Modeling Study of Electrocoagulation System For Treating Wastewater

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Effective treatment of wastewater from households, communities, and industries is vital to preserve our environment. Chemical treatment to add coagulants into the wastewater is the most popular treatment method, but due to the high operating cost and secondary contamination issue, a novel method to solve those issues is required. In this study, we revisited the electro-coagulation (EC) system which has promising features of low system/operating cost and environment friendly process. EC was actively developed once, but due to the low efficiency and scaling-up issues, it could not be fully utilized. In this study, physics-based mathematical model was developed to elucidate the underlying physics of the EC process and to define key control parameters which enables to resolve those issues fundamentally.

Multi-physics coupled with electrochemical reactions at electrodes, chemical reactions in bulk solution, diffusive and convective transport of ionic species were implemented to develop a two-dimensional unsteady mathematical model supported by Langmuir isotherm theory for the first time. The developed model was utilized to analyze the effect of geometry parameters of the EC reactor (i.e., distance between electrodes) and operating conditions (i.e., applied current intensity, flow rate and pollutant concentration in wastewater) on distribution of intermediate ionic species generated from each electrode, and adsorption behavior between generated coagulants and
arsenic/phosphorus pollutants in the wastewater. It is expected that results from this extensive research will be utilized as key information for EC reactor developers to develop their systems effectively.
MODELING STUDY OF ELECTROCOAGULATION SYSTEM FOR
TREATING WASTEWATER

BY

SWACHWA DEY
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A THESIS SUBMITTED TO THE GRADUATE SCHOOL
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FOR THE DEGREE
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Thesis Director:
Kyu Taek Cho
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DEDICATION

To my wife Disha Mony Dey, parents Sujit Kanti Dey & Rina Kana Chowdhury, sister Moumita Sonia Deb, and brother-in-law Snehasis Biswas.
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CHAPTER 1: INTRODUCTION

1.1 Treatment of Contaminated Water

The access to drinking water is under stress. Water pollution is responsible for unbalanced aquatic ecosystems as well as scarcity of healthy water. There is always a need to develop efficient treatment process for managing wastewaters to maintain quality and improve quantity at broader scale by safeguarding environment and sustainability (Hakizimana et al., 2017). The treated wastewater can be reused, which depends on the efficiency of treatment process. This process is very crucial for sustainable environmental balance and safety. Industrial wastewater is more often treated under various processes to meet the environmental, state, or municipal moreover international regulations (ISO 23043:2021). Wastewater treatment procedures can be divided into major three parts, which are physical treatment, biological treatment, and chemical treatment (Moussa et al., 2017).

Physical treatment which is pretreatment or primary treatment of water, is done by sedimentation or flotation of solid waste within water. This pretreated water is passed through several filters to separate larger solid wastes. After separating larger solid wastes, the water is flown through a chemical process which separates smaller solid particles by generating larger flocs (Adejinle, 2019). Physical process does not cause significant change of the chemical or biological composition of the wastewater. Biological treatment processes are used to degrade contaminants through microorganisms and the key purpose is to reduce organic contents or
nutrients. The available biological processes are, trickling filters, aerated lagoons, activated sludge, rotating biological contactors. The chemical treatments are known as additive processes, as these processes are performed by adding chemicals to react with the contaminant for removal. Chemical process includes coagulation/flocculation, chlorination, adsorption and ion exchange (Moussa et al., 2017).

One of the chemical process called coagulation, which is performed by adding certain chemicals named coagulants to form flocs which adsorbs pollutants from wastewater. There is a current technique called electrocoagulation (EC), which combines coagulation and electrochemical procedures where additional coagulants are not required. Electricity was used for water purification back in 19th century, due to high capital cost and electricity cost this technique was abandoned for long period of time (G. Chen et al., 2004). Recently, this technique has gotten enormous attention due to its favorable environment condition which provides less footprint. Moreover, availability of cheap electricity nowadays, which ensures the process economically sound also. This current study will focus on a two-dimensional mathematical model of EC process which analyzes mass transfer of key species generated during EC process and their consequent effects on pollutant removal capacity under different operating conditions. As the EC process is the combination of coagulation and electrochemistry, the following section is going to briefly overview about coagulation process and EC.

1.2 Chemical Coagulation Process and Electrocoagulation

Over 100 years ago the modern use of coagulants for water treatment started with ferric chloride and aluminum sulphate as the coagulants for water treatment (Jiang, 2015). A
chemical coagulation process is shown in Figure 1. When coagulant is added to wastewater, it precipitates with trapped pollutants. The reactions occur when alum or ferric salt is added to the impure water which is influenced by several operating conditions such as mixing intensity, pH, temperature, alkalinity, and the nature and amount of turbidity (Pizzi N. & Lauer, W., 2013). To occur aggregation of particles, there are four coagulation mechanisms, namely 1) double layer compression; 2) sweep flocculation; 3) adsorption and charge neutralization; and 4) interparticle bridging. The overall coagulation process involves the reaction among the colloids and the added coagulants which destabilize and neutralize the electric charges in particles. The added coagulants are responsible for the creation of small scattered particles which come together into larger and more stable particle flocs (Tetteh & Rathilal, 2019).

Electrocoagulation (EC) on contrary is used as an alternative technique of chemical coagulation for treating wastewater. This process includes the combining effects of coagulation, flotation, and electrochemistry (Hakizimana et al., 2017). The major difference
with the coagulation and electrocoagulation is that; no addition of coagulants required for EC process as coagulants are being generated in-situ when current is applied (Moussa et al., 2017). A simple EC cell is shown in

Figure 2 below, which is consists of anode and cathode electrodes and a DC power supply.

![Figure 2. Schematic representation of a basic EC cell. (Moussa et al., 2017)](image)

While current is applied on an EC cell, metallic hydroxides are generated in-situ via electro-dissolution of a soluble sacrificial anode, which immersed in wastewater. Through the electrochemical reactions, generated metallic ions hydrolyze near the anode to form series of metal hydroxides, those have capability to destabilize the dispersed particles present in the water (Chou et al., 2010). Among those hydroxides or species, the most stable and solid faced hydroxides extract the pollutant on their surfaces, and the hydrogen gas bubbles generated during chemical reactions carry the flocs formed to the surface in an adsorption process. The rate of generation of flocs is dependent on the applied electric current, and it can be controlled according to the requirements, which is a fascinating technology for water or wastewater treatment (Balasubramanian et al., 2009).
As in EC process additional chemical is not necessary, there is lack of chance of secondary pollution occurring, which is also another key advantage of EC system (Holt et al., 2005). During the hydrolysis reactions, the evolution of hydrogen gas bubbles occurs at the anode with every reaction. These gas bubbles then help to remove the pollutants by floating them on the surface of the solution (Mollah et al., 2004). Due to the simplicity of operation of EC process, it allows complete automation of the entire system (Bazrafshan et al., 2015). In EC process the flocs filtration is easier with compared to the chemical coagulation, because flocs generated from EC process are larger than normal chemical coagulation (Mollah et al., 2004). EC system also delivers less sludge volume compared to coagulation process (Bazrafshan et al., 2015). The process is also faster than other treatment process and more smaller pollutant particles can be removed as the reactions occurs in ionic level (Holt et al., 2005). However, the replacement of sacrificial anode is necessary since it dissolves in the solution during EC process (Mollah et al., 2004).

The efficacy of an EC system depends on several operating conditions and other factors, which are current density/applied current intensity, cell arrangement, flow rate of a continuous system, cell gap, current density, current efficiency, initial concentration of pollutant, pH condition of the solution, material properties of pollutant, type of anode, type of power supply, and other wastewater features (Hakizimana et al., 2017). Most of these factors are operating conditions. Among those, some of the crucial factors are going to be discussed in the following section which are studied during this research for optimization of EC technique.
1.2.1 Effect of Applied Current/Current Density and Current Efficiency

Current density or amount of applied current fixes the dosage of the coagulants generated from the anode and the evolution of the hydrogen gas at the cathode (Hakizimana et al., 2017). Hydrodynamics of the system depends on the generation of hydrogen bubble, which influences the mass transfer between pollutants and species generated during chemical reactions and affects the collision rate of coagulated particles that results in floc formation (Holt et al., 2002). For optimum output from EC process, current limit must be determined carefully for proper optimization. The level of optimum current intensity also affected by several operating conditions as like as pH, temperature, and water flowrate (G. Chen, 2004). Due to super faradic behavior of electrochemical system, it is often observed that metallic ions generated during EC process is more than the amount calculated the Faraday law. Super faradic behavior was found to be valid by Graça et al., 2019. This phenomenon is more often defined by current efficiency.

1.2.2 Effect of Distance Between the Electrodes

The distance between electrodes is also a key factor for proper optimization of an EC system. Though there are many types of cell arrangements are available in electrochemical systems but the gap between the main anode and cathode, affects mass transfer and mass generation of key species a lot. Energy consumption also decreases with a small cell gap system (Hakizimana et al., 2017). With small cell gap, more electrochemically generated gas bubbles bring about turbulent hydrodynamics which leads to more mass transfer as well as chemical reactions between the coagulant species and pollutants (Martínez-Villafañe et al., 2009).
1.2.3 Effect of Initial Pollutant Concentration

Initial pollutant concentration also found to be an important factor that affects the overall performance of the EC system. The removal efficiency of the system depends on how much pollutant the system needs to abate. The removal rate of an EC system reaches to a steady state position in different times, which fairly depends on the operating condition and nature of the pollutant. The performance of the EC system varies whether it is dealing with high initial pollutant concentration or low, though nature of the pollutant remains same. The level of initial pollutant concentration abatement also determines whether the EC system is suitable for primary, secondary, or tertiary treatment according to requirement of usage of treated water.

1.2.4 Effect of Influent Velocity

The influent velocity of wastewater in any continuous water treatment plant is a vital factor for its performance. The relevant technologies or other equipment of water treatment system hugely depend on this key parameter. The magnitude of flow rate affects the formation and growth of the flocs generated during EC process and the floatation effect (Song et al., 2018). Both in bench scale testing and industrial sectors, effects of flow rate are studied in broad range. High flow rate often observed to be inefficient as it provides less time of mixing and treatment whereas low flow stream provides more time of mixing which affects mass transfer as well mass generation of key species. Sometime too low flow rate would not be effective due to other operating conditions or related other machineries in an industrial plant.
1.3 Literature Review

Ensuring sufficient drinking water for all is one of the most critical and predominant issues in the world. Most of the population in the world still do not have access to proper drinking water. The realization of this difficult issue leads to huge effort for developing cost-effective, reliable, and environmentally friendly wastewater treatment technologies that would be able to reuse a significant amount of water produced from various industries (Moussa et al., 2017). There are many available technologies to treat the wastewater for providing mass access to reuse. However, those technologies are quite costly due to high maintenance requirements. At that point electrocoagulation system appears as one of the best alternatives for recycling wastewater for its favorable environmental and financial features.

Due to the complexity of underlying physics of the EC process, the development of mathematical models able to describe all the mechanisms related to the process within single model are not substantial (Graça et al., 2019). Lack of theoretical understanding of underlying physics of this process is the major obstacle for proportionating the technique in industrial as well as other large sectors. Numerous publications can be found on EC process development, which primarily focus on laboratory scale experiment to provide proof for effectiveness of the technology for removing specific pollutant. Few other researchers tried to look into the kinetics, modeling, cell design, electrode arrangement and materials, cost analysis, integrating electrocoagulation with other existing methods (Moussa et al., 2017). Some of the distinctive research and analysis conducted on modeling of EC system are reviewed prior and during this current research.
A zero-dimensional (0D) mathematical model on EC system for removing arsenic content was developed by Graça et al., 2019. They investigated total and dissolved aluminum concentration at different applied current by considering hydrolysis reactions. That model did not include the mass transfer effects of the intermediate species generated during the EC process. The Langmuir adsorption isotherm was though included with model to evaluate performance of the system. The model predicted the concentrations of total and soluble aluminum satisfactorily.

A two-dimensional (2D) EC model was formulated by Lu et al., 2017 by considering mass transfer effects of interim species generated during EC in a steady state condition. They evaluated effects of current density, residence time and pH of the solution to analyze the mass distribution of key species at different locations of EC domain. The model did not include any kinetics for adsorption mechanism for pollutant removal. Recently, another 2D model was developed by McBeath et al., 2020 for removing organic pollutant by considering mass transfer effect of the species generated during EC process. This model also did not add any adsorption mechanism for consequent evaluation for their mathematical model regarding removal efficacy. They studied the current distribution of species at different operating conditions i.e., different cell gap, arrangement, turbulent flow modeling etc.

Some researchers developed phenomenological models depending on the kinetics of overall EC process (Hakizimana et al., 2017). Mameri et al., 1998 attempted to model EC kinetics of removing fluoride anions. They found an exponential relation with time, so that it was a first-order kinetic model with fluoride concentration. Essadki et al., 2010 also computed a kinetic model on defluoridation kinetics in an external-loop airlift reactor. They observed
that the kinetic constants were increased with the increment of electric current while the values of those constant decreased with the increment of initial fluoride concentration.

Most of the adsorption mechanism related research works for EC process depend on experimental evaluation for better fitting of data. It is surprisingly observed that adsorption mechanism was not under focus of EC modelers when they were developing numerical models on EC technique. For removing COD from the wastewater of semiconductor manufacturing plant, Chou et al., 2010 studied adsorption mechanisms focusing on different adsorption techniques and their properties. The study was conducted by comparing experimental data with Pseudo-first-order (Lagergren et al.) and Pseudo-second-order (Ho & Mckay, 1998) adsorption kinetic models and Langmuir (Langmuir, 1916), Freundlich (Freundlich et al.) and Dubinin-Raduskevich (Dubinin & Radushkevich, n.d.) isotherm models. The pseudo-first-order and the pseudo-second-order kinetic models were also adopted by Khatibikamal et al., 2010, Murthy & Parmar, 2011, and Vasudevan et al., 2011. The pseudo-first-order adsorption kinetic model assumes that the rate of occupation of the adsorption sites is proportional to the number of unoccupied sites, on the other hand the pseudo-second order model describes the adsorption equilibrium (Hakizimana et al., 2017). A statistical model of EC process was introduced by Balasubramanian et al., 2009, which combined experimental data and different adsorption mechanisms comparison, and by doing that they formulated some empirical relations. This kinetic and statistical model for removing arsenic derived through response surface methodology (RSM). Aluminum (Al) and mild steel anodes were used for comparing EC performance and empirical relationships were developed by RSM. It was found that Al electrode had better performance over mild steel electrodes and Langmuir isotherm more well
fitted with experimental data for describing adsorption mechanism. Hu et al., 2007 introduced a new adsorption kinetic model which is known as variable-order-kinetic model (VOK). The model was derived from existing adsorption isotherm models and Faraday’s law. The VOK model initially developed for defluoridation, later it was seen that, the model is quite efficient to estimate time for fluoride removal by using EC mechanism (Hakizimana et al., 2017).

Some other researchers also conducted statistical modeling of EC system based on RSM but with different names or approaches for design optimization. Daghrir et al., 2013 and Garg & Prasad, 2016 developed their statistical model by full or partial factorial design (FD). Central composite design (CCD) was adopted by Garg & Prasad, 2016, Amani-Ghadim et al., 2013, Gengec et al., 2012, Olmez-Hanci et al., 2012, Bhatti et al., 2009, and Bhatti et al., 2011. D-optimal design (DOP) and Box-Behnken design (BBD) also utilized by several other researchers for RSM modeling (Tir & Moulai-Mostefa, 2008, Chavalparit & Ongwandee, 2009, Zodi et al., 2010, Garg & Prasad, 2016a, and Tak et al., 2015). FD was used to identify the effects of independent variables and their interactions and CCD, DOP, and BBD were used to determine the optimum operating conditions (Hakizimana et al., 2017).

Analysis on electrochemical properties of EC system also conducted by few researchers. Electrolysis voltage of EC system was analyzed by X. Chen et al., 2002 by adopting Butler-Volmer equation. They demonstrated that pH and flow rate have little effects on electrolysis voltage within large range. Inter-electrode distance, conductivity of the solution, current density and surface condition of electrodes play vital role for determining electrolysis voltage. Dubrawski et al., 2014 also conducted research on electrochemical properties of EC system for relating potential and current in continuous parallel EC system for evaluating overall
performance under different operating conditions. They performed their analysis at cell potentials of 2-20 V. It was found that, their model deviated highest 9% when system was adjusted with low flow rate, narrow electrode gap, polished electrodes and 150 mg/L NaCl supporting electrolyte. Highest deviation occurred when the electrode gap was enlarged, unpolished electrode was used and Na$_2$SO$_4$ provided as supporting electrolyte.

There are some available studies which includes financial analysis of the EC process with utilization of operating conditions. Uludag-Demirer et al., 2020 did a techno-economic analysis of EC on water reclamation from organic wastewater experimentally. Their work found quite satisfactory result in terms of removing turbidity, total phosphorous, total chemical oxygen demand removal, but it was able to remove total nitrogen insufficiently from organic waste. Recently, McBeath et al., 2020’s 2D model for determining current density distribution of species and fluid modeling of EC process and consequently its effect on removal of natural organic matter from drinking water as well as power consumption analysis. This particular study, identified that more uniform current distribution achieved in an EC process with a larger electrode gap due to the influent flow uniformity and it was also found that the removal of natural organic matter was reduced when the inter electrode gap was reduced to from 10 to 1 mm.

These literature studies indicate that, most of the physics of EC system have never been analyzed together by combining mass transfer effects of the intermediate species generated during EC process and consequently adsorption kinetics occurring for pollutant removal within the EC domain. Another key observation is that for modeling of EC mechanism, all models
consider some specific pollutant removal. There is no scholarly article found on modeling of a novel EC model which can be utilized with any kind of pollutant removal.

1.4 Objective of Study

The main objective of this study is to analyze the EC mechanism by considering electrochemical reactions, chemical reactions, diffusive, and convective mass transfer effects of intermediate species generated during EC process. In this research the operating conditions are optimized by considering important physical phenomena of EC process. To enhance the performance of the EC system, even distribution of key species generated during EC process is necessary. The effects of important operating conditions; current density or applied current, the initial concentration of the pollutant, and flow rate and geometric parameter (cell gap) are evaluated to achieve more even distribution of key species to increase the efficiency of the system. The adsorption mechanism is also included in this research for evaluating performance of the EC system. The Langmuir adsorption isotherm is successfully simulated with 2D model to calculate the efficiency of the system with more accuracy. It is seen that; specific pollutant removal was usually focused on most of the previous EC related studies to prove the effectiveness of the technique. The following study, both organic and inorganic pollutants are considered for evaluation of the system. For the detrimental characteristics of arsenic (inorganic) and phosphate (organic), which are the major components of most of the wastewater sources; the current research is conducted for reducing their concentration significantly through EC treatment. This research focuses on analyzing and determining the optimum operating conditions for applied current, cell gap, initial concentration of pollutant,
and influent velocity for evaluating the key factors that influencing the performance of the EC process through a 2D mathematical model.
This current study is completed in three phases, which are shown in Table 1. In 1st phase zero-dimensional (0D) model is built in unsteady state for both arsenic and phosphate removal. The experimental data from Graça et al., 2019 regarding arsenic removal are analyzed through the 0D model. For phosphate removal the experimental work done by Shalaby et al., 2014. are validated at four different current densities. The operating conditions and relative parameters are collected and analyzed from their experimental data.

In 2nd phase, the operating conditions are analyzed two dimensionally (2D) for both arsenic and phosphate removal with consideration of mass transfer effect in batch reactors. For batch EC reactors, only diffusive mass transfer effect is considered. Then, on this model effects of current intensity, cell gap, and initial pollutant concentrations are observed.

During 3rd phase of work a continuous EC reactor model is developed. In this 2D model diffusive and convective mass transfer effects of species are considered. Same operating conditions are kept for both arsenic and phosphate removal. The performance of the EC cell is evaluated at three different inlet velocities. The analysis on distribution of key species generated during EC process are performed at different locations of the EC domain and different inlet velocities.
Table 1: Operating conditions analyzed for three modeling phases (unsteady state) for arsenic and phosphate removal.

<table>
<thead>
<tr>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D (batch reactor)</td>
<td>2D (batch reactor)</td>
<td>2D (Continuous reactor)</td>
</tr>
<tr>
<td>Effect of current</td>
<td>Effect of current intensity for</td>
<td>Convection effect in</td>
</tr>
<tr>
<td></td>
<td>batch system reactor</td>
<td>continuous reactor</td>
</tr>
<tr>
<td>Initial concentration of</td>
<td>Cell gap effect in batch</td>
<td></td>
</tr>
<tr>
<td>pollutant</td>
<td>system reactors</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Effect of initial pollutant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>concentration in batch system</td>
</tr>
<tr>
<td></td>
<td></td>
<td>reactors</td>
</tr>
</tbody>
</table>

It is mentioned that this numerical study is carried out for both batch and continuous EC cell reactors. Due to the high conductivity of the solution as supporting electrolyte is provided, and the system is considerably low in size, for those reasons the migration effect for mass transfer is omitted. The structure of our study for batch system EC process is shown in Figure 3. Aluminum electrodes are considered for this model. For arsenic removal, the batch EC cell has 11 cm of height and cell gaps are maintained at 4, 6, and 8 mm while for treating phosphate electrode height is considered to be 20 cm and cell gaps are kept at 2 cm, 2.5 cm and 2.75 cm. The volume of the solution treated in batch systems are 3000 ml for arsenic removal and 1500 ml for phosphate removal, whereas for continuous system 100 ml solution is processed for both pollutants. The effective electrode surface areas considered in batch systems is 0.0152
m^2 and 0.022 m^2 for arsenic and phosphate, respectively. The continuous system’s structure consists of an opening of 1 cm x 1 cm channel for inlet and 1 cm opening for outlet (Figure 4). The electrodes are 9 cm long and distance between the electrodes is kept at 8 mm. The currents intensities considered for arsenic removal are 190, 100, and 40 mA and for phosphate treatment they 750 mA, 500 mA, and 250 mA in batch reactors. For continuous cell for both pollutants, the current intensity is fixed at 300 mA. During examining the effect of convection, the continuous EC cell reactor is run for 10 minutes to remove arsenic and 20 minutes for phosphate. Initial pH of the solution is assumed to be 7 for all of the cases, because EC process performs better at neutral pH (Graça et al., 2019). The effect of convective mass transfer on pollutant removal is studied for three different influent velocities, 1 × 10^{-4}, 5 × 10^{-5}, and 1 × 10^{-6} ms^{-1}. Effect of supporting electrolyte is neglected throughout the analysis.

Figure 3: 2D EC model for batch reactor.
2.1 EC Mechanism

In the EC cell when current is applied metal ions are generated from sacrificial anode; these ions further generate monomeric and polymeric species through hydrolysis reactions and finally transformed into flocs or insoluble hydroxides (Lu et al., 2015; van Genuchten et al., 2012) (Figure 5). Those flocs carry enough potential for adsorption of pollutants (Lakshmanan et al., 2010). Later these hydroxide precipitates remove pollutants by adsorption or settling process (Merzouk et al., 2011). During EC process the main electrochemical reactions occur at the surface of sacrificial anode and inert cathode are shown below:

\[
\text{Anode: } Al \rightarrow Al^{3+} + 3e^- \tag{1}
\]

\[
\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}
\]

The amount of generated aluminum ions can be calculated by Faraday’s law (Graça et al., 2019):

\[
[Al^{3+}] = \frac{I}{FZV} \varepsilon_c \tag{3}
\]

Where, \(I\) is the applied current (mA), \(\varepsilon_c\) is current efficiency, which is considered to be 1.6 (Graça et al., 2019), \(F\) is the Faraday constant (96485 C mol\(^{-1}\)), \(Z\) is charge number and \(V\) is the volume of the solution (m\(^3\)).
The electro generated ions from equation (1) and (2) will generate monomeric and polymeric hydroxides by hydrolysis which are \( \text{Al(OH)}^{2+} \), \( \text{Al(OH)}_{2}^{+} \), \( \text{Al(OH)}_{3} \), \( \text{Al(OH)}_{4}^{-} \), \( \text{Al(OH)}_{5}^{2-} \), \( \text{Al}_{2} \text{(OH)}_{4}^{+} \), \( \text{Al}_{6} \text{(OH)}_{15}^{3+} \), \( \text{Al}_{7} \text{(OH)}_{17}^{4+} \) and \( \text{Al}_{8} \text{(OH)}_{20}^{4+} \) (Mechelhoff et al., 2013). The reaction rates and hydroxide products are governed by pH condition of the solution (Gomes et al., 2007; Kobya et al., 2006). In this study for simplification purpose, \( \text{Al(OH)}_{4}^{-} \) is considered as the final hydrolysis species. Formation of soluble and insoluble hydroxides’ reactions shown in Figure 5, are given below:

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}^{2+} + \text{H}^{+} & (4) \\
\text{Al(OH)}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_{2}^{+} + \text{H}^{+} & (5) \\
\text{Al(OH)}_{2}^{+} + \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_{3} + \text{H}^{+} & (6) \\
\text{Al(OH)}_{3} + \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_{4}^{-} + \text{H}^{+} & (7) \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^{+} + \text{OH}^{-} & (8)
\end{align*}
\]

The reactions rates for the chemical reactions shown from equation (4) to (8) are given below (Graça et al., 2019):

\[
\begin{align*}
R_1 &= k_{1-f}\left(\frac{\text{Al}^{3+} - \text{Al(OH)}^{2+} \cdot \text{H}^{+}}{K_1}\right) & (9) \\
R_2 &= k_{2-f}\left(\frac{\text{Al(OH)}^{2+} - \text{Al(OH)}_{2}^{+} \cdot \text{H}^{+}}{K_2}\right) & (10) \\
R_3 &= k_{3-f}\left(\frac{\text{Al(OH)}_{2}^{+} - \text{Al(OH)}_{3} \cdot \text{H}^{+}}{K_3}\right) & (11) \\
R_4 &= k_{4-f}\left(\frac{\text{Al(OH)}_{3} - \text{Al(OH)}_{4}^{-} \cdot \text{H}^{+}}{K_4}\right) & (12) \\
R_w &= k_{wf}\left(1 - \frac{\text{OH}^{-} \cdot \text{H}^{+}}{K_w}\right) & (13)
\end{align*}
\]

Where, $R_i$, $k_{i-f}$, and $K_i$, are the reaction rates, kinetic constant of hydrolysis reaction, and thermodynamic equilibrium constants, respectively. The values of kinetic constants and equilibrium constants are shown in Table 2 below.

Table 2: Kinetic constants and thermodynamic equilibrium Data for the hydrolysis reactions

<table>
<thead>
<tr>
<th>i</th>
<th>$k_{i-f}$ (Abodi et al., 2012)</th>
<th>$K_i$ (Xiao et al., 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$4.2 \times 10^4$ 1/s</td>
<td>$9.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>$4.2 \times 10^4$ 1/s</td>
<td>$5.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>$5.6 \times 10^4$ 1/s</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>4</td>
<td>$2.5 \times 10^{-7}$ 1/s</td>
<td>$2.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>w</td>
<td>$1.52 \times 10^6$ 1/s</td>
<td>$1.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>s</td>
<td></td>
<td>$4.6 \times 10^{-33}$</td>
</tr>
</tbody>
</table>

Figure 5: The three stages of a complete EC process. (Adejinle, 2019)
2.2 Governing Equations

Nernst-Planck equation for mass transfer flux of species is given below:

\[
\mathbf{N}_i = -D_i \nabla c_i + z_i \mu_{m,i} F c_i ( -\nabla \Phi ) + u c_i
\]  

(14)

Where, the 1\textsuperscript{st} term on the right-hand side of the equation describes mass transfer flux due to diffusion, 2\textsuperscript{nd} term defines mass transfer flux due to migration and the last one denotes flux due to convection effect. In equation (14) \(D_i\) is diffusion coefficient (m\(^2\) s\(^{-1}\)), \(c_i\) is the species concentration (mol m\(^{-3}\)), \(z_i\) is the charge number of species, \(\mu_{m,i}\) is the ionic migration rate or mobility (m\(^2\)V\(^{-1}\)s\(^{-1}\)), \(\Phi\) is the electric potential (V), \(u\) is the flow velocity vector (ms\(^{-1}\)), and \(F\) is the Faraday constant.

In this study for batch system EC systems only mass transfer due to diffusivity is considered whereas for continuous flow EC cell accounts diffusion and convection effects. The migration effect is omitted for both cases as the EC domain is relatively small, solutions are highly conductive due to supporting electrolyte is provided to the solution.

The mass balance equation for the species can be written as:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_i
\]

(15)

Where, \(R_i\) is the reaction term.

The condition for electro neutrality is given below:

\[
\sum_{i=1}^{n} z_i c_i = 0
\]

(16)

The total current density arising from each species is given below:

\[
i = F \sum_{i=1}^{n} z_i \mathbf{N}_i
\]

(17)

The mobility of ionic species can be calculated from this following equation:
\[ \mu_{m,i} = \frac{D_i F}{RT} \]  

(18)

Where, \( R \) is universal gas (8.314 J mol\(^{-1}\) K\(^{-1}\)) constant and \( T \) is the temperature (K).

The reaction term mentioned in overall mass balance equation (15) can be calculated for each species through the following mass balance equations (Graça et al., 2019):

\[ R_i|_{i=Al^{3+}} = \frac{d[Al]_D}{dt} - R_1 \]  

(19)

\[ R_i|_{i=Al(OH)^{2+}} = R_1 - R_2 \]  

(20)

\[ R_i|_{i=Al(OH)^{3+}} = R_2 - R_3 \]  

(21)

\[ R_i|_{i=Al(OH)_3(s)} = R_3 - R_4 \]  

(22)

\[ R_i|_{i=Al(OH)^{4-}} = R_4 \]  

(23)

\[ R_i|_{i=H^+} = R_1 + R_2 + R_3 + R_4 + R_w \]  

(24)

\[ R_i|_{i=OH^-} = R_w + 3 \cdot \frac{d[Al]_D}{dt} \]  

(25)

[Al]_D is the amount of dissolved aluminum concentration. The dissolved aluminum is calculated by the following equations (Graça et al., 2019):

\[ \frac{d[Al]_D}{dt} = \frac{1}{FZV} \varepsilon c - k_{cg}([Al]_D - [Al]_{sat}) \]  

(26)

In equation (26), [Al]_{sat} denotes saturated aluminum concentration at certain pH level, and \( k_{cg} \) is the coagulation constant.

The saturated aluminum depends on the pH condition of the solution. It is measured from the following equation (Graça et al., 2019):

\[ [Al]_{sat} = K_s K_w^{-3} (10^{-3pH} + K_1 \cdot 10^{-3pH} + K_2 \cdot 10^{-pH} + K_3 + K_4 \cdot 10^{pH}) \]  

(27)

For continuous EC cell reactor, the flow inside the EC channel is checked by calculating the Reynold’s number (Re), Re is ensured to be laminar. The incompressible Navier-Stokes (NS)
equation and continuity equation are used in this study to describe the flow pattern and pressure inside the EC channel.

\[
\rho \frac{\partial u}{\partial t} + \rho (u \cdot \nabla) u = \nabla \cdot [-pI + \mu (\nabla u + (\nabla u)^T)] + F \tag{28}
\]

\[
\rho \nabla \cdot (u) = 0 \tag{29}
\]

Where, \(\rho\) is the density of the fluid (kg m\(^{-3}\)), \(u\) is the influent velocity (m s\(^{-1}\)), \(p\) is pressure (Pa), \(\mu\) is dynamic viscosity of the fluid (Pa · s), \(T\) is the temperature (K), \(F\) is the volume force vector (N m\(^{-3}\)) and \(I\) denotes identity matrix.

### 2.3 Boundary Conditions

The current density at anode surface is set as uniform current density.

\[
i = F \sum_{i=1}^{n} z_i N_i = i_0 \tag{30}
\]

Flux condition at anode surface:

\[
N_i |_{i=Al^{3+}} = \frac{i_0}{3F}, \quad N_i |_{i=other species} = 0 \tag{31}
\]

Similarly, at cathode surface the uniform current density condition is applied.

\[
i = F \sum_{i=1}^{n} z_i N_i = -i_0 \tag{32}
\]

Flux condition at cathode surface:

\[
N_i |_{i=OH^-} = -\frac{i_0}{F}, \quad N_i |_{i=other species} = 0 \tag{33}
\]

No slip boundary conditions are applied on the electrode surfaces and insulated boundaries. No flux conditions for all species are implied on insulated boundaries in case of continuous reactor.

Initial condition:

Initial concentration of arsenic = 10, 15, and 20 mg/L.
Initial concentration of phosphate = 10, 15, and 20 mg/L

Initial concentration of all species is 0 mol/m$^3$ except $H^+$ & $OH^-$. The initial concentrations of $H^+$ & $OH^-$ are calculated from the initial pH condition of the solution.

For continuous system EC reactors, inlet and outlet boundaries are specified and following boundary conditions are provided:

At inlet: A uniformly distributed velocity normal to the inlet boundary is prescribed. Three different inlet velocities are set to examine the effect of influent velocity/convective flux on EC process for arsenic removal.

At outlet: The mass transfer at outlet is only convection dominant and there is no mass transfer due to diffusive flux, and pressure is set to zero.

$$D_i \nabla c_i = 0, \quad p_o = 0$$

(34)

### 2.4 Adsorption Kinetics (Langmuir Isotherm)

The general physical procedure of adsorption mechanism is shown in Figure 6. In this study for describing adsorption kinetics and calculating pollutant removal rate the Langmuir adsorption isotherm is used. The Langmuir isotherm considers monolayer deposition of adsorbate on homogeneous adsorbent surface (coagulant) with a finite number of identical adsorption sites (Chou et al., 2010; Graça et al., 2019). It was developed to represent chemisorption at a set of well-defined localized sites with the same adsorption energy, independent of the surface coverage, and with no interaction between adsorbed molecules (Chou et al., 2010). There are several other isotherms available for describing pollutant flocculation and precipitation mechanisms. In the study conducted by Balasubramanian et al., 2009 with aluminum electrodes, it was found that
Langmuir isotherm model matches more perfectly than other models with experimental data. Carmona et al., 2006 considered that concentration of the pollutant in the particle is always in equilibrium with liquid phase concentration which was also adopted in Graça et al., 2019’s model and the same approach is considered in this study. From this approach the mass balance of solid and liquid phase concentrations of species can be written as:

\[ C_0 - C^* = q^* [Al]_s \]  

(35)

In this equation \( C_0 \) is the initial concentration of pollutant (arsenic and phosphate) and \( q^* \) and \( C^* \) are the equilibrium pollutant concentration in solid and liquid phase, respectively. The concentration of solid aluminum hydroxides is denoted by \([Al]_s\). This \([Al]_s\) can be calculated from the following equation (Graça et al., 2019):

\[ [Al]_s = [Al]_T - [Al]_D \]  

(36)

Where, \([Al]_T\) is the total aluminum concentration which can be calculated from Faraday’s equation (3). The amount of dissolved aluminum is obtained by computing equations (19) to (25).

The adsorption equilibrium concentration according to the Langmuir isotherm is given below (Graça et al., 2019):

\[ q^* = \frac{QKC^*}{C_0 + (K-1)C^*} \]  

(37)

Where, \( Q \) is the solid capacity and \( K \) is the separation factor.

By equating equations (35), (36) and (37) we get,

\[ C^* = -\frac{C_0(2-K) + QK[Al]_s}{(K-1)} + \frac{C_0^2}{C^*(K-1)} \]  

(38)

Finally, the pollutant removal rate (RR) can be calculated from the following equation:

\[ RR = \frac{C_0 - C^*}{C_0} \times 100 \]  

(39)
Figure 6: The adsorption process in EC.

2.5 Numerical Tools

For solving the non-linear PDEs and consequently calculating arsenic removal rate, the finite element based commercial software COMSOL Multiphysics 5.3 is used. ‘Transport of Diluted Species’ module for computing the equations for concentration of species, ‘Laminar Flow’ module to calculate velocity profile and pressure and ‘Domain ODEs and DAEs’ modules are employed for adding Langmuir isotherm into the model. Time dependent studies for different times are computed for batch and continuous reactors. Parameters used during modeling are given in Table 3.
Table 3: Parameter values for modeling

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient of H⁺</td>
<td>$9.308 \times 10^{-9}$ m$^2$/s</td>
<td>(Lu et al., 2017)</td>
</tr>
<tr>
<td>Diffusion coefficient of OH⁻</td>
<td>$5.280 \times 10^{-9}$ m$^2$/s</td>
<td>(Lu et al., 2017)</td>
</tr>
<tr>
<td>Diffusion coefficient of Al$^{3+}$</td>
<td>$1.011 \times 10^{-9}$ m$^2$/s</td>
<td>(Lu et al., 2017)</td>
</tr>
<tr>
<td>Faraday Constant, F</td>
<td>96485 C/mol</td>
<td></td>
</tr>
<tr>
<td>Solid Capacity, Q (for arsenic)</td>
<td>7 mg$<em>{Al}$ \cdot$mg</em>{As}^{-1}$</td>
<td>(Graça et al., 2019)</td>
</tr>
<tr>
<td>Separation Factor, K (for arsenic)</td>
<td>1.1</td>
<td>(Graça et al., 2019)</td>
</tr>
<tr>
<td>Coagulation constant, k$_{eg}$</td>
<td>$1 \times 10^{-3}$ 1/s</td>
<td>(Graça et al., 2019)</td>
</tr>
</tbody>
</table>

For calculating solid capacity (Q), and separation factor (K) of phosphate, the experimental data of Shalaby et al., 2014 are analyzed. According to the Chou et al., 2010, the regression analysis is conducted to identify the unknown coefficients of Langmuir isotherm. By equating the equation (37) $1/C^*$ versus $1/q^*$ values are plotted and the regression coefficient values for every current density are calculated. For all 1000 mA, 750 mA, 500 mA, and 250 mA current the values of $R^2$ are 0.9679, 0.9798, 0.9949, and 0.9781, respectively (Figure 7). From the slopes and intercepts of the following images the values Q and K are identified. As for the last three current intensities’ regression coefficients are more tentative to 1.00, for that reason at those applied current, average of Q and K are calculated as parameters for 2D modeling. The average of Q and K are found to be 0.547 mg$_{Al} \cdot$ mg$_{P}^{-1}$ and 0.172, respectively.
Figure 7: Regression analysis plots at different current intensities for phosphate removal.
In an EC experiment conducted by Graca (2019), the total and soluble aluminum concentrations were determined for three different current intensities (40 mA, 100 mA, 190 mA) to analyze the best of the three. The optimum current intensity is used to determine the removal rate of arsenic. The experiment was run for 90 minutes. For first 30 minutes current was turned on and next 50 minutes current was turned off. During the 1st phase of research, the experimental data was validated by the 0D model. The 0D model can predict the amount of total and soluble aluminum concentration satisfactorily. The figures of total aluminum (Figure 8), soluble aluminum concentration (Figure 9), and removal rate (Figure 10) comparison for different initial pollutant concentration at an optimum current intensity are given below. The total aluminum concentration increased with proportion to time till the current was on (for 30 minutes) (Figure 8). The amount of dissolved aluminum also increased till the current was on. When the current was turned off, the amount of dissolved aluminum was seen to be dropping as those were undergoing chemical reactions and turned into solid hydroxides (Figure 9). It was also observed that, the overall removal rate was decreased, when the initial pollutant (arsenic) concentration in the contaminated water was high (Figure 10).
Figure 8: Total aluminum concentration at different applied current for arsenic removal.

Figure 9: Soluble aluminum concentration at different applied current for arsenic removal.

Figure 10: Arsenic removal rate for different initial concentration of arsenic, applied current: 190 mA.
3.1.2 0D Model for Phosphate Removal

Though there are lots of experimental works performed on phosphate removal by EC process, but there is lack of scholarly numerical modeling work available on phosphate removal till to date. Most of the research focused on proving the efficacy of EC technique for phosphate removal. Due to this reason, there are so many unavailable information regarding phosphate removal procedure. At 1st phase of this current research, an experimental study performed by Shalaby et al., 2014 was analyzed. The unknown parameters are deduced from the experimental data they provided. It is mentioned on section 2.5. For phosphate removal they worked on a batch reactor and checked the effect of current at 250 mA, 500 mA, 750 mA, and 1000 mA for removing initial phosphate concentration of 20 mg/L. They ran their experiment for 180 minutes and observed that with higher current density the removal rate was increased. In this current work, the 0D model is utilized to observe the effect of current intensity for phosphate removal. It is found that with the increment of current intensity, the phosphate removal rate increases (Figure 11) which was also found by Shalaby et al., 2014. The total aluminum and soluble aluminum generation during phosphate removal are also studied (Figure 12 & Figure 13). It is mentioned that during phosphate removal all over the time the current was turned on. From the modeling result it is seen that though total aluminum concentration increases with respect to time, but soluble aluminum reaches in steady state after some time. This observation can indicate that, all aluminum ions generated during the EC process can never be turned into solid metallic hydroxides due to the side reactions or dilution of aluminum ions occurring during the EC process.
Figure 11: Phosphate removal at different applied current, initial phosphate concentration: 20 mg/L.

Figure 12: Total aluminum concentration at different applied current for phosphate removal.

Figure 13: Soluble aluminum concentration at different applied current for phosphate removal.
3.2 Results from Phase 2 (2D Model for Batch Reactors)

3.2.1 Effect of Applied Current.

3.2.1.1 Mass Distribution of Key Species

3.2.1.1(a) Distribution of Al\(^{3+}\)

Along the anode to cathode distance in the batch EC system, the distribution of coagulants at different current intensities are shown in Figure 14 for both arsenic and phosphate removal. It is seen that the generation of Al\(^{3+}\) is higher near anode surface and decreases from anode to cathode direction. The average generation of coagulants is proportional with applied current. Chen et al., 2002’s study can be mentioned to explain the characteristics of this type of distribution trend of coagulants. Near electrode surface there is no convective flux present. A diffusion layer is formed near electrode surface by electrochemically active species, which is the coagulant itself. The concentration of coagulants changes rapidly within the diffusion layer while current is applied. Due to the diffusive mass transfer effect, Al\(^{3+}\) ions have some tendency to travel towards the bulk solution. The surface plots of coagulant are given in Figure 15, which shows that Al\(^{3+}\) concentration is high near the anode surface.

![Figure 14: Al\(^{3+}\) distribution from anode to cathode direction (a) Arsenic removal model at 50 minutes, b) phosphate removal model at 200 minutes)](image-url)
3.2.1.1(b) Distribution of OH$^-$

During the EC process when current is applied OH$^-$ ions are being generated simultaneously from inert cathode surface along with coagulants from sacrificial anode surface due to the reduction reactions occurring at cathode surface. Similar trends like Al$^{3+}$ ions are observed regarding distribution of OH$^-$ ions as shown in Figure 16. However, the OH$^-$ ions are more distributed over the EC region with compared to the Al$^{3+}$ ions, and this is due to the diffusive property of OH$^-$. As it is known that OH$^-$ ion has higher diffusivity than Al$^{3+}$, for that reason OH$^-$ ions can be distributed more evenly. It is also seen that with higher intensity of applied current the generation of OH$^-$ ions increases.

Figure 16: OH$^-$ distribution from anode to cathode direction (a) Arsenic removal model at 50 minutes, b) phosphate removal model at 200 minutes)
3.2.1.1(c) Distribution of Al(OH)$_3$

The key component for removing pollutant through electrocoagulation is the insoluble aluminum hydroxides generated from the chemical reactions of ionic species. Al(OH)$_3$ is the most stable and only solid phase (flocs) aluminum species among all other species generated during EC process. The pollutants are adsorbed on the surface of insoluble aluminum hydroxides or flocs during EC process. Due to its vital role during EC process, in this study the generation and distribution of Al(OH)$_3$ is also studied. It is observed that, with a higher current intensity the amount of insoluble Al(OH)$_3$ increases. At the middle of the EC channel the concentration of Al(OH)$_3$ is seen to be higher (Figure 18 & Figure 19). Due to diffusive flux, the primary species generated from electrochemical reactions, tend to move towards the bulk solution and undergo chemical reactions at every layer and stabilize somewhere near the middle of the EC cell. For phosphate removal the Al(OH)$_3$ distribution is different from arsenic removal though both have higher concentration near center of the region. As the distance for arsenic removal model is 8 mm and 2 cm for phosphate removal, the primary ionic species face difficulties to travel more distance.
and to participate in chemical reactions. But due to high current intensity for phosphate removal and more treatment time, the model for phosphate removal generates more \( \text{Al(OH)}_3 \) compared to arsenic removal model. For this reason, the following trend of distributions for \( \text{Al(OH)}_3 \) shown in figures are observed.

**Figure 18:** \( \text{Al(OH)}_3 \) distribution from anode to cathode direction (a) Arsenic removal model at 50 minutes, b) phosphate removal model at 200 minutes.

**Figure 19:** Surface plot of \( \text{Al(OH)}_3 \) distribution from anode to cathode direction for arsenic removal model at 50 minutes, applied current: 190 mA, cell gap: 8 mm.
3.2.1.2 Effects of Applied Current on Pollutant Removal Rate

In this model, overall arsenic removal rate is calculated by adopting Langmuir isotherm. It is found that the removal rate is increased with higher applied current. The overall removal efficiencies obtained for 10 mg/L initial arsenic concentration are 90.2%, 85.6%, and 75.72% at 190 mA, 100 mA, and 40 mA applied currents, respectively (Figure 20) and for 10 mg/L phosphate removal, the removal efficiencies are found to be 92.5%, 89.9%, and 84.1% at 750 mA, 500 mA, and 250 mA current intensities, respectively (Figure 21). The surface plot generated from the model for removal rate can be used to demonstrate where removal rate is decreased and the reasons behind. From Figure 22 it is seen that the removal rate is reduced near anode surface. Due to the diffusion layer formed by Al$^{3+}$ ions, there is lack of chance to adsorb the pollutants by the insoluble aluminum hydroxides, which are highly concentrated at middle of the EC channel. Another reason might be due to the side reactions occurring during EC process. For higher concentration of Al$^{3+}$ ions near anode surface, there are high possibilities of side reactions occurring near that area. There is another key observation also seen for different pollutant removal. Due to different material properties of arsenic and phosphate more efforts like more current intensity, more treatment time, etc. are needed. For that reason, it can be stated that, the performance of EC treatment process not only depends on operational conditions but also the nature of the effluent or pollutant, according to which the operating conditions must be determined.
Figure 20: Arsenic removal at different applied current, cell gap: 8 mm, initial arsenic concentration: 10 mg/L.

Figure 21: Phosphate removal at different applied currents, cell gap: 2 cm, initial phosphate concentration: 10 mg/L.
Figure 22: Surface of removal at applied current: 190 mA, distance between the electrodes: 8 mm, time: 50 minutes.

3.2.2 Effects of Cell Gap

3.2.2.1 Mass Distribution of Key Species at Different Cell Gap

This current study finds that an EC system with less cell gap provides better performance in terms of pollutant removal. The pollutant removal efficacy of an EC system depends on the generation of metallic hydroxides or flocs. To generate more flocs, even distribution of species or better mixture of species generated during EC process is mandatory. Other observations are done by maintaining a cell gap 8 mm for arsenic removal. Later systems with 4 mm and 6 mm cell gaps are analyzed and 4 mm system found to be more efficient than other systems. The species distribution of key elements generated during EC process are analyzed at different cell gaps. From Figure 23, it is seen that less amount of Al$^{3+}$ ions remain near anode surface when cell distance is kept at 4 mm. With a higher cell gap all Al$^{3+}$ ions cannot travel far distance, and it is difficult for them to mix with bulk solution and to participate in chemical reactions. When small cell gap is provided, these ions have more chances to mix with bulk solution as they do not need to travel more distance and can participate in chemical reactions occurring during EC process due to
diffusive flux. More chemical reactions can generate more insoluble flocs, which will provide more pollutant removal. Similar observation is seen for OH⁻ ion distribution. In 4 mm cell gap system the concentration of OH⁻ ion near cathode surface is around 80 mol m⁻³ whereas in 6 mm cell gap system it is around 100 mol m⁻³ (Figure 24).

Figure 23: Coagulants (Al³⁺) concentration distribution at a) 4 mm and b) 6 mm cell gap, applied current: 190 mA, time: 50 minutes.

Figure 24: OH⁻ concentration distribution at a) 4 mm and b) 6 mm cell gap, applied current: 190 mA, time: 50 minutes.

Due to higher mixing of primary species Al³⁺ and OH⁻ in a lower cell gap system it is obvious that more insoluble aluminum hydroxides or flocs can be produced. This observation is
proved when mass distribution of Al(OH)$_3$ is checked in different cell gaps. Figure 25 shows that more Al(OH)$_3$ is generated in 4 mm cell gap system with compare to 6 mm cell gap. More even distribution of Al(OH)$_3$ is also achieved in 4 mm cell gap system.

![Graph](image1.png) ![Graph](image2.png)

Figure 25: Al(OH)$_3$ concentration distribution at a) 4 mm and b) 6 mm cell gap, applied current: 190 mA, time: 50 minutes.

3.2.2.2 Effects of Cell Gap on Pollutant Removal Rate

The higher concentration of insoluble hydroxide generation leads to more pollutant removal in an EC system. As the 4 mm cell gap system produces more insoluble hydroxides compare to 6 mm and 8 mm cell gap system, higher removal rate is attained in 4 mm EC cell system. For 8 mm cell gap with initial arsenic concentration of 10 mg/L the removal rate is found to be 90.2% (Figure 20) whereas 4 mm and 6 mm cell gap systems provide 98.9% and 96.2% efficiencies, respectively. Comparison of arsenic removal rates at different cell gaps are shown in Figure 26. The effect of different cell gap on the overall performance of EC cell also evaluated for phosphate removal. The overall removal rates are calculated at cell gaps of 2 cm, 2.5 cm and 2.75 cm and the removal rates obtained are 92.5%, 85.5%, and 82%, respectively (Figure 27).
Figure 26: Arsenic removal rate at different cell gaps, initial arsenic concentration: 10 mg/L, applied current: 190 mA.

Figure 27: Phosphate removal at different cell gap, initial phosphate concentration: 10 mg/L, applied current: 750 mA.
3.2.3 Effects of Initial Pollutant Concentration

The current study is also analyzed the effect of initial concentration of pollutant on overall removal rate to evaluate the system’s effectiveness whether it can be utilized as primary, secondary, or tertiary treatment process. It is seen that with a higher initial pollutant concentration the removal rate decreases. This model is evaluated for 10 mg/L, 15 mg/L, and 20 mg/L as initial arsenic concentrations and the removal rates are found to be 90.2%, 86.5%, and 83.9% respectively. For same amount of phosphate removal, the removal rates are found 92.5%, 90.4%, and 87.7%, respectively. From this analysis it is seen that with a higher initial concentration of pollutant, EC performance is reduced, for this reason it can be said that EC process should be more effective if it can be applied as a secondary or tertiary treatment system to remove fine particles and for using at large scale.

Figure 28: Arsenic removal rate with different initial concentration, distance between the electrodes: 8mm, applied current: 190 mA.
Figure 29: Phosphate removal with different initial concentration, distance between the electrodes: 2 cm, applied current: 750 mA.

Table 4: Summary of arsenic removal at different conditions in batch reactors

<table>
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<tr>
<th>Model no.</th>
<th>Applied Current (mA)</th>
<th>Cell Gap (mm)</th>
<th>Initial Pollutant Concentration (mg/L)</th>
<th>Removal Rate (%)</th>
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Table 5: Summary of phosphate removal at different conditions in batch reactors

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<th>Applied Current (mA)</th>
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3.3 Results from Phase 3 (2D model for Continuous Reactors)

3.3.1 Mass Distribution of Species Generated during EC Process in a Continuous Reactor

3.3.1(a) Distribution of Al$^{3+}$

A different structure is developed to study the convective mass transfer effect on EC process. The geometric detail of this structure is given at Figure 4. A lower mass generation of species is seen with a higher inlet velocity in a continuous EC cell reactor. Three different locations are selected to observe the mass distribution of key species. 1$^{st}$ location is near the inlet of the EC channel at $X = 1$ cm, the 2$^{nd}$ location is at $X = 2$ cm after the inlet and last location is near the outlet of the EC channel which is $X = 9$ cm. The following Figure 30 shows the distribution of Al$^{3+}$ distribution in three different inlet velocities at three different locations of the EC channel. At $1 \times 10^{-6}$ ms$^{-1}$ inlet velocity, it is observed that near inlet the generation of Al$^{3+}$ is lower than other two locations. The distribution of Al$^{3+}$ is almost identical for locations at 2 cm and 9 cm at lowest inlet velocity, but at $1 \times 10^{-4}$ ms$^{-1}$ and $5 \times 10^{-5}$ ms$^{-1}$ inlet velocities the difference at those locations regarding Al$^{3+}$ distributions become more distinguishable. More species are gathered for high velocity stream near the outlet region. The surface plots can provide more clarity of distribution of Al$^{3+}$ at different inlet velocities. The two surface plots shown in Figure 31 are at inlet velocity $1 \times 10^{-4}$ ms$^{-1}$ and $1 \times 10^{-6}$ ms$^{-1}$, respectively. Due to higher residence time at low velocity, more Al$^{3+}$ ions can move towards bulk solution and participate in chemical reactions due to their diffusive properties. While at high velocity stream a great portion of Al$^{3+}$ ions depleted along the flow stream and experience less chances to participate in chemical reactions in bulk solution due to reduced residence time.
Figure 30: Al$^{3+}$ distribution at three locations at different inlet velocities: a) $1 \times 10^{-6}$ ms$^{-1}$, b) $5 \times 10^{-5}$ ms$^{-1}$, & c) $1 \times 10^{-4}$ ms$^{-1}$ applied current: 300 mA, distance between the electrodes: 8 mm, time: 10 minutes.

Figure 31: Surface plots of Al$^{3+}$ distribution at $1 \times 10^{-4}$ ms$^{-1}$ and $1 \times 10^{-6}$ ms$^{-1}$ inlet velocities, applied current: 300 mA, distance between the electrodes: 8 mm, time: 10 minutes.
3.3.1(b) Distribution of OH⁻

The distribution of OH⁻ ions have the similar course like Al³⁺ distribution. At higher inflow velocity, near inlet region, OH⁻ concentration is lower with compared to other two locations. Due to the higher velocity stream most of the OH⁻ ions gathered near outlet region. At lowest i.e., $1 \times 10^{-6}$ ms⁻¹ inlet velocity except inlet, the concentration distribution of OH⁻ remain same at other two locations. The explanation provided for Al³⁺ distribution, can be used for OH⁻ distribution also. The distribution of OH⁻ at three different locations at three different inlet velocities are shown in Figure 32. With higher velocity streams the difference between OH⁻ distribution at upstream locations expands more. The surface plots of OH⁻ distribution at $1 \times 10^{-4}$ ms⁻¹ and $1 \times 10^{-6}$ ms⁻¹ inlet velocities are shown in Figure 33.

Figure 32: OH⁻ distribution at three locations at different inlet velocities: a) $1 \times 10^{-6}$ ms⁻¹, b) $5 \times 10^{-5}$ ms⁻¹, & c) $1 \times 10^{-4}$ ms⁻¹, applied current: 300 mA, distance between the electrodes: 8 mm, time: 10 minutes.
3.3.1(c) Distribution of Al(OH)₃

The generation of Al(OH)₃ mostly depends on proper mixture of primary species generated while current is being applied. With lower velocity, the solution has higher residence time to stay within the EC channel. For this reason, more Al³⁺ and OH⁻ ions can move towards the bulk solution and can undergo chemical reactions and ultimately produce more insoluble metallic hydroxides. From Figure 34 it is seen that more aluminum hydroxides are generated at 1 × 10⁻⁶ ms⁻¹ with compared to other two higher inlet velocities at regions X = 2 cm and X = 1 cm. At lowest inlet velocity after the inlet, the distribution of Al(OH)₃ remains similar along the EC channel while with high flow streams, the concentration varies according to the extent of the velocity streams. More insoluble aluminum hydroxides are accumulated near the outlet region with higher flow rate. It is also seen that Al(OH)₃ is more concentrated near cathode surface with compare to the overall distance between the electrodes from each other. This kind of distribution also dominated due to mass transfer properties of the species. Al(OH)₃ is the final product of chemical reactions occurring
among the primary species, though in this study $\text{Al(OH)}_4^-$ is considered to be final product. $\text{Al(OH)}_4^-$ is generated due to side reactions of $\text{Al(OH)}_3$ and it is not stable. Due to unstable characteristics of $\text{Al(OH)}_4^-$, it again turns to $\text{Al(OH)}_3$ by reacting with $\text{OH}^-$ ions. When $\text{Al}^{3+}$ ions undergo chemical reactions, at final stage they converted into stable solid hydroxides. Due to dominant convective mass flux these hydroxides cannot stay around middle of the EC channel which results higher concentration near cathodic surface.

Figure 34: $\text{Al(OH)}_3$ distribution at three locations at different inlet velocities: a) $1 \times 10^{-6}$ ms$^{-1}$, b) $5 \times 10^{-5}$ ms$^{-1}$, & c) $1 \times 10^{-6}$ ms$^{-1}$, applied current: 300 mA, distance between the electrodes: 8 mm, time: 10 minutes.
3.3.2 Effects of Inlet Velocity on Removal Rate

The overall generation of insoluble metal hydroxides or flocs controls the overall performance of the EC system. With the generation of highly concentrated metal hydroxides, more removal efficiency can be achieved. From the species distribution analysis at different flow streams, it is identified that with a low influent velocity, the EC system can generate more Al(OH)$_3$. This additional number of insoluble hydroxides can adsorb more pollutants. In Figure 36 the arsenic removal rates at different influent velocities are shown. It is found that at $1 \times 10^{-4}$ ms$^{-1}$, $5 \times 10^{-5}$ ms$^{-1}$, and $1 \times 10^{-6}$ ms$^{-1}$ the EC cell provides 90.2%, 93.9%, and 97.5% respectively for 10 minutes run time. From Figure 37 for phosphate removal, it is seen that the removal rates with same operating condition and more run time (20 minutes) are 62.2%, 72.6%, and 84%, respectively. Due to the nature of phosphate more treatment time is required for its removal. Initially, the removal rates are almost same for different inlet velocities for certain period. The reason is that, as the
species generated in-situ, due to this, the key species have similar concentrations for that period under same current intensity. But due to dominant convective flux the concentration of key species starts to change according to the residence time at respective inlet velocity. From that point the removal efficiency starts to change for different inlet velocities. The surface plots (Figure 38) of removal rate at $1 \times 10^{-4}$ ms$^{-1}$ and $1 \times 10^{-6}$ ms$^{-1}$ are generated to investigate the locations and the reason behind reducing of removal efficiency. At $1 \times 10^{-6}$ ms$^{-1}$, it is seen that there is lack of removal around the anode surface region. The explanation is that due to diffusive boundary layer formed by Al$^{3+}$ ions near the anode surface where Al$^{3+}$ ions have more concentration. Due to higher concentration of Al$^{3+}$ ions there are more chances of side reactions occurring near that region, which eventually affect the removal rate efficacy. The removal rate at higher inlet velocities is mostly hampered at inlet region due to high flow stream. All over the EC channel the removal rate remains uniform due to more mixing of solution at high inlet velocity. So, the cause behind low efficiency of EC system at high inlet velocity is the high flow stream itself, which provides the solution less residence time to stay within the EC domain for treatment.

Figure 36: Arsenic removal rate at different inlet velocities, applied current: 300 mA, distance between the electrodes: 8 mm, treatment time: 10 minutes.
Figure 37: Phosphate removal rate at different inlet velocities, applied current: 300 mA, distance between the electrodes: 8 mm, treatment time: 20 minutes.

Figure 38: Surface plots of removal rate at $1 \times 10^{-4}$ ms$^{-1}$ and $1 \times 10^{-6}$ ms$^{-1}$ inlet velocities, applied current: 300 mA, distance between the electrodes: 8mm, time: 10 minutes.
Table 6: Summary of arsenic removal at different inlet velocities in continuous reactors

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<th>Model no.</th>
<th>Applied current (mA)</th>
<th>Cell gap (mm)</th>
<th>Initial pollutant concentration (mg/L)</th>
<th>Run time (min.)</th>
<th>Inlet velocity (ms⁻¹)</th>
<th>Removal rate (%)</th>
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Table 7: Summary of phosphate removal at different inlet velocities in continuous reactors

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CHAPTER 4: CONCLUSION AND FUTURE WORK

4.1 Conclusion

In this study, electrocoagulation (EC) process was investigated through three computational models for both a conventional batch-type reactor and a new continuous reactor. The batch reactor is a well-stirred closed system, and once wastewater is fed into the system, it gets fully treated before the discharge from the system. The system was simulated through an unsteady zero-dimensional model due to the uniform spatial distribution of participating chemical species. The effect of species-generating current intensities, chemical chain-reactions evolving various species, and their adsorption reactions with impurities in wastewater was studied in the developed zero-dimensional model.

The continuous reactor is a new open system in which wastewater circulates continuously between storing containers and the reactor while it is being treated. Non-uniform species distribution in the reactor is highly possible and understanding of its effect on removal efficiency is required to develop the reactor. Two-dimensional models were developed to analyze the distribution of chemical species for various cell geometries and operating conditions, and their effect on the pollutant removal was studied systematically through two 2-D models.
The first 2-D model was developed to include physics of species diffusion which allows to study the species distribution without getting disturbance of convective bulk flow. The model clearly predicted the effect of various conditions such as current intensities, cell gap (i.e., distance between electrodes in each side), and pollutant concentration in wastewater. It was found that high removal rate was resulted at the high current intensity, small cell gap, and low pollutant concentration.

The second 2D model considered convection effect in addition to the species diffusion, and thus it included all the physics involved in the EC process such as electrochemical reactions on each electrode, chemical chain-reaction in the bulk fluid, species transport through diffusion and convection, and physical adsorption of pollutants into the coagulants. This comprehensive model allowed to predict the removal rates in realistic conditions. It was found that low inlet velocity is favorable for maximizing pollutant removal in a continuous system because it provides longer residence time for species to undergo the reactions completely.

The physics-based models in this study were developed originally for arsenic removal from wastewater due to abundant experimental data available in literature, but the developed models were successfully utilized to analyze phosphate which is known as a main component “cultural eutrophication” (Chislock et al., 2013), resulting in disastrous pollution in water. The nature and material properties of arsenic and phosphate are different. More current intensity and treatment time are required to remove phosphate to reach a required level, whereas due to higher solid capacity and metallic properties of arsenic, it requires less current intensity as well as treatment time for removal.
It was one of the purposes in this study to develop a set of models which can be utilized as a platform to analyze the EC system for various pollutant species, and the research target was achieved. I hope that the results in this study could suggest as a guideline for the EC system developers.

### 4.2 Future Work

Electrocoagulation (EC) and chemical coagulation (CC) processes are considered as more efficient and less time-consuming water treatment systems. Nowadays, EC is being treated as a better alternative of CC due to its environmental and financial advantages. To utilize this system for using at large scale, the efficiency of this system needs to be increased while dealing with high concentration of pollutant, and high influent velocity. For this reason, turbulent flow condition of influent for better mixing of the species can be a major point of research to achieve this goal. Moreover, often in industrial sectors, the wastewater consists of mixture of several types of pollutants. To tackle this issue, uniform pollutant treatment model can be developed for mixed pollutant contents.

In this current study due to the small size of the EC domain, mass transfer due to migration effect has not been accounted, but in a large electrochemical system, voltage rise is a common problem. To check its effect, mass transfer due migration effect can be added to the system for calculating concentration of intermediate species.

In current work, it was seen that there are side reactions occurring at highly concentrated regions of coagulants. The side reaction often degrades the performance of EC system. In-depth analysis can be made to mitigate side reaction issues in EC system. The life of the electrodes is
also an important part for successful implementation of this system in industrial application. More studies can be conducted to determine the life span of electrode for estimating proper timing and manner to change or replace them.
REFERENCES


2) Adejinle, A. E. (2019). THE TREATMENT OF CONTAMINATED WATER USING ELECTROCOAGULATION. *Department of Mechanical Engineering, Northern Illinois University, DeKalb, IL.*


