, which are larger pipes separated from the waste water pipes. Due to this separation rainfall can be lead directly back to nature, without any repercussions. Treatment plants deploy several steps to filtrate and clean the waste water, before leading the cleaned effluent back to nature, via lakes, creeks or the ocean. An overall process can be seen on figure 3.1, which show a simplified image for waste water cycle in Odense.

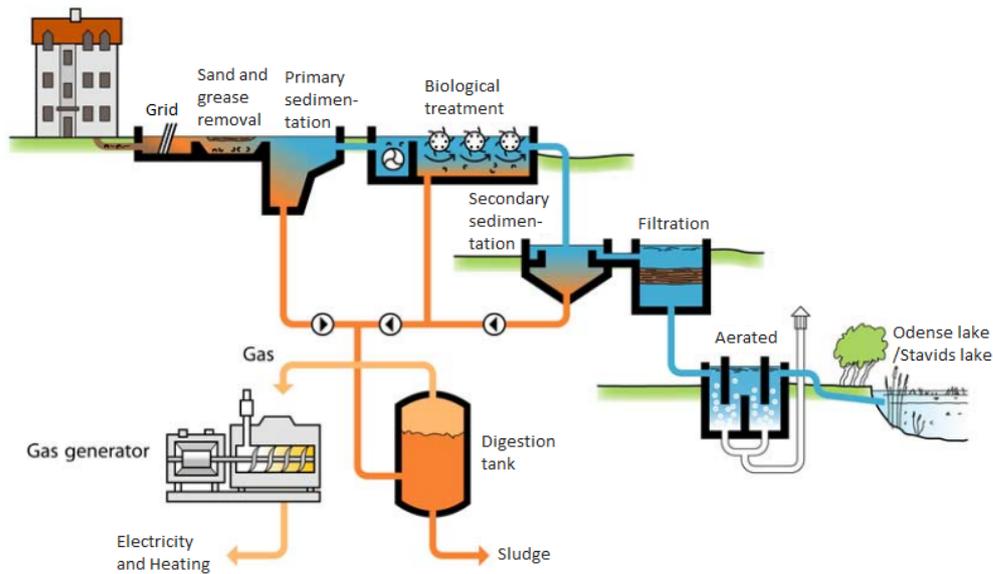


Figure 3.1: Schematic of a treatment plant in Odense, the waste water enters the plant from top left and leaves the treatment plant to the lower right. [1]

The process will be described further, with respect to figure 3.1. The first step in a treatment plant is removal of rags and waste, such as plastic, paper, twigs, sand and gravel. The grids withholds the waste, after which the removed mass is transferred to a container for later disposal at a specific landfill.

The water is lead to the first tank for primary sedimentation or settlement, which are designed to reduce the velocity of the waste water flow, allowing heavier solids to settle at the bottom as raw sludge. The water from the primary sedimentation tank is lead to biological treatment, where bacteria present in the waste water is employed to remove organic matter and reduce nitrogen and phosphor in the water. This process alternates between anaerobic and aerobic conditions, while mixing the water greatly to keep the process going.

The water is than lead to a secondary sedimentation tank, which works the same as the primary sedimentation. However parts of the sludge, which still contain microorganisms, are lead back to the biological process to be reused. The effluent is lead to a final filtration and aerated before being lead back into nature. Sometimes chemicals are added here to remove excess phosphor, if needed, such as iron or aluminum coagulation salts. [8]

The sludge from the primary and secondary sedimentation tanks are lead to digesters or digestion tanks. The sludge is left for digestion for an extended period of time depending on the treatment plant, before being dewatered, often by a screw press, seen on image 3.2, where the water is being lead back to the start of the treatment cycle and the sludge mass is send to specific landfill.

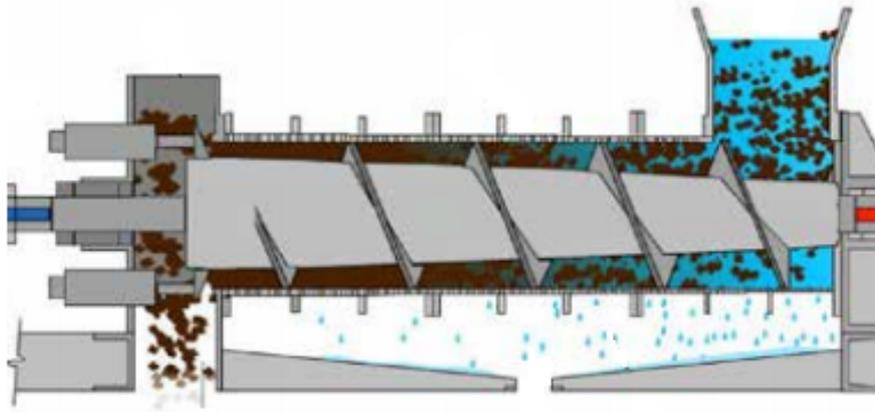


Figure 3.2: In the screw press the water enters from the right and forced to the left, while water is rejected out the sides. [10]

During the digestion process large amounts of bio gases are generated. This bio gas are often used to operate the treatment plant itself and for heating the houses around the treatment plant workstations.

3.0.2 Coagulation

During dewatering of the sludge, coagulation agents are added such as iron chloride or aluminium sulphate to promote the sedimentation of suspended solids. These agents are used to neutralize charged particles which allow for precipitation and decrease the total suspended solids, TSS, while these agents can also be deployed to decrease residue phosphor in the water, if needed. The coagulant agents are often added during heavy mixing to improve the collision, which promotes destabilisation of the suspended particles. Afterwards mixing is slowed to allow flocs to form and precipitate. The mixing times depend on the treatment plant and type of agent used, where dispersion of coagulation agent is often 30-60 seconds. [8] The use of inorganic salts such as iron chloride $[\text{FeCl}_3]$ or aluminum sulphate $[\text{Al}_2(\text{SO}_4)_3]$ are often acidic in nature and require safety methods for handling when used and stored, and alters the pH level of the treated wastewater.

The most common coagulation agents are Iron or aluminium salts used in chemical coagulation, CC, which alter the pH level of the stream and leave residue sulphate or chloride from respectively. Sulphate is undesired in the effluent, as it is coupled with other inorganic metal cycles, which in turn can influence phosphorus concentration in the lakes and rivers. Sulphate can redox between itself, sulfide and thiosulfate. Sulfate can depending on the condition of the water generate hydrogen sulfide gas, a toxic compound at high concentrations, which is followed by an distinctive smell of rotten eggs. [3] Large amounts of chloride, which can either react with organic matter to form toxic chlorinated compounds, while chlorine $[\text{Cl}_2(\text{g})]$ is a highly toxic gas, should the conditions for the later be available. Another newer coagulation method is electrocoagulation, shortened EC in this project, which have gained increasing interest due to efficiently removing suspended particles in water, while negating excess amounts of chloride and sulphate.

An interesting feature reported from previous research on EC, show the pH level to adjust during operation. [5, 20] The commonly noted range adjusted to is between 7 and 8 pH for EC, compared to CC which often is acidic, lowering the pH. The change in pH is

not yet known, though some theories have been suggested by authors [5, 7, 9, 20] for the mechanisms taking place. The most prominent theories suggest hydrogen gas evolution, with the electrodes working as catalysts.

As EC is operated using cathodes and anodes of either iron or aluminium, the anodes are sacrificed providing the source of metal ions, while the cathode reduces water to hydroxides and hydrogen gas.[12, 17] Research suggest during operation a passivation layer form at the cathode, indicated by an increase in potential and an overall reduce in efficiency of the EC cell.[18] During operation it is favoured to keep the potential as low as possible, to avoid side reactions occurring.

Previous designs of an EC cell include batch reactors and continuous flow reactors, which have investigated surface water, ground water, wastewater and sludge. [5, 11, 15, 16]. The designs evolve around passing the water near the electrodes and release the metal ions into the solution, generating the coagulation agents. EC show promising results having fewer residue chemicals compared to CC and, produced ion, e.g Fe^{2+} , have shown to readily hydrolyse to Fe^{3+} , for precipitation, when oxygen is present.

3.1 Problem statement

How can an EC cell be designed as a viable alternative to CC? The project will aim to design an EC cell, with respect to the following:

- The current density, current, surface area and flow time for the overall efficiency.
- Computer simulations of an EC cell investigating the fluid dynamics.
- Investigate the concentration influence on the electrolytic cell potential using Nernst equation.

3.2 Approach

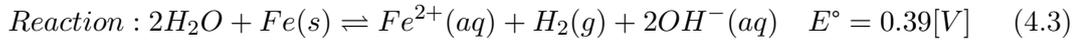
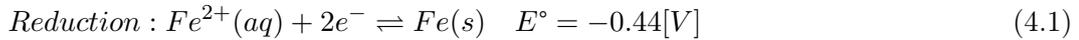
The EC cell will be designed virtually in COMSOL multiphysics for investigating the fluid dynamics and an approach to determine dimensions of an EC cell based on theory.

Theory 4

This section will outline initial approach for investigating the reaction mechanics occurring during an operation of an EC cell, where the EC cell is adopt the initial conditions of an electrolytic cell. The concentration and pH influence is investigated using Nernst equation and the equation for cell potential. Any reduction potential are given in volt [V] vs. a standard hydrogen electrode [S.H.E], unless otherwise stated.

4.1 Electrochemistry with sacrificial electrodes

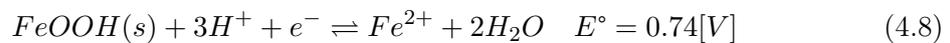
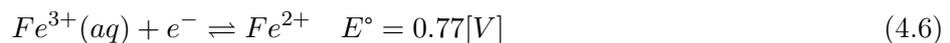
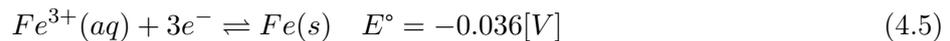
An EC cell can be considered to be an electrolytic system, where the release of ions happens at the anode and the reaction at the cathode is a reduction of water. In an electrolytic system using sacrificial iron electrodes, the iron will be oxidized to Fe^{2+} at the anode, and water will be reduced to hydrogen gas (H_2) and hydroxide ions (OH^-). [6] The standard S.H.E. reduction potentials and combined overall reaction can be seen in equation 4.1, 4.2 and 4.3 [].



The overall cell potential for an electrolytic cell is given using the following equation 4.4:

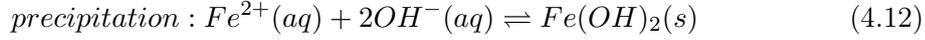
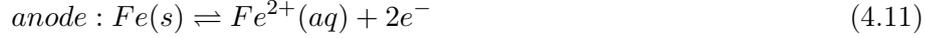
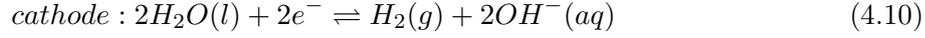
$$E^\circ_{cell} = E^\circ_{red} - E^\circ_{oxi} \quad (4.4)$$

The reduction with the lowest potential will be oxidized while the other reaction will be reduced, giving the overall cell potential for the reaction. In this case hydroxides would be oxidized generating iron and having an overall potential of 0.39 [V]. The inverted reaction, for generation of Fe^{2+} this potential must be applied from a power source. The reduction potential is standardized value, measured against a S.H.E, which is the reference value for all other reduction potential measured, set to 0 [V] in reduction tables. Few notable reduction potential between water and iron are the following [14]:

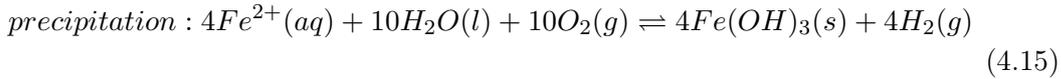


The above potential show the difference in reduction potential to generate Fe^{3+} instead of Fe^{2+} in the cell, increasing the potential to from 0.39 [V] to 0.8 [V]. While the generation of

Fe^{2+} is more likely, depending on the pH of the solution and the oxygen level, iron is likely to hydrolyse suggest by [6]. Under basic conditions they suggest the following reactions take place:



While under acidic:



The two lower reduction potentials are other likely reactions to take place if iron is present in the cell, without a power source. The cell potential for iron and chlorine should the latter be available would be 1.8 [V] seen from the above reduction potentials, suggesting at increased potentials generation of chlorine gas is a possible side reaction.

4.2 Concentration, ohmic potential and overpotential for electrolytic cells

In an electrolytic cell the relationship between free energy difference and the electric potential difference can be measured using equation 4.16

$$\Delta G = -nFE \quad (4.16)$$

Here ΔG is Gibbs free energy of the system, n is the transferred electrons, F is Faraday's Constant and E is the potential difference between electrodes in the cell. When operating an electrolytic cell, the potential difference will vary, due to changes at the surface of the electrodes, the bulk concentration, the mass transfer and conductivity of the electrolyte. These parameters are related in the following equation:

$$E = E_{cathode} - E_{anode} - I \cdot Res - V_{ov} \quad (4.17)$$

Here $E_{cathode}$ and E_{anode} is the reduction potentials for each the cathode and anode respitvely, IR is the Ohmic potential and V_{ov} is the total overpotential of the system from several contributors, which will be discussed further later that must be overcome by the system. In the electrolytic cell the concentration influence the potentials of the anode and cathode, which can be calculated using Nernst equation 4.19, for each half cell reaction depicted as 4.18:



$$E = E^\circ - \frac{RT}{zF} \cdot \log \frac{\gamma_B^b}{\gamma_A^a} \quad (4.19)$$

Here E° represent the reduction/oxidation potential of the cathode or anode respectively under standard conditions, R is the gas constant, T is temperature, z electron transferred,

F is Faradays constant and γ_B and γ_A is the activity of the product and reactants. This give the effective electrode potential for a given electrolytic cell reaction, as the concentration increase, specifically seen with batch reactions, such as batteries. The Ohmic potential is effected by the operation current used and the resistance of the electrolyte, which will be discussed in section 4.3 The reaction suggested from previous research taking place, is the formation of Fe^{2+} and generation of hydroxides and hydrogen gas. When hydrogen gas is catalysed the overall current density influence the overpotential needed to drive the reaction. An example is the hydrogen gas evolution using an platinum electrode, at current density of $10 \left[\frac{\text{A}}{\text{m}^2}\right]$ and $100 \left[\frac{\text{A}}{\text{m}^2}\right]$ the overpotential are known to be 0.015 [V] and 0.03 [V] respectively [13]. The overpotential for an eletrolytic predicts the thermodynamic energy required to promote the reaction, often being larger energy than standard reduction potentials. Three main contributors to the total overpotential are described in equation 4.20 [20].

$$V_{ov} = V_{E_a} + V_c \quad (4.20)$$

Here the total overpotential are summerized by the activation energy V_{E_a} for the electron transfer to take place, V_c is the concentration overpotential which is limited by the mass transfer from the surface of the electrode to the bulk of the electrolyte. This along with the ohmic potential generates an overpotential for operation of the EC. The Ohmic potential is seen as the IR-drop in solution from equation 4.17.

4.3 Current and Current Density

Electronic circuits apply a potential difference [V] to move a current of electrons [I] over a distance, within a material, which have an inert resistance to movement [R] or the electrons. This correlation is described by Ohm's law:

$$U = I \cdot Res \quad (4.21)$$

This applies to potential difference in a circuit as seen on image 4.1 or when the current moves through a galvanic cell as seen on image 4.2, creating a potential difference.

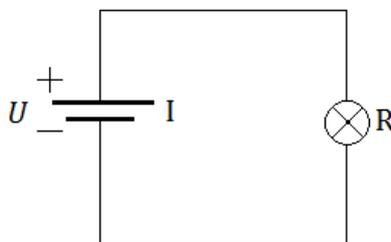


Figure 4.1: Potential drop in an electrical circuit.

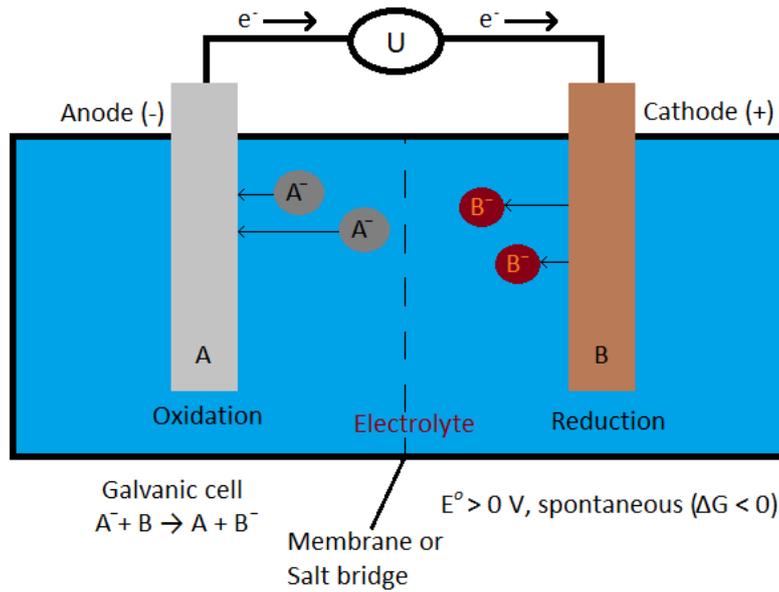


Figure 4.2: Potential difference in a galvanic cell, separated by an membrane or salt bridge.

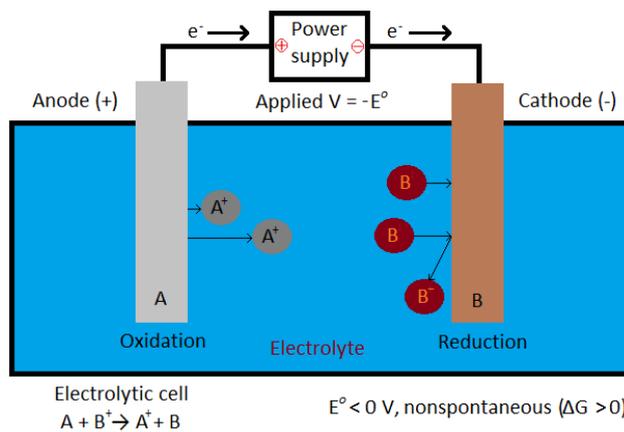


Figure 4.3: Potential difference in an electrolytic, no separation is membrane or salt bridge, as the process is against the favourable reaction.

When this is applied to solutions, where the current is moving through an electrolyte, the resistance is determined by the pure solution, whereas for this project is wastewater, which as mentioned, contain ions and organic matter that would increase or decrease resistance. The resistance in a solution can be estimated by the length and cross section area between electrodes and the resistivity of the solution, shown on figure 4.4.

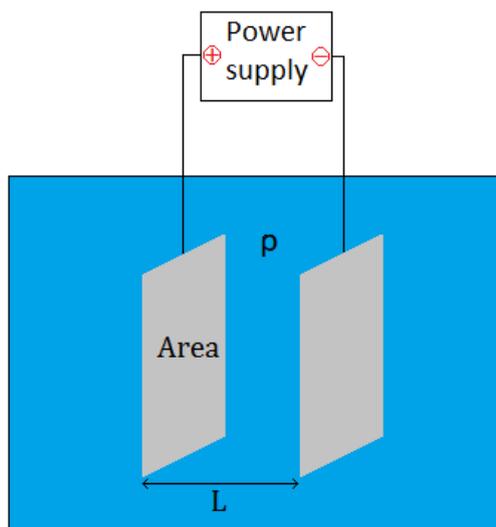


Figure 4.4: Resistance between two electrodes suspended in a medium, based on the distance between the two, cross section and resistivity of the medium.

The resistivity of a solution is the specific materials resistance to electric flow, where low resistivity allows a material to readily conduct electricity. The following equation 4.22 show the relation between resistance, resistivity and the distance and cross section area of the electrodes.

$$Res = \frac{L}{A} \cdot \rho \quad (4.22)$$

Here [L] is the distance between the electrodes, [A] is the cross section and [ρ] is resistivity of the solution. The inverse of resistivity in a solution is conductivity, which are related in equation 4.23.

$$\kappa = \frac{1}{\rho} \quad (4.23)$$

This allow for the conductance to be measured to determine the resistance of the system. The current related to the amount of moles generated can be seen in equation 4.24.

$$n = \frac{I \cdot t}{z \cdot F} \quad (4.24)$$

Where [z] is the valence for the generated ion, [F] is Faradays constant and [n] is the amount of moles for the generated ions. If no side reactions taking place and with 100% faradaic efficiency considered, the required current for a dosage of iron generation, equation 4.24, is rearranged in the following equations:

$$I_{Fe^{2+}} = \frac{n_{Fe^{2+}} \cdot z \cdot F}{t} \quad (4.25)$$

$$dosage_{Fe^{2+}} = Q \cdot c \tag{4.26}$$

$$\frac{n_{Fe^{2+}}}{t} = \frac{dosage_{Fe^{2+}}}{M_{Fe^{2+}}} \tag{4.27}$$

$$I_{Fe^{2+}} = \frac{Q \cdot c \cdot z \cdot F}{M_{Fe^{2+}}} \tag{4.28}$$

Here [Q] is the flow in $[\frac{L}{s}]$, [c] the concentration of iron at the outlet in $[\frac{g}{L}]$ and [M] is the molar mass of iron. Equation 4.28 then determines the current needed for a specific effluent concentration.

4.4 Reactor settings and configurations

For setting up the EC cell the connection and setup of the electrodes can be varied. The electrodes can be monopolar and bipolar attuned shown on figure 4.5.

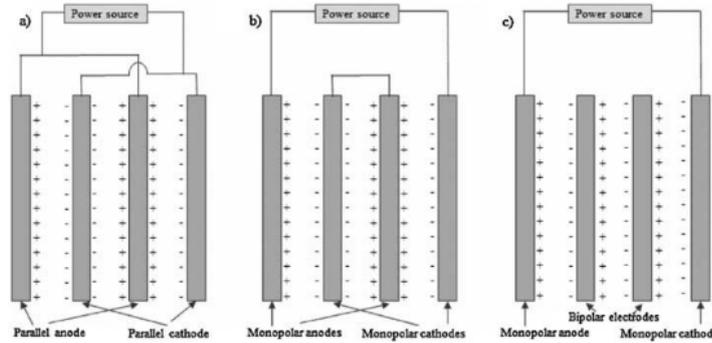


Figure 4.5: Different electrode configuration shown in an electrochemical setup by [6].

The configuration setup showed bipolar electrodes require higher voltage but lower current to operate, hence the best electrode arrangement is based on yield, cost or efficiency. Bipolar in a series connection showed to be favouring yield, while monopolar is the most cost effective, due to the lowest energy consumption and high pollutant removal. [6] Since the current is related to the amount of ions released seen from equation 4.28, keeping the potential of the system at a low value to diminish side reactions from taking place, it is needed to either reduce the distance between the electrode or have a larger surface area, as seen from equation 4.22. The distance between the electrodes should as short as possible, while still allowing a stream to pass by them. To create an electrode in reasonable size, additional electrodes used will give the surface area of one large electrode, but is easier to replace when the electrodes decompose. Other research have been made using multiple electrode sets, e.g. 3 anodes and cathode sets. With multiple electrodes used the circuit path for the electrons are changed and defined by either being serial or parallel connected. For the following equations the subscript [sys] denotes the whole system. For electrodes connected in a serial connected circuit the current, resistance and potential would follow

equations 4.29 to 4.31:

$$U_{sys} = U_1 + U_2 + U_n \dots \quad (4.29)$$

$$Res_{sys} = Res_1 + Res_2 + Res_n \dots \quad (4.30)$$

$$I_{sys} = I_1 = I_2 = Constant \quad (4.31)$$

The potential of the whole system is determined by the each potential drop in the whole system, see figure 4.6, while the current of the system remain constant. This is due to the electrons only having one path to take through the system, and as such will not change.

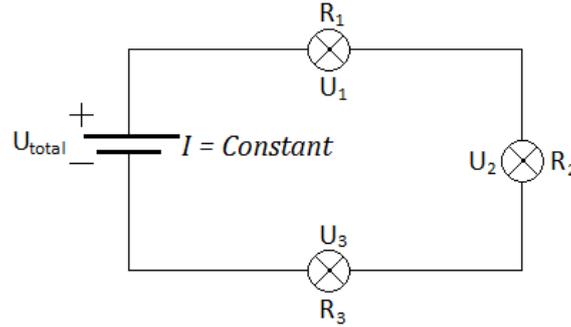


Figure 4.6: Schematic of a series connected circuit. R in the figure are the same as Res.

For electrodes in a serial connected circuit, the resistance of the system determines the potential, and as the resistance change due to passivation layer, concentration increase and distance between the electrodes change as they corrode, a serial connection is not favourable. If the electrodes however are connected in a parallel circuit, the potential, resistance and current of the system is related in equation 4.32 to 4.34:

$$U_{sys} = U_1 = U_2 = Constant \quad (4.32)$$

$$\frac{1}{Res_{sys}} = \frac{1}{Res_1} + \frac{1}{Res_2} + \frac{1}{Res_n} \dots \quad (4.33)$$

$$I_{sys} = I_1 + I_2 + I_n \dots \quad (4.34)$$

For this system, the electrons can take several paths across the electrolyte, with the current of the whole system being a representation of each these paths. Since the resistance still can change like described before, the potential will remain less affected by this, as the increase in resistance might be around one electrode. However in parallel circuits the potential for the system will stay the same, even with multiple paths, as such the current would be the one to drop when the resistance increase at the electrodes. For electrochemistry the potential determines the reaction taking place, which means the parallel connected circuit give a larger control of potential side reactions taking place. Therefore this project will choose parallel connected circuits. A parallel circuit can be seen figure 4.7.

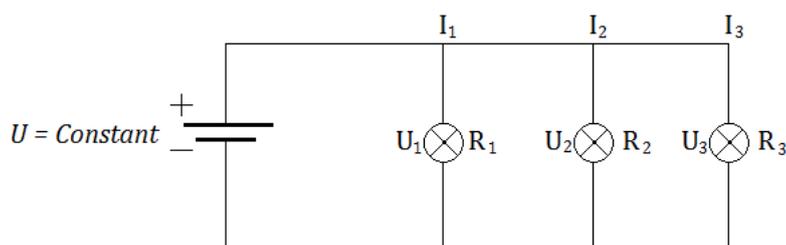


Figure 4.7: Schematic of a parallel connected circuit.

For this project the aim is to connect all electrodes in a parallel circuit, to have a constant potential to avoid generation of unwanted side reactions at high potentials.

4.5 Circuit

When looking at the electrocoagulation cell, a large area is desired, creating a large reactive surface. However, with increasing quantity of solution and concentrations, the area have to increase. Often plates are used, which have a directing flow, but with a large plate, the flow might become laminar at large distances, which would be undesirable for the concentration of ions, since the diffusion and electron migration would be the primary forces to move ions from the surface to the bulk solution. In this project a cell with rods, placed in a array with a predefined distance between each rod, would create a more turbulent flow, as seen in picture 4.8.

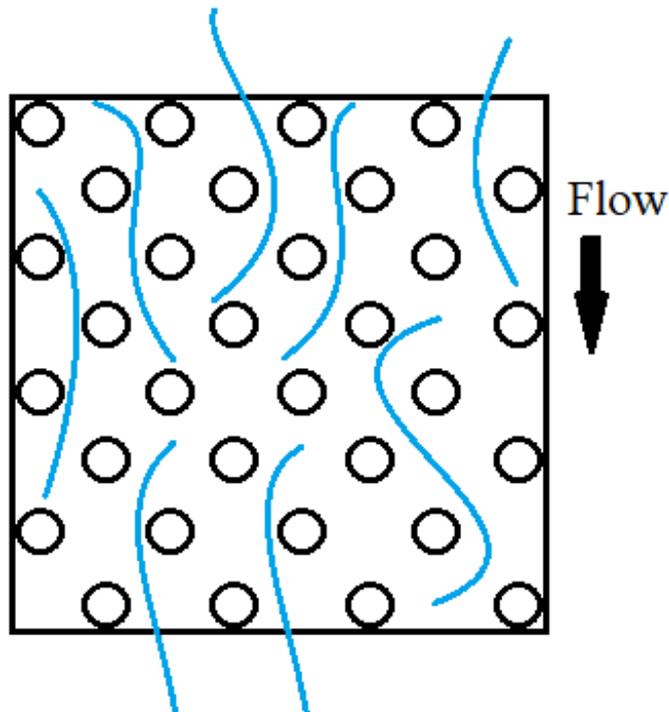


Figure 4.8: The flow through the cell, seen from the side.

The circles in the figure 4.8 represent the electrodes, each row alternating being cathode

and anode. The distance used for predicting the resistance between the electrodes will be defined as follows:

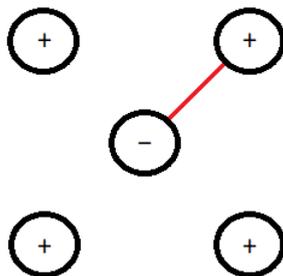


Figure 4.9: The shortest distance between an anode and a cathode with the red line.

Figure 4.9 have the shortest distance between an anode and cathode, while the electrode is enclosed by 4 opposite electrodes. This setup for the flow will disrupt the flow through the cell and help with mixing of the bulk.

4.6 Electrocoagulation process limits

When working with EC previous research covered a number of parameters which may influence the overall efficiency of the cell.

4.6.1 Degradation of electrode

During the continued use of the EC cell, the sacrificial anode will be start to corrode, while the cathode have shown to create an oxide layer[18], which decrease the efficiency. This will lower the overall release of ions, since less generation of hydroxides will also decrease the generation of Fe^{2+} , since the reaction is stoichiometric to keep the electron balance.

4.6.2 Alternating and Direct Current

The use of alternating (AC) or direct(DC) current contributes to the overall operation cost for the EC. DC is the most commonly used power supply for EC, but [19] reported that AC can be superior in operation, where they reported an removal efficiency increase when using AC, and the power consumption lowered overall. This can be due to the decrease of the passivation layer which might form on the cathode, and was reported by [11, 17].

4.6.3 Mass transport limit

4.7 COMSOL

In this project COMSOL multi-physics 5.5 will be used to create virtual models of EC cells. All simulated designs can be found in the enclosed appendix folder. The aim for the COMSOL simulations is to evaluate fluid dynamics and in place of physical construction. In COMSOL two physic studies will be used, Laminar and turbulent fluid flows. For the laminar flow model, this physics is simply selected in the COMSOL multiphysics interface,

using a mesh system to solve the continuum mechanics of the generate structure. When measuring the turbulence fluid dynamics, a selection of models are available:

- Algebraic γ Plus model.
- L-VEL model.
- $\kappa - \varepsilon$ model.
- $\kappa - \omega$ model.

The first two models, L-VEL and γ Plus, simulate the eddy viscosity using algebraic expressions using the local fluid velocity against the distance to the closest wall. Transport equations are not solved in these models. These models are the least expensive in computation power, however also least accurate models.

The $\kappa - \varepsilon$ and $\kappa - \omega$ model are similar in solving. Here two variables are calculated, first the turbulent kinetic energy, k , and the rate of dissipation of turbulence kinetic energy ε or specific rate of dissipation of kinetic energy ω . In these models wall functions will be used, which is computation for fluid dynamics near the wall, see figure 4.10. As simulation approach the wall, the mesh of the geometry needs to be finer, increasing simulation times. These are the most common used turbulence models used in COMSOL, while also being the least computation expensive. For this project the $\kappa - \varepsilon$ is used, as the model is well suited for flow around complex geometries, where $\kappa - \omega$ model are used for strong curvature seen in pipes.[4]

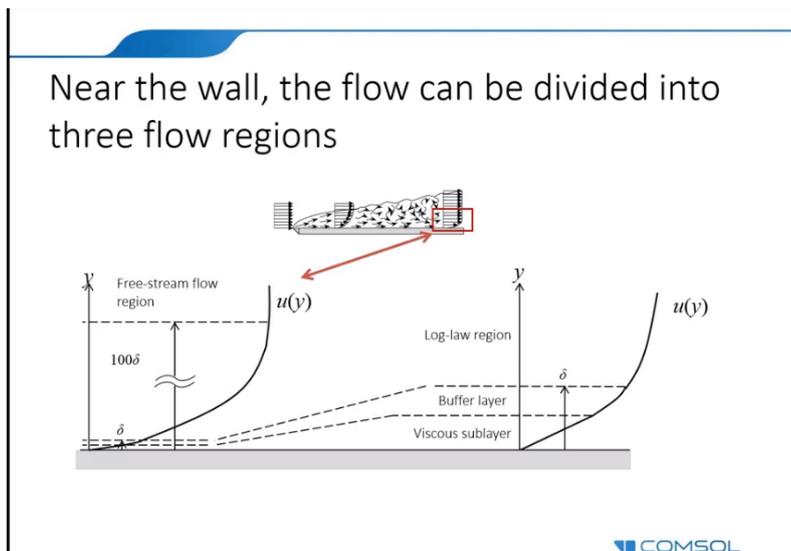


Figure 4.10: Schematic of the layers and wall functions which are used by COMSOL.[2]

Experimental setups 5

This section will cover the simulation setup for each simulation in COMSOL multiphysics where the fluid dynamics will be investigated. Fluid dynamics will simulate the flow through an EC, and measure the pressure difference between laminar and turbulent flow. Parametric sweeps models will be applied, to increase the flow through the cell, to investigate the flow patterns around the electrodes.

5.1 COMSOL - Cell building

This section will cover the aspects of building a EC cell in COMSOL multiphysics. First a model wizard is used to create a 3D model.

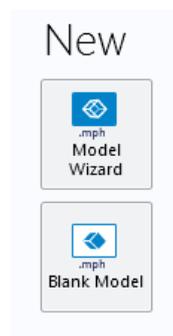


Figure 5.1: The wizard setup from new file in COMSOL multiphysics. Model wizard is selected.

Afterwards a 3D model is selected and physics are selected.

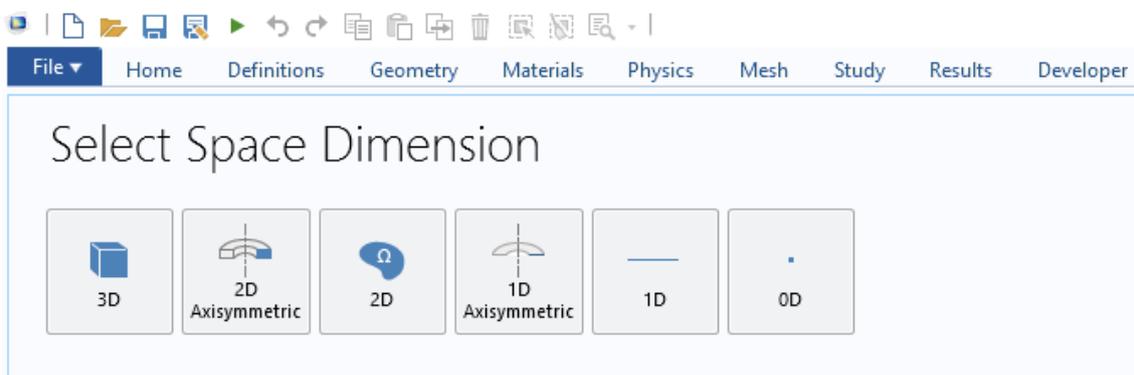


Figure 5.2: Selection of dimension, 3D for this project.

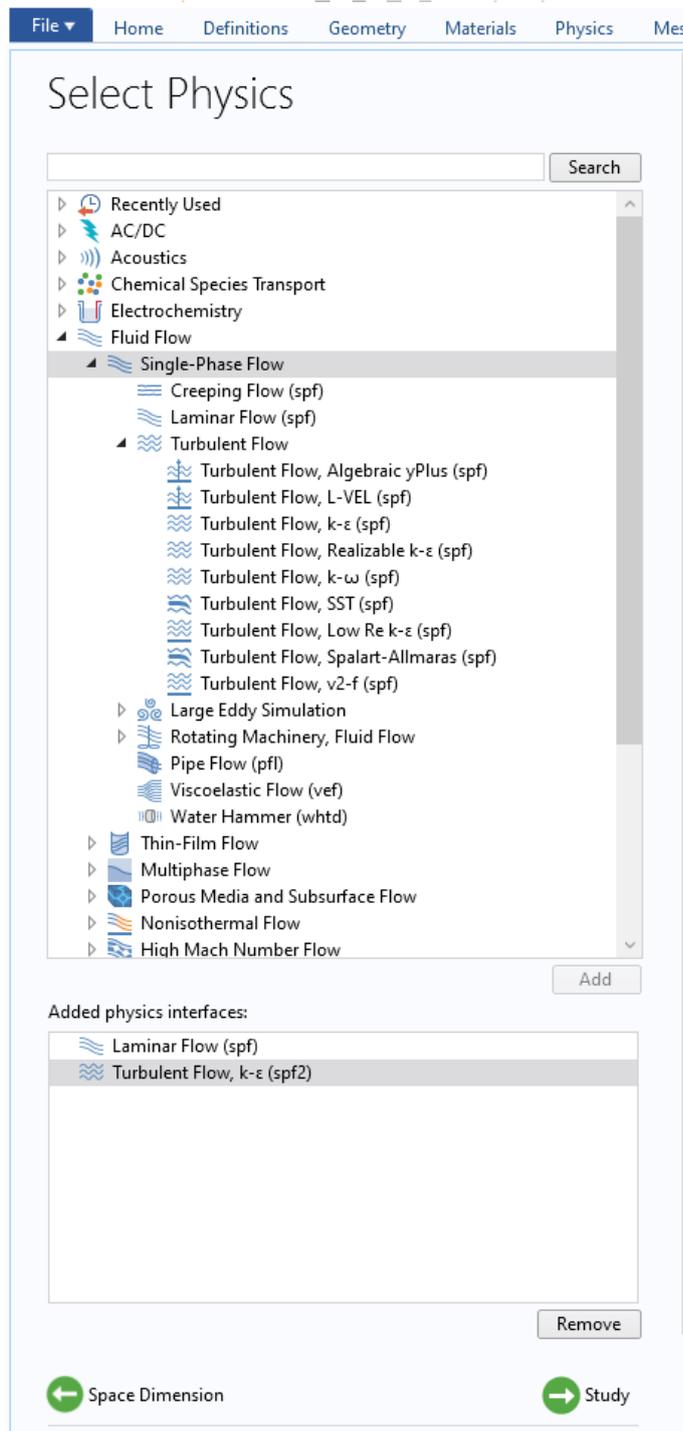


Figure 5.3: The figure show a list of physics COMSOL can use, for these simulations turbulent and laminar flows will be used under Single-Phase Flow. When physics are selected they appear in the lower confirmation box.

Laminar physics is a singular physics model which is selected, however for the turbulent model several physics can be chosen, where each model from top to bottom, will increase the computation time, but increase the precision and accuracy of the model. For this simulation the turbulent flow $\kappa - \varepsilon$ is used. When all physics are selected the Study button is clicked in figure 5.3 to select a study, which is either time dependant or stationary. For

this project stationary is used, as this will assume equilibrium state for operation. This will create the following setup from figure 5.4

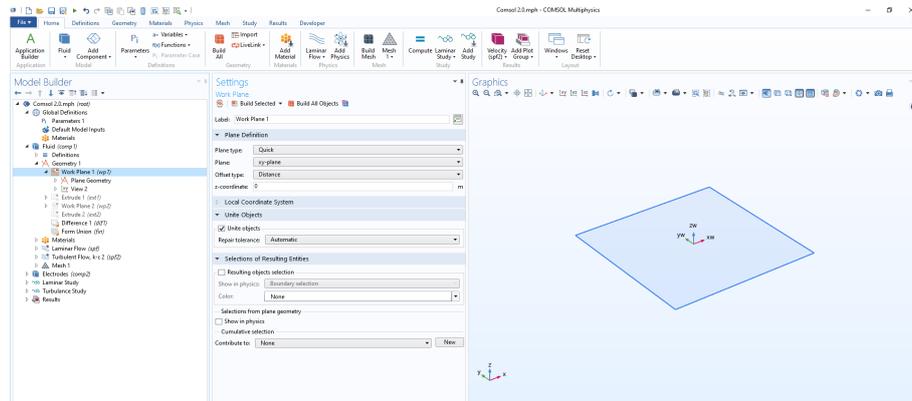


Figure 5.4: The model builder on the left include parameters, geometries and used models measured. Graphics on the right show the work plane used to draw and visualise the geometries in COMSOL multiphysics 5.5.

From the geometry a 2D workplane can be added, which allows to build frame of the cell and position the electrodes before extruding geometry. The extruded model is based on the length of the electrodes, since any length beyond the cell is unaffected by the fluids. The calculations for the height, length and depth of the cell can be found in the enclosed appendix folder under appendix; A1 and A2. This cell is build using a $M \times M$ rod setup, where M is equal to 4 electrodes for this specific setup. Figure 5.5 show the electrodes in the extruded model of the cell.

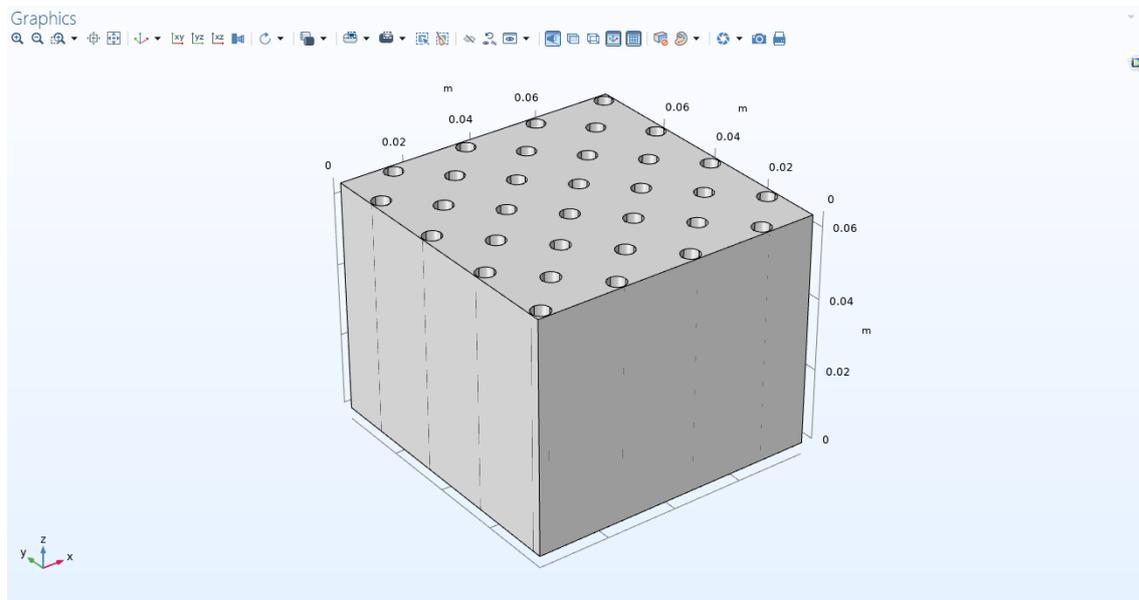


Figure 5.5: The model as build in COMSOL multiphysics, the void in the geometry is representing the electrode positions.

Figure 5.6 in and out flow for the cell.

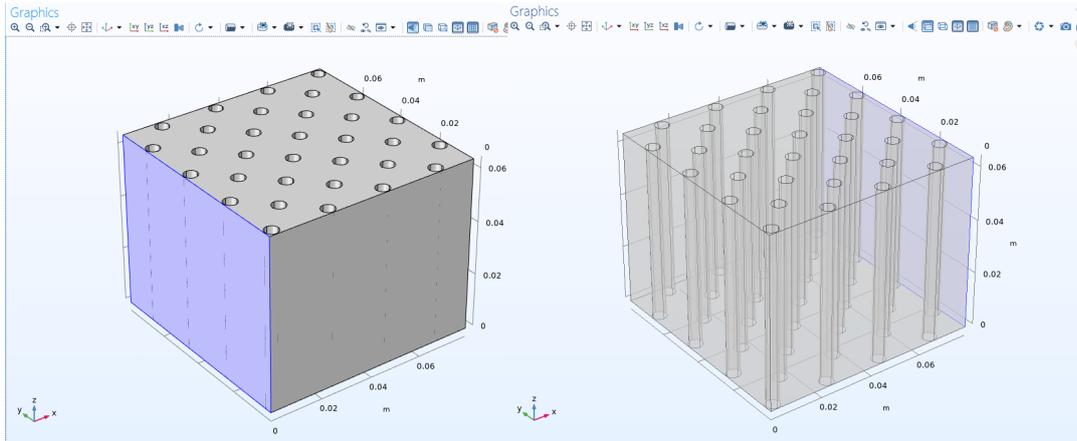


Figure 5.6: The blue area on the left figure show inlet and the right figure show the outlet.

A mesh is then generated for the structure, as small control volumes, which are used for measuring the continuum mechanics affecting the fluid dynamics of the water through the cell. The mesh generated are shown in figure 5.7.

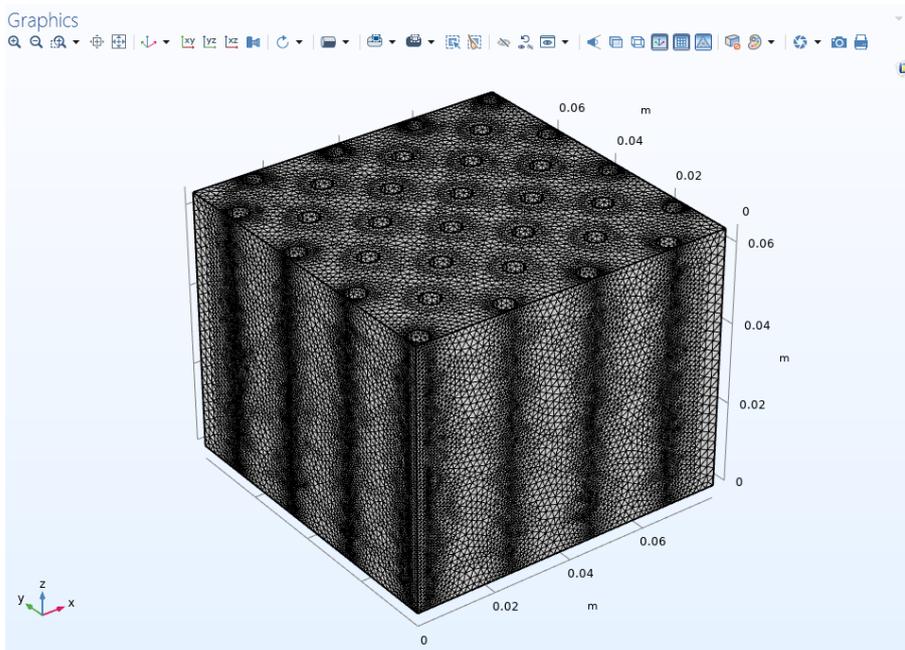


Figure 5.7: Illustrates the *coarse* mesh modelled on the cell. The tetrahedrons are refined near the surfaces and boundaries using a mapped generation of *finer* mesh, due to the distance between the electrodes and the walls of the cell, where coarse is free tetrahedrons are too large to model sufficiently.

Once a mess is generated under each physics, laminar and turbulent respectively, inlet and outlet surfaces are selected. Under each study a parametric sweep is added, which will run the simulation multiple times, and increase the flow through the cell.

Results 6

6.1 Cell design

In this project the cell design was based on having as much surface area available as possible, while using predefined parameters. The following table show the initial selected values for the cell.

| Parameter | Value | Unit | variable range |
|---------------------------|-------|---------------------|--|
| Flow | 0.05 | $[\frac{g}{L}]$ | 0.05 $[\frac{g}{L}]$ to 3 $[\frac{g}{L}]$ |
| Current Density | 17.78 | $[\frac{Amp}{m^2}]$ | 15 $[\frac{Amp}{m^2}]$ to 20 $[\frac{Amp}{m^2}]$ |
| Conductivity | 0.1 | [S/m] | - |
| Concentration | 0.1 | $[\frac{g}{L}]$ | - |
| Diameter of rods | 0.6 | [cm] | 0.5 [cm] to 0.6 [cm] |
| Electrode sets | 16 | - | 16 anodes and 16 cathodes |
| Cathode Anode distance | 1.00 | [cm] | 0.9 [cm] to 1.0 [cm] |

Using the parameters, the cell for COMSOL was designed with the rod setup. First the current were determined by equation 4.28, which gave a current for the system to be:

$$\frac{Q \cdot c \cdot z \cdot F}{M_{Fe^{2+}}} = I_{Fe^{2+}} \quad (6.1)$$

$$\frac{0.05 \frac{L}{min} \cdot 0.1 \frac{g}{L} \cdot 2 \cdot 96485 \frac{C}{mol}}{55.85 \frac{g}{mol} \cdot 60[s]} = 0.288 Amp \quad (6.2)$$

This allowed to determine the required surface area needed, to generate the current, at the predefined current density.

$$J = \frac{I}{A} \Leftrightarrow A = \frac{I}{J} \quad (6.3)$$

$$\frac{0.288 Amp}{17.78 \frac{Amp}{m^2}} = 161.9 [cm^2] \quad (6.4)$$

This surface area will be divided by the desired amount of electrodes, for this case 16 anodes and cathodes will be used giving a total surface area of a single electrode to be $10.12 cm^2$. The length of each electrode was determined using the surface area, and the desired diameter. The following equation r is the radius of the cylinder shaped rods, and the height is the length of the rods.

$$A_{surface} = 2 \cdot \pi \cdot r \cdot h \Leftrightarrow h = \frac{A_{surface}}{2 \cdot \pi \cdot r} \quad (6.5)$$

$$\frac{10.12 [cm^2]}{2 \cdot \pi \cdot 0.25 cm} = 5.36 [cm] \quad (6.6)$$

This was used to generate the structure in COMSOL and the fluid dynamics was calculated on this. The length of the cell was made to have the electrodes in an array matrix with cathode/anode distance being 0.9 [cm]. They were setup in a 4X4 array.

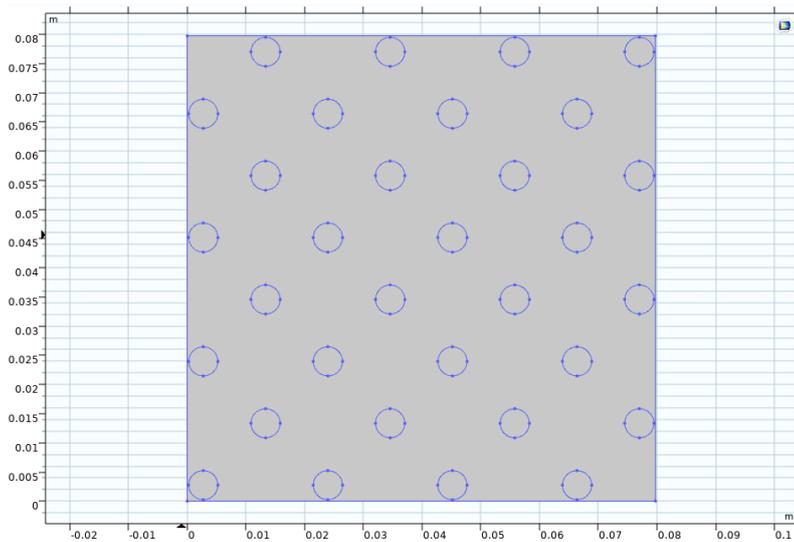


Figure 6.1: COMSOL worksheet of the build cell, with the electrodes in a 4X4 array setup.

The distance between each electrode was used to decide the length of the cell and width of the cell. The height of the cell was set to the length of the electrodes, as anything beyond would not be simulated, or affect the simulations. The distance between two cathodes were determined using figure 6.2

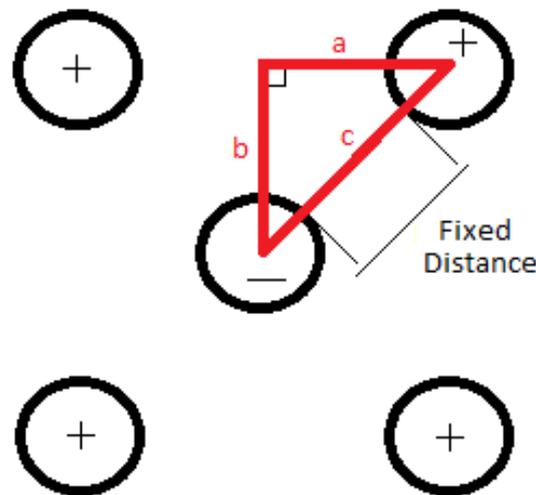


Figure 6.2: The fixed distance is set at the surface of the electrodes. The distance c is based on the space between electrodes to the mass center of the rods. Distance b is the mass center distance between two rows of electrodes and distance a is the mass center distance between two columns. The angles on distance c are set to 45° .

The distance between two same polarity electrodes are equal to distance "a" times 2. For

the first and the last electrode in each set, the length of the cell must be increased by the radius of the rods, since the distance "a" include half the distance of the current rod and the next rod. The length of the cell calculated using:

$$a = c \cdot \cos(45^\circ) \quad (6.7)$$

$$c = 0.9[cm] + 0.6[cm] \quad (6.8)$$

$$a = 0.9[cm] + 0.6[cm] \cdot \cos(45^\circ) \Rightarrow a = 1.06[cm] \quad (6.9)$$

$$length_{cell} = a \cdot 2 \cdot (4 - 1) + d \quad (6.10)$$

$$length_{cell} = 1.06[cm] \cdot 2 \cdot 3 + 0.6[cm] \Rightarrow length_{cell} = 7.92[cm] \quad (6.11)$$

Here the distance between electrodes is 0.9 [cm] and the diameter is 0.6, as the radius of each rod are used, to get to the center for each. This was the dimensions used for generating the cell in COMSOL.

6.2 COMSOL simulations

In COMSOL for the study, everything was measured at stationary, assuming the reactor is at steady state.

6.2.1 laminar

For laminar simulations a single model in COMSOL is used, assuming a everything in the reactor flows at laminar conditions. The model simulates the change in velocity and the pressure through the cell, which can be seen from figure 6.3 and 6.4.

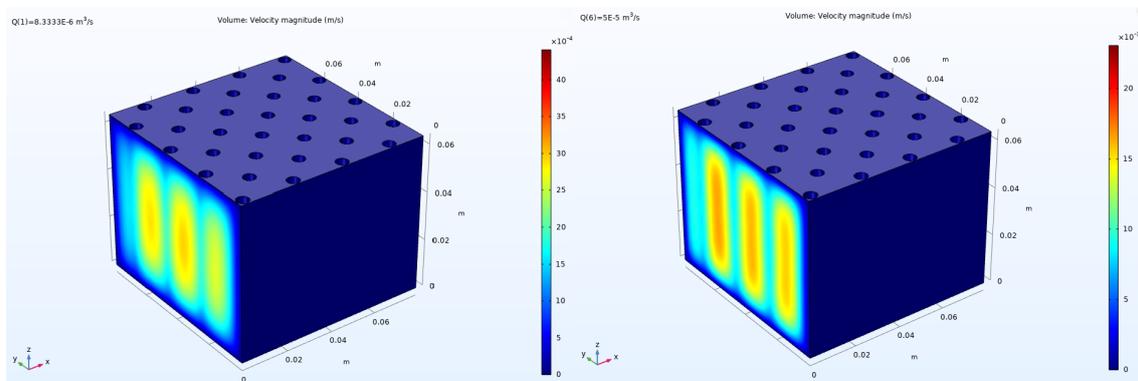


Figure 6.3: COMSOL simulation of the velocity change through the cell. The flow of the cell can be seen in the top left corner for each Cell defined as Q. The legend show the velocity measured in $\frac{m}{s}$ and how it increases from blue to red.

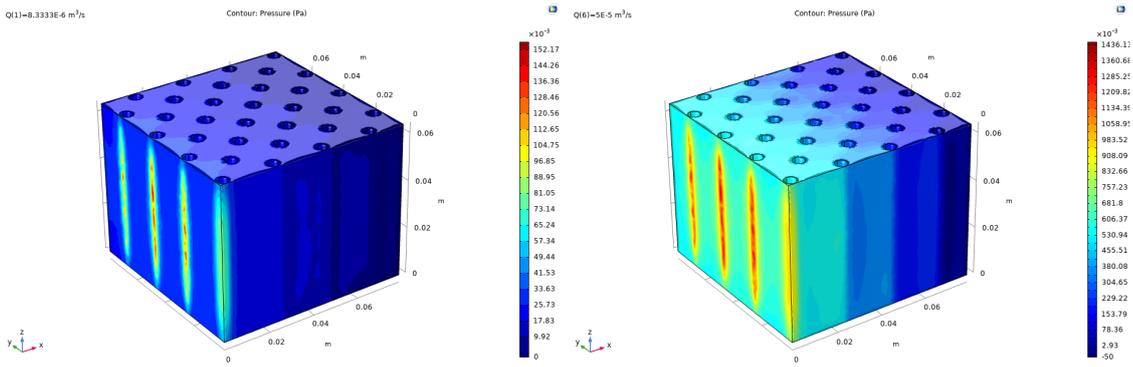


Figure 6.4: COMSOL simulation of the pressure change through the cell. The flow of the cell can be seen in the top left corner for each Cell defined as Q. The legend show the pressure measured in [Pa] and how it increases from blue to red.

For the velocity in laminar conditions, the functions near the wall are not calculated, which is seen as the no change in velocity on both high and low speed, however, inside the cell, the increase in velocity does happen around rod, this is shown in a slice velocity seen in figure 6.5

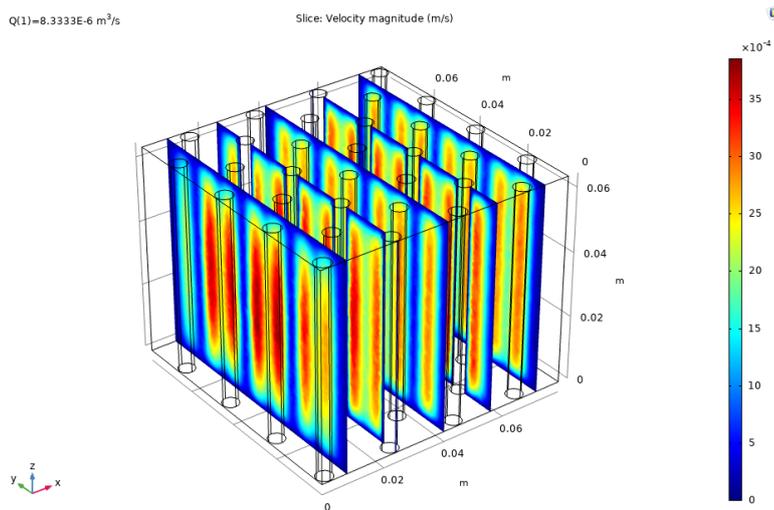


Figure 6.5: It can be seen around the rods the velocity increase, due to the disturbance of the rods.

From the pressure simulation, it seems the first half of the cell is under higher pressure, and dissipates as the fluid passes the next set of rods.

6.2.2 turbulent

For the turbulent simulations, the $\kappa - \varepsilon$ model is used. Evaluating the data from COMSOL are made using convergence plots and wall resolutions, when simulating turbulent fluid dynamics. In COMSOL the wall resolution should be low as possible, otherwise the computational domains exceed the walls, and movement is calculated through

the boundary layers, such as the electrodes. For this model the wall resolution showed promising results, seen in picture 6.6.

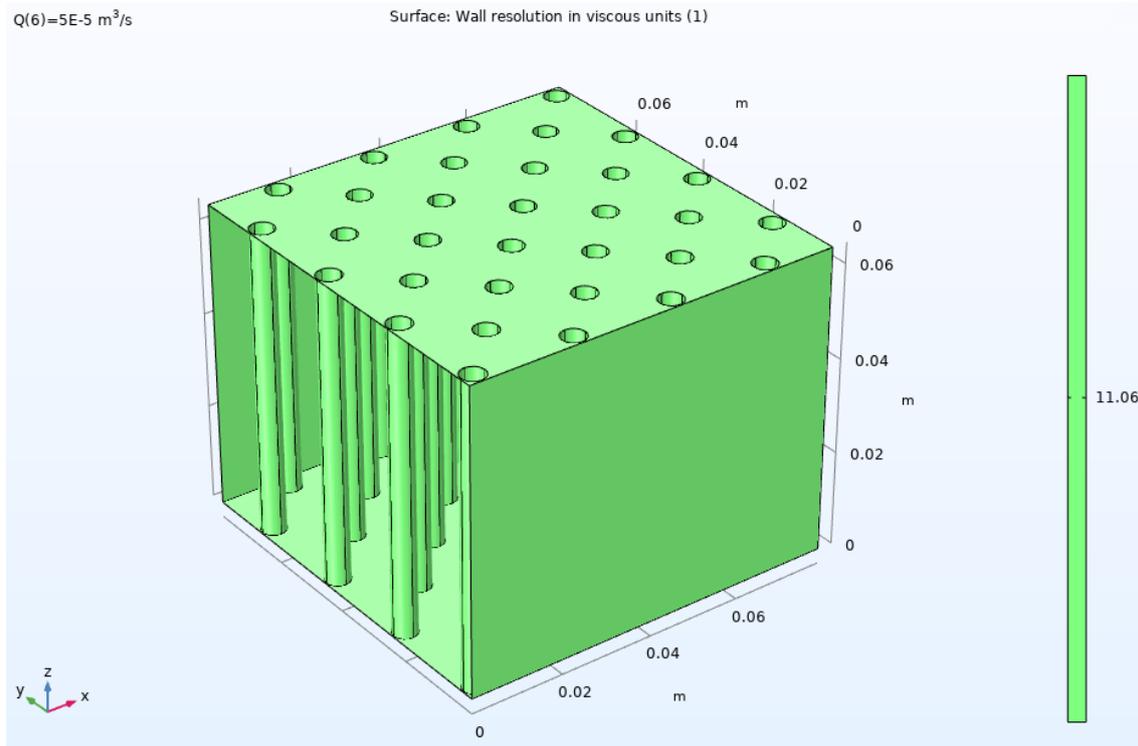


Figure 6.6: COMSOL simulation of the wall resolution for the highest flow turbulent model, with a flow of $3 \frac{L}{min}$.

It can be seen from this picture that the wall resolution is 11.06 everywhere, which is the lowest value and best resolution in COMSOL. This is seen at the highest flow rate of $3 \frac{L}{min}$, which means this meshing is fine enough for fluid simulations. As mention in section 5, the meshing generated for this model is Coarse in the bulk and made a finer mapped mesh near the electrodes and walls, to improve the accuracy of the model and decrease the computation time. Next figures show the velocity of the lowest and highest flow rate through the cell, figure 6.7.

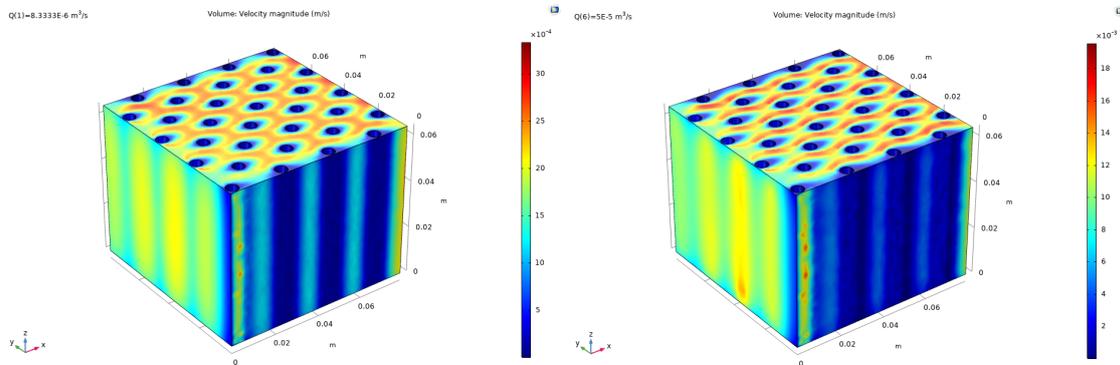


Figure 6.7: COMSOL simulation of velocity for the highest and lowest flow rates of $0.5 \frac{L}{min}$ to $3 \frac{L}{min}$.

Around the rods, the velocity can be seen to change, and increase as the stream meets new rods. On the front of the rods, the velocity seem to increase near the surface of the rod, compared to the back of the rods. The rods around the edges of the cell, experience the least change in velocity, while for the cell setup, a slight space is made between the rods on the edges and the wall of the cells. The low flow rate have the higher velocity of the near the rods at the wall of the cell.

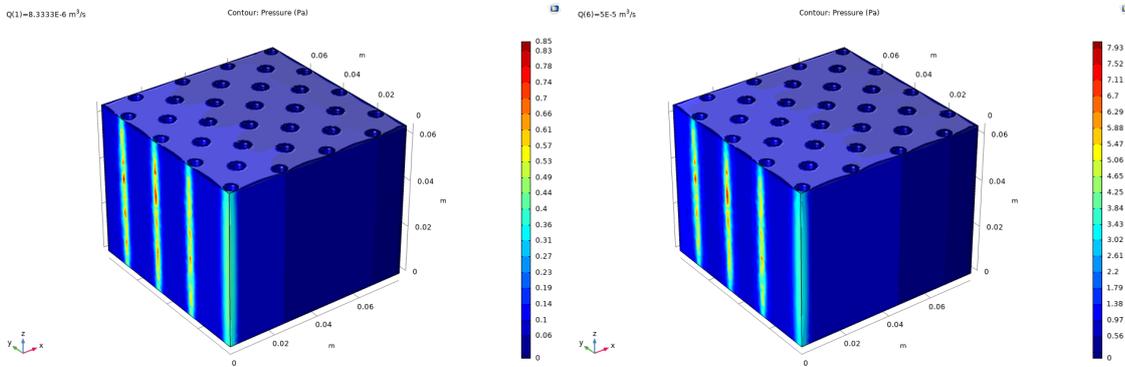


Figure 6.8: COMSOL simulation of pressure change for the highest and lowest flow rates of $0.5 \frac{L}{min}$ to $3 \frac{L}{min}$.

The pressure in the cell is less affected by the rods, compared to the laminar flow model, and the pressure change decrease through the cell. "

Discussion 7

7.1 Discussion

The potential attained by generating the COMSOL model, have a current of 0.288 [Amp], and with the specific conductivity of wastewater from [], the resistance of the circuit can be determined as 98.90 [Ohm], however as the cell is using 16 electrodes the resistance of the system become as equation 4.33.

$$\frac{1}{R_{sys}} = \frac{1 \cdot 16}{98.9[ohm]} \Rightarrow R_{sys} = \frac{98.9[Ohm]}{16} \quad (7.1)$$

$$R_{sys} = 6.18[Ohm] \quad (7.2)$$

This means the effective resistance of the parallel system is far lower, then the resistance for a single electrode set. The potential can now be estimated using Ohm's law.

$$U_{sys} = I \cdot Res \quad (7.3)$$

$$0.288[Amp] \cdot 6.18[Ohm] = 1.78[V] \quad (7.4)$$

$$(7.5)$$

This would allow the operation of releasing iron into the solution, having the operation potential at 1.78 [V], and getting a concentration in solution to 0.1 [$\frac{g}{L}$]. However, as the resistance is dependant on the conductivity of the electrolyte, as the concentration of iron and hydroxides increase near the surface of the electrode, the resistance will increase. Between the two circuits, series and parallel, the parallel will experience less overall resistance increase, as each electrode will be a single circuit, as the current will remain the same. To get the most accurate conductivity of the electrolyte, it is better to use the molar conductivity, seen in equation 7.6.

$$\Lambda_m = \frac{\kappa}{C} \quad (7.6)$$

Here the Λ_m denotes the molar conductivity and κ is the conductivity of the electrolyte and C is the molar concentration of the electrolyte.

7.1.1 COMSOL

In COMSOL the fluid dynamics was only simulated, as the species transport model was not giving proper results. To simulate the electrolytic resistance, change in potential, and release of iron and hydroxides in COMSOL some limitations were observed. The passivation layer which have been reported in [18], cannot be simulated in COMSOL, as the simulation will only show the operation at steady state.

The cell was designed to avoid having flow behind the edges of the electrodes near the wall, since the no counter electrode would be near. This was due to ensure most of the fluid flow in passed near an electrode, within the shortest distance of 1 [cm]. But when simulation, to avoid a meshing difficulties near the electrodes at the wall and the wall, a space was added to encounter that.

Conclusion 8

It can be conclude the theoretical creation of a cell based on a fixed current density and concentration generated a structure in a parallel circuit, showing a potential being lower than 1.8 [V]. COMSOL multiphysics as strong tool to simulate the fluid dynamics.

Perspectives 9

To work further with this project a physical cell would be build of the same dimensions as the one generated in COMSOL. Here the release of iron ions based on the current and flow rate would be measurable and compared to COMSOL simulation. This would be done on wastewater, taken from before primary sedimentation, secondary sedimentation and dewatering treatment. The release of iron could be measured using qualitative inorganic analysis using thiocyanate, to create coordination complexes in a spectrophotometer. This complex follows Le Chatelier's principle, and along with ICP can determine Fe^{2+} and Fe^{3+} in solution. Treating the wastewater with oxygen to measure the change in $\text{Fe}^{2+}/\text{Fe}^{3+}$ compared to untreated wastewater. For COMSOL the simulations of mass transport using either Primary, secondary or tertiary current distribution. This can be used to understand the how the composition of the fluid, concentration overpotential and kinetics affect the overall process. This can be seen from figure 9.1.

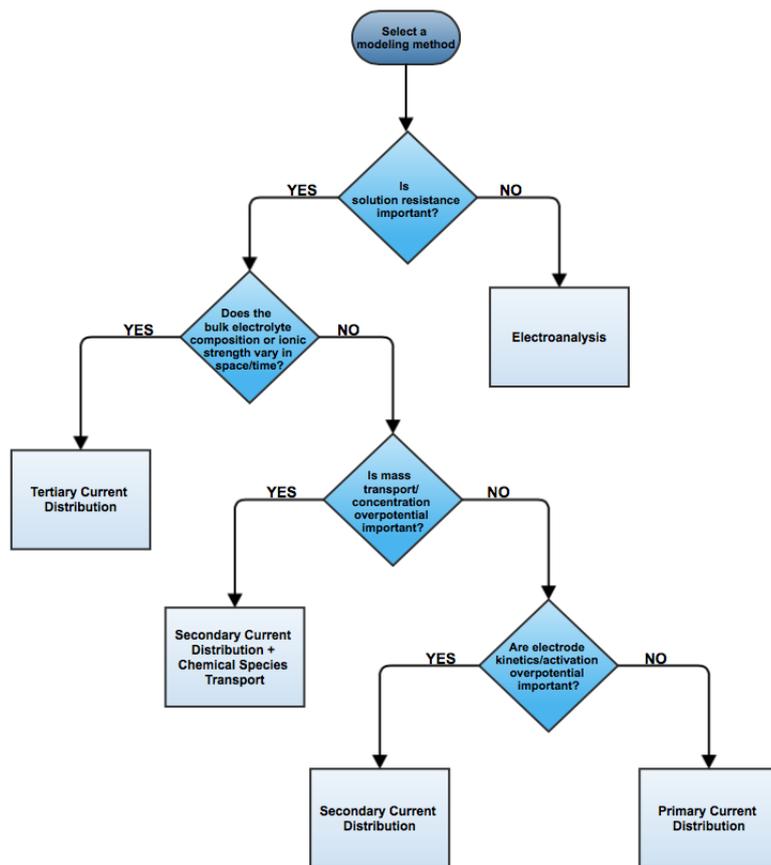


Figure 9.1: This figure is a guideline for which model to use depending on model variables and parameters. [4]

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