Wastewater Treatment using a Novel Combined Electro-Oxidation, Electro-Coagulation, and Electro-Filtration Process

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Abstract

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Wesley Meertens

This research designs a novel electrochemical wastewater treatment reactor, combining Electro-Oxidation (EO), Electro-Filtration (EF), and Electro-Coagulation (EC), which was then evaluated through the anti-fouling capabilities of EF and through the removal capabilities for dye materials and Chemical Oxygen Demand (COD). The reactor is facile, does not require chemical additions, has minimal training requirements, is modular, and plainly removes contaminants.

The main findings showcase the capabilities of this novel reactor design, the anti-fouling characteristics of a conductive membrane, and the enhanced removal capacities of electrochemical wastewater treatment as compared to the popularized membrane processes. The normalized flux decrease due to fouling was around 20.51% for the standalone UF processes, compared to an average normalized flux decrease of 9.99% for EO-EF and 33.44% for EO-EC-EF reactor set ups. This shows the anti-fouling capabilities of a conductive membrane, as the average normalized flux decrease was more than half in the EO-EF set up, as compared to the UF set up. Methylene blue removal was around 33% for the UF set up, whereas it was over 95% for all electrochemical reactor set-ups. Finally, for COD removal, UF removed around 12% as compared to an average 77% removal rate using electrochemical processes. These improved removal capacities and flux ratings when using electrochemical processes have validated the reactor designs while confirming the anti-fouling and removal abilities of electrochemical wastewater treatment designs. At the time of submission, this combination of electrochemical processes has not been investigated to the best of our knowledge.

Acknowledgements or Dedication

I would like to thank my initial supervisor, Dr. Rahaman, for inviting me to join his research group and supporting me throughout. I would also like to give thanks to Dr. Mahbubour Choudhary for helping me conceptualize these ideas and walking me through the initial phases of creating a research project. Finally, I would like to thank Dr. Nokken for her exceptional feedback and recommendations for my research.

All the members in the Rahaman research group could receive their own acknowledgement. Of course, I need to thank my partner who maintained my caffeine and happiness levels throughout. Shouts out Masai. Finally, I would like to thank Hydro Quebec and Concordia University for their financial contributions to this research.

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1. Introduction and Research Objective

1.1 Background

Access to clean drinking water is a basic human right, and with water and energy exploitation increasing concurrently, water scarcity and the environmental impacts associated with energy production will continue to worsen over time. To add on to these existing issues, certain industrial players within the pharmaceutical, energy production, and textile industries (among others) are polluting the remaining freshwater sources. For example, industries creating or using synthetic dyes create many negative environmental impacts, mainly due to the discharge of wastewater. It hampers light penetration, distresses biological processes, and have known hazardous, toxic, and carcinogenic effects, all of which impairs the aquatic environment quality[1-4].

Water bodies receiving these industrial effluents are now carrying trace to large concentrations of pathogens, organic matter, and aesthetic pollution, requiring purification steps before the water is safe to drink. In addition, trace contaminations may remain after wastewater treatments, even after highly effective membrane processes are used, which present toxic hazards to the environment and people alike[5]. This could also be caused by outdated treatment facilities not being designed to remove emerging contaminants simply due to the lack of knowledge of these contaminants during the design phase[6]. In order to maintain these outdated treatment facilities while still addressing these new contaminants, a cost-effective solution could consist of an uncomplicated addition at the end of water treatment processes to remove these contaminants, or to impose a simple improvement onto existing facility operations.

Pollution and insufficient water purification are worldwide issues, but even in water rich countries such as Canada, access to drinking water remains a challenge for marginalized communities. For example, the number of overall gastrointestinal infections in Indigenous communities due to drinking water quality was 26 times greater than the rest of Canada, a figure that is likely underreported[7]. Furthermore, even with the Truth and Reconciliation Commission prioritizing clean water for indigenous communities, most are still without clean drinking water. The solutions recommended by the government are still taking settler-colonial approaches to this issue, when governments, researchers and Indigenous communities need new approaches and improved relationships to move forward on issues of health and safe drinking water[7].

These issues are pushing the water-energy nexus to be a focal point of research[8]. Cheap, environmentally and socially friendly, and efficient access to water purification methods is becoming a priority. Ideally, the implementation of a facile, transportable, and affordable treatment option could provide an opportunity for marginalized communities to choose for themselves how to source their access and basic human right to water, while further providing a solution to address trace contaminants at the end of outdated treatment facilities.

To address these issues, electrochemical advanced oxidation processes (EAOPs) have presented themselves as a potential solution and have plainly displayed their ability to completely remove dye materials and organic materials from wastewater streams. These techniques, if combined, may offer scalability, mobility, efficiency, and simplicity as these concepts show the potential to contribute a feasible solution to both sides of the water-energy nexus.

1.1.1 Electrochemical Advanced Oxidation Processes

Electrochemical wastewater treatment, namely electro-oxidation (EO), electro-coagulation (EC), and electro-filtration (EF), are collectively known as Electrochemical Advanced Oxidation Processes (EAOP) and have been heavily researched recently for their abilities in many treatment scenarios. Conductive membranes used in EF show anti-fouling abilities[9], EO is able to efficiently oxidize organic materials[10], and EC can precipitate suspended solids out of waste streams without the need of chemical handling[11]. Projects have been published using EC, EF, or EO (or a combination of these) for a myriad of different wastewaters, including wastewaters containing electroplating effluents[12], trace emerging contaminants[13], bacteria[14], dyes[15-22], pharmaceuticals[23], industrial effluents[24], and agriculture effluents[25] among others.

Electrooxidation requires an induced charged placed on an electrode that is submerged in wastewater. This electrode adsorbs and oxidizes pollutants when they come in direct contact with the anode[26], while concurrently producing a power oxidizer in the •OH radical[27]. These processes are separated as such into direct oxidation (comes in contact with the electrode) and indirect (•OH radical production). The •OH radical is one of the most powerful oxidants in wastewater treatment and has a high oxidation potential to degrade organic pollutants in wastewater, such as chemical oxygen demand and chemical dyes[28,29]. One main benefit of using EO would be the in-situ production of the oxidizing compound, as compared to more traditional wastewater oxidation processes such as Ozone or hydrogen peroxide oxidation, which requires the production, handling, and transport of these chemicals. Another key benefit is that essentially, the only requirement for the functionality of both direct and indirect EO is the applied charged placed onto the submerged electrode, making this powerful treatment technique very simple to use.

Coagulation techniques are used to remove solids from wastewater by manipulating the charges of the particles suspended in water to conjoin, thereby creating larger solids[30]. These larger solids more readily settle out of the water simply through gravity[31,32]. Electrocoagulation (EC) takes advantages of this by generating coagulants via electrically dissolving aluminum (Al) or iron (Fe) from electrodes[32]. The general advantage of the EC method is that this technique generates the coagulants in-situ, meaning it does not require any chemical transport or handling. Furthermore, research shows other advantages over chemical coagulation processes such as EC produces flocs over a wider pH range, a reduction in sludge volume, and flocs are produced at a more rapid rate[33]. Finally, as with the EO process, the only requirement is inducing a charge onto a submerged iron or aluminum electrode for it to electrically dissolve to provide the coagulant, making this a very straightforward and easy process.

Fouling has plagued the membrane industry, widely believed to be the main hurdle keeping membrane processes from clearly being the most efficient wastewater treatment option. To address this, anti-fouling techniques such as membrane surface coatings, tangential cross-flow, and even electrochemical techniques have been investigated[34-36]. EF uses an applied electric field from an electrode to encourage charged colloidal particles to maneuver away from the membrane, keeping the surface of the filtration membrane free from fouling[37]. EF is based on the principle that almost all colloidal materials in wastewater are negatively charged, therefore, by applying a charged electric field which envelops the membrane surface, the colloidal particles will move away from the membrane surface[38]. Interestingly, when applying this current to a conductive membrane surface to create the electric force, it both repels all the charged colloids in the wastewater away from the membrane (through EF) but also any organic foulant that comes in contact with the conductive membrane surface undergoes direct electro-oxidation[39]. Again, these electrochemical techniques only require the ability to apply an electric charge onto an electrode to create the electric field, or in the case of a conductive membrane, to apply the electric charge onto the conductive membrane.

Conductive membranes and conductive membrane surface coatings have been investigated to combine EF-EO, but surface coatings suffer from physical deficiencies such as brittleness and very rough surfaces[40]. The brittleness disqualified this method for membrane wastewater treatment as it would always break, and the surface roughness leads to adsorption into the membrane introducing a gateway for foulants to latch onto membrane surfaces[40,41]. Inorganic conductive membranes have also been investigated, but they are very expensive to manufacture, difficult to produce, and cannot be sized to typical membrane filtration units[40]. However, with the introduction of the easy to make, inexpensive, and conductive carbon nanotubes (CNT), multiwalled carbon nanotube (MWNT) sheets can be used as either a membrane or a membrane surfactant for EF processes[35].

1.1.2 Combined Electrochemical Processes

Researchers have attempted to combine electrochemical treatment in sequence to remove dyes and organic content from wastewaters, with varying degrees of success [12-25], but commonly they completely oxidize dye materials while also obtaining minor to major chemical oxygen demand reductions as well. Typically, if an electrochemical treatment is used, it is used in sequence with another conventional treatment as a pre-treatment, post-treatment, and/or a fully integrated treatment[43]. While EAOPs are effective in any sequence, there are clear benefits in using a single, fully equipped electrochemical treatment reactor. If there is a need for increased capacity, you can add however many modules needed to address the need for increased capacity. Furthermore, the footprint of a single reactor is clearly less when compared to two (or more) sequential treatment operations. When considering all EAOPs simply need an induced charge onto electrodes, there is clear potential for a single combined EAOP reactor which is inherently modular, scalable, mobile, efficient, and easy to use[1,2,45-47]. However, there are clear challenges for EAOPs to address before being recklessly combined. Limitations such as EF using expensive yet brittle conductive membrane materials[40], or the large suspended particles created through EC inherently and clearly foul membrane processes if within the same reactor[32,33], EO faces mass transfer difficulties as the direct oxidation process requires direct contact to the electrode[45], while all EAOPs also have electric current requirements.

1.2 Objective of Thesis

The motivation of this research comes from seeing the benefits of electrochemical wastewater treatment, such as no need for chemical additions, high oxidation capacity, anti-fouling characteristics, the ease of use, and investigating the validly of combining them into one mobile, easy-to-use module. By combining these systems, it will reduce the footprint by incorporating several treatment methods that typically utilise separate reactors. If this system can address trace contaminant pollution sufficiently, it may see potential usage in northern communities or municipalities alike.

The first research goal is to design a combined reactor which incorporates as many EAOPs as possible. Different reactor designs, sizes, and configurations were investigated until a modular all-in-one design able to incorporate EF, EC, and EO was discovered. This reactor must address all the major inhibiting hurdles holding back each EAOP. For EF, a new MWNT membrane surface is used as a surfactant on a commercially available membrane, removing the brittleness concerns[14]. For EO, a cross-flow reactor design negates the mass transfer challenge by actively cycling the wastewater onto the electrode surface[39,42]. Finally, the fouling concerns of EC combined with a membrane is addressed by using as many anti-fouling agents as possible, including EF and a cross-flow reactor [34,40]. This novel combination in a single reactor has not been researched to the best of my knowledge.

The next goal was to make the reactor facile to use, following a plug-and-play directive. A plug-and-play directive implies very easy use, allowing the user to simply plug in the reactor and expect results. This allows any community access to this water purification technology by not requiring heavy training or supervision to use it. Electrochemical treatment processes are unique in that they only require a power source to start treatment operations, which quite literally follows a plug-and-play directive[43].

Another key goal is to evaluate the anti-fouling capacity of the conductive filter used in this research. Even if the overall reactor does not provide suitable treatment, any cross-flow reactor implementing anti-fouling techniques is imperative research for water purification knowledge. A common validation step for fouling control is monitoring the clean permeate flux rates and the propensity in which flux decreases over time[13,23].

Finally, the reactor must be validated through the removal capacities of the setup. Synthetic dyes and trace organic materials are pesky polluting materials which can be toxic, carcinogenic, and problematic for environmental and human health alike[1-4,13]. Therefore, the reactors capabilities will be tested on removing dyes and organic compounds from wastewater.

The following traits of the reactor are inherent in this research work;

1. Minimally trained supervision required for the utilisation of the wastewater reactor, following a “plug-and-play” directive,

2. Reactor designed to be mobile, with the ability to be used in northern communities or as a posttreatment purification step alike,
3. No chemical additions needed for adequate treatment,
4. No start-up time required, and
5. Adequate removal capacity for several common wastewater pollutants.

The following key findings have been investigated in this research work;

1. Reactor designs including the combination EO, EC, and EF were validated. The combination of these electrochemical techniques has not been previously reported in literature to the best of our knowledge, where these reactor set-ups were tested with various common wastewater pollutants including colour and COD,
2. The unconventional pairing of coagulation (EC) and filtration (EF) within the same reactor was investigated for trace contaminant and synthetic dye removal, and
3. The anti-fouling capabilities of conductive membranes were validated.

2. Literature Review

2.1 Synthetic Textile Wastewater

Industries creating or using synthetic dyes create many negative environmental impacts, mainly due to the discharge of wastewater. It hampers light penetration, distresses biological processes, and have known hazardous, toxic, and carcinogenic effects, which impairs the aquatic environment quality by changing its color and creating conditions for eutrophication, low reoxygenation and a decrease in the solar light penetration[1-4]. Furthermore, colour is one of the critical public concerns for drinking water, due to the clear visibility of dyes, known as aesthetic pollution. Although colour is not often the most dangerous health hazard for human consumption, due to the clear visibility to the naked eye, it is often the most important public concern for drinking water characteristics. These well documented issues are a call for the facile and environmentally friendly removal of dyes from waterbodies.

Negative environmental impacts are often associated with the textile dyeing industry, mainly due to the discharge of these wastewaters containing a large concentration of dyes. Wastewater containing these synthetic dyes from industry are significant sources of aesthetic pollution. The growth of dye polluting industries such as textiles, food, cosmetics, papers, and pharmaceuticals, among others, has led to the increasingly large challenge of widespread dye removal[3]. Many processes have been used to remove synthetic dyes from waterbodies, such as membrane filtration, chemical coagulation, biological oxidation, electrochemical processes, sonolysis, photolysis, and ozonation, among others. The advantages and disadvantages of all these techniques have been researched in detail[2-4]. However, it was found that not one of the individual physical or chemical techniques can be used to treat wastewater effluents with good economics or energy efficiencies[47]. To be able to address the clean water access challenge properly, there remains plenty of room to consume less energy at a higher removal efficiency. One potential has been identified in the electro-chemical oxidation of these dyes.

2.2 Trace Contamination

Trace contaminations are simply pollutants or elements in minute concentration. Drinking water regulations have mandatory requirements for COD or colour content before the water can be safely consumed. Or, effluent standards are placed on municipalities and industries alike to ensure the waterbody receiving these effluents are not affected drastically by remaining contaminants. While minor in concentration, trace contamination can be a tricky problem for treatment facilities [6,7,31]. On one hand, additional treatment is clearly required to reached certain standards. On the other hand, investing into additional equipment or implementing new treatment facilities may appear to be excessive when considering the minute amount of pollution that is being addressed.

2.3 Traditional Wastewater Treatment Practices

Municipalities and industries are combatting their generated wastewater streams by applying treatment processes before discharging to waterbodies. There are many options to address these wastewater effluents and choosing the correct treatment practice for each situation boils down to wastewater characteristics, cost and size restraints, and effluent standards.

2.3.1 Membrane Filtration

Membrane based separation processes have become one of, if not the most, popular treatment technique of the 21st century. Membrane processes are a selective separation technique mainly based upon membrane porosity, which uses hydraulic pressure as the driving force for clean permeate water flux. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are widely applied across almost all water purification sectors for wastewater treatment[34]. Membrane processes are effective in reducing the unit operations, recycling process water, and can recover valuable constituents, all while lowering pollutant levels effectively, from pharmaceutical effluents to salinity from sea water. However, fouling remains a major obstacle for the efficient use of membrane technologies, which severely hampers the efficiency of this process[34-36,40,41,48]. Fouling forces many maintenance activities and chemical cleaning, which consumes additional energy, produces concentrated waste streams, and shortens the membranes lifespan. Fouling also causes a rapid decline in permeate flux over time. Many studies have been conducted to reduce fouling propensity to eliminate the need for chemical cleaning to increase the longevity of membranes increase economic efficiencies[35,36]. The removal, or even reduction, of fouling from membrane based wastewater treatments would directly assist in increased accessibility to water treatment worldwide.

High membrane shear rates have been well researched and are understood as an efficient method to increase permeate flux[39,42]. These shear rates are obtained by tangential fluid velocity along the membrane, which creates axial pressure gradients. These gradients reduce concentration polarization in UF, NF, and RO, while also removing foulants from MF surfaces. While an effective method to increase permeate flux, it has a power requirement using pumps[39,42].

Electrofiltration is a process utilizing an electric field across the membrane process to reduce fouling. Almost all colloids and suspended solids, including microorganisms, have a charge (more commonly negatively charged). Therefore, by producing a similar charge as the constituents in the wastewater stream, they are repulsed from the membrane surface, removing their opportunity to foul the membrane surface. For quick and efficient cleaning of electro-filtration membranes, theoretically, polarity reversal can be applied to remove these foulants[49]. Invasive and persistent foulants may need to be scrubbed off if the fouling becomes excessive[49]. Furthermore, the organic material that comes in direct contact with the charged membrane surface may be oxidized via electro-oxidation, which will be discussed further.

2.3.2 Biological Treatment

Activated sludge treatment is a commonly used biological wastewater treatment involving the addition of microorganisms to pretreated wastewater for the oxidization of carbonaceous biological and nitrogenous matter[50]. These microorganisms convert the (sometimes problematic) organic matter through aerobic and anaerobic wastewater processes into more congenial products. Biological treatment is heavily influenced on operating parameters, including retention times, wastewater composition, and temperature[50]. Regarding dye treatment options, this biological treatment is considered the standard or conventional choice. While aerobic treatment of dyes is typically quite difficult, studies have found that under anaerobic conditions, dyes can be readily biodegraded[51]. To be an effective treatment, biological treatment methods should be paired with other processes removing the inorganic constituents[52], such as pretreatment or using the MBR. Furthermore, there are some disadvantages regarding the slow treatment kinetics, the necessity of constant highly trained personnel on site, pre-treatment, and regular maintenance of microorganisms[53].

2.3.3 Membrane Bioreactors

Membrane Bioreactors (MBR) are a common biological wastewater treatment that utilizes both sludge treatment and a membrane separation process[50]. It essentially combines fine screening to the established wastewater treatment method of activated sludge biological processes, removing some time and space requirements needed for the sedimentation process (a common requirement in biological treatment). The added membrane removes the suspended particles and bacteria from the liquid. While aerobic treatment of dyes is typically quite difficult, studies have found that under anaerobic conditions, dyes can be readily biodegraded[51]. In terms of dye removal, anaerobic membrane bioreactors (AnMBRs) are shown to be able to readily remove COD and remove aesthetic pollution relatively easily, even at high salinity, albeit with the disadvantages of heavy membrane fouling in addition to the traditional biological treatment obstacles[51].

2.4 Chemical Treatment

2.4.1 Chemical Coagulation

Chemical coagulation is a process which encourages suspended materials in wastewaters to floc together and naturally settle. Suspended particles in water carry a negative charge, which tend to stabilize and repel other suspended particles. Flocs are created by destabilizing the charged suspended particles through the application of chemical coagulants, allowing these materials to collide. The coagulant carries an equal but opposite charge of these suspended particles to neutralize the negatively charged particles. To encourage further collisions, typically, a rapid mixing tank is used[32]. Of course, a large chemical input is required, which has associated costs and environmental impacts. A sludge layer of all the settled materials will need to be processed as well. The reduction of chemical use and sludge production would greatly improve the efficiency of this process.

2.4.2 Chemical Oxidation/Disinfection

Chemical oxidation is mainly governed by the production, or chemical input, of oxidizing or disinfecting species, such as hydroxyl radicals, chlorine, or ozone. These species have relatively non-selective oxidation capabilities, allowing near-complete oxidation of organic materials[54]. They possess relatively fast reaction rates, although these processes are relatively costly, require chemical inputs (and transport/management of oxidants, except for ozone if produced on site), and creation of some disinfection by-products[55].

2.4.3 Chemical Adjustments

Many wastewater treatment processes need to operate under specific operating parameters, especially considering wastewater characteristics. For example, some membrane materials can only operate within certain pH levels. Many oxidation reactions, such as electro-oxidation, chemical oxidation, or even biological methods, also require pH adjustments to ensure the necessary reactions are taking place.

2.5 Electrochemical Wastewater Treatments

Electrochemical processes for wastewater treatment have been gaining momentum in recent years due to their robust performance and environmentally friendly methods[1,2]. Research has shown these processes to have a lot of interesting qualities, such as operations at ambient temperature, no pressure requirements, easily adjustable to influent compositions and flow rates, require no auxiliary chemicals, and produce less waste, if any at all, when compared to traditional methods[44].

Specifically, electro-oxidation (EO), electro-coagulation (EC), and electro-filtration (EF) can plainly remove problematic pollutants from many different types of wastewater[44-46].

2.5.1 Electro-Oxidation

The heavily researched EO uses an anode with an induced charge that poses as an electron acceptor, which adsorbs and oxidizes pollutants when they come in direct contact with the anode[45]. The anode will also produce a powerful oxidizer, •OH radicals, which further oxidizes pollutants[27]. These two EO processes are separated as such into direct oxidation and indirect oxidation. Direct oxidation (or direct electron transfer to the anode) is a clean oxidation process without the addition of chemicals, or otherwise, asides from the electron. Direct oxidation refers to the wastewater stream needing to come in direct contact with the electrode for the oxidation process to take place, even at low potentials (typically, this oxidation takes place when the OEP, to be discussed further, is lesser than what is needed for water splitting and oxygen evolution). The direct contact requirement may introduce an inefficiency based on diffusion limitations, of which can be addressed by using cross-flow mechanics[39,42], as opposed to static or batch reactors. Indirect oxidation is associated with the formation of •OH radicals, and most organics can be degraded by these •OH radicals, which is formed as an intermediate of H_2O at the surface of anodes. The •OH radicals, along with the electrically produced Metal Oxides (MO), react with organics up to their full mineralization (converting them to CO_2, water, and inorganic ions) without any selectivity, following Eqs. (1-1 to 1-3)[56]. These processes may lead to electrode fouling, leading to further electrode contamination. Furthermore, some toxic by-products may be formed in these processes[44].

$$M + H_2O \rightarrow M(\bullet\,\mathrm{OH}) + H^+ + e^- \rightarrow MO + H^+ + e^- \tag*{[1-1]}$$

$$R + M(\bullet\,\mathrm{OH}) \rightarrow Products\ (CO_2 + H_2O + H^+ + e^-) \tag*{[1-2]}$$

$$R + MO \rightarrow RO + M \tag*{[1-3]}$$

where M is the metal surface and R is an organic species.

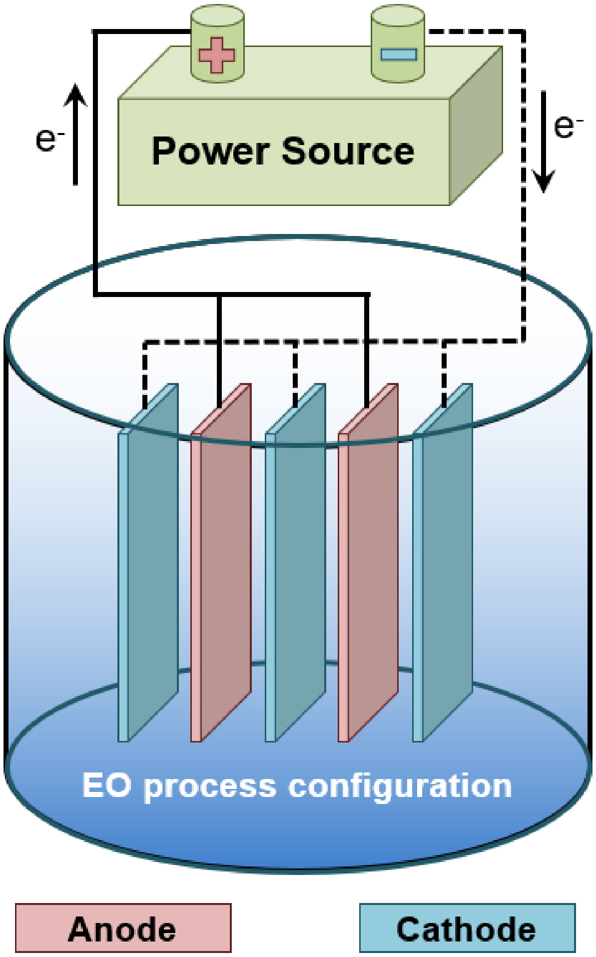

Figure 1 Electro-Oxidation process configuration

The efficiency of •OH radical production is connected to the O_2 evolution overpotential (OEP) of the electrode materials. The electrolysis of water, which is the separation of oxygen from water due to an electric current, takes place at 1.23 V. Electrodes with high OEP are connected to the fast and easy mineralization of organics. Table 1 shows a classification of several anodic materials based on their OEP[57,58].

Table 1 Anode Materials and their Respective Oxygen Evolution Potential, V vs. SHE

Material	**Oxygen Evolution Potential, V vs. SHE**
RuO_2	1.47
FeO_2	1.52
Pt	1.60
Graphite (Pyrolytic Oriented)	1.70
PbO_2 - PbO_2/Ti	1.8 – 1.9
Ti/Ce/Sb/SnO2	2.16
Ti/Nd/Sb/SnO2	2.28
Boron Doped Diamond (BDD)	2.40

2.5.2 Electro-Fenton

A similar process to EO, the Electro Fenton[56-58] also includes direct and indirect pollutant reduction processes, just taking place on the cathodic surface, albeit at a much less efficient rate. The indirect oxidation is governed by the classical Fenton reaction, which can occur when a small quantity of Fe (II) is introduced as a catalyst to an acidic solution (~pH 3) that contains electrically generated H_2O_2. The Fe (II) and H_2O_2 react to produce •OH radicals, as well as Fe (III), the former acting as an oxidizing agent.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad [2\text{-}1]$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet\mathrm{OH} + \mathrm{OH}^- \qquad [2\text{-}2]$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad [2\text{-}3]$$

$$RH + \bullet\mathrm{OH} \rightarrow mCO_2 + H_2O + \mathrm{pX} \qquad [2\text{-}4]$$

2.5.3 Electro-Filtration

Many membrane surface alterations have been tested for anti-fouling properties, such as implementing hydrophilic/hydrophobic properties, biocidal properties, or other surface modifications[40,41,48]. In electrofiltration (EF), a produced electric field envelops the membrane surface for anti-fouling properties. EF uses an applied electric field from an electrode to encourage charged colloidal particles to maneuver away from the membrane, keeping the surface of the filtrating membrane free from fouling[37]. Traditionally, EF is used by producing an electric field applied perpendicularly to the membrane surface by placing electrodes on the permeate and retentate sides of the membrane, thereby producing an electric force on the charged molecules or colloids in the wastewater stream[new1]. This technique has shown the ability to decrease fouling rates and increase permeate flux rate in cross-flow reactors[13,14,23,40,48]. The traditional EF method is shown in Figure 2.

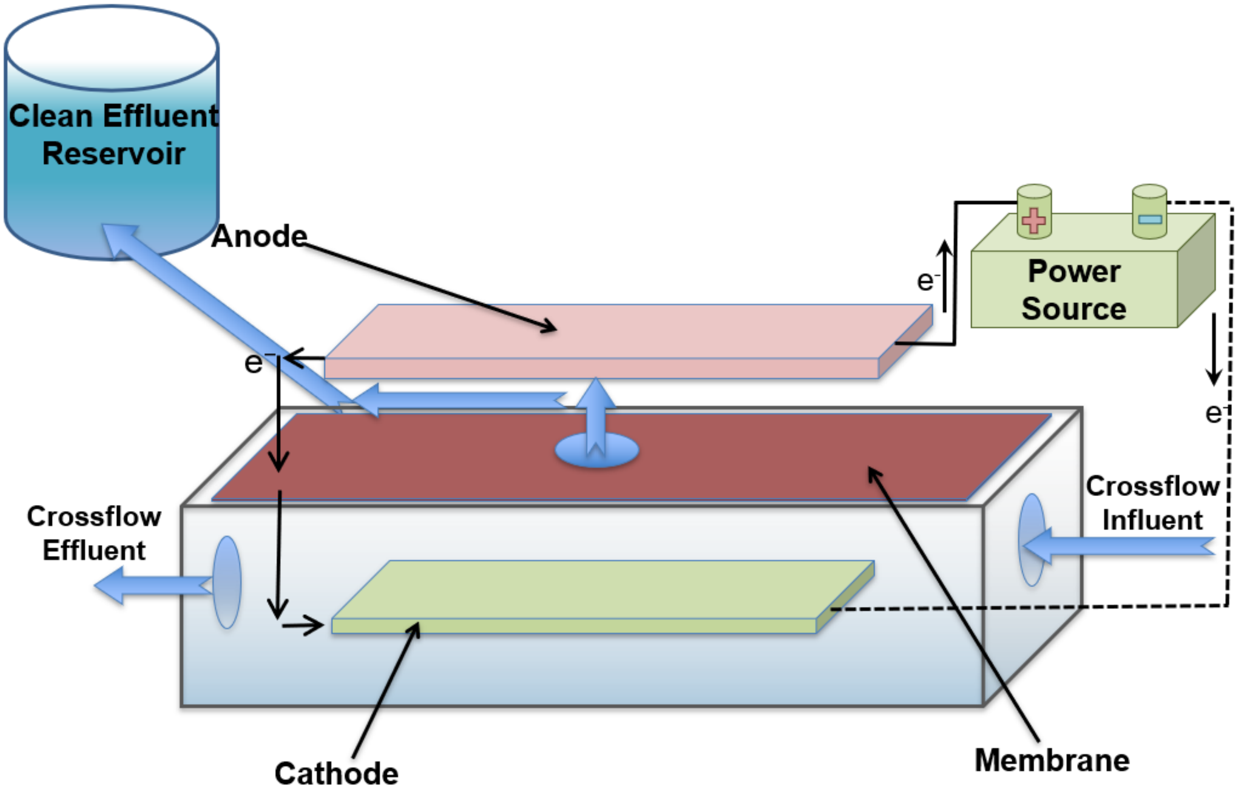

Figure 2 Traditional Electro-Filtration method represented, with the anode on the permeate side of the membrane and the cathode on the retentate side of the membrane

The use of a conductive membrane surface would be able to harness both EF and EO techniques at the same time. When applying a current on a conductive membrane, not only would the electric force still be applied onto the charged colloids, but any organic foulant that comes in contact with the conductive membrane surface undergoes electro-oxidation (direct), reacting with organics up to their full mineralization[39]. This updated version of EF is shown in Figure 3.

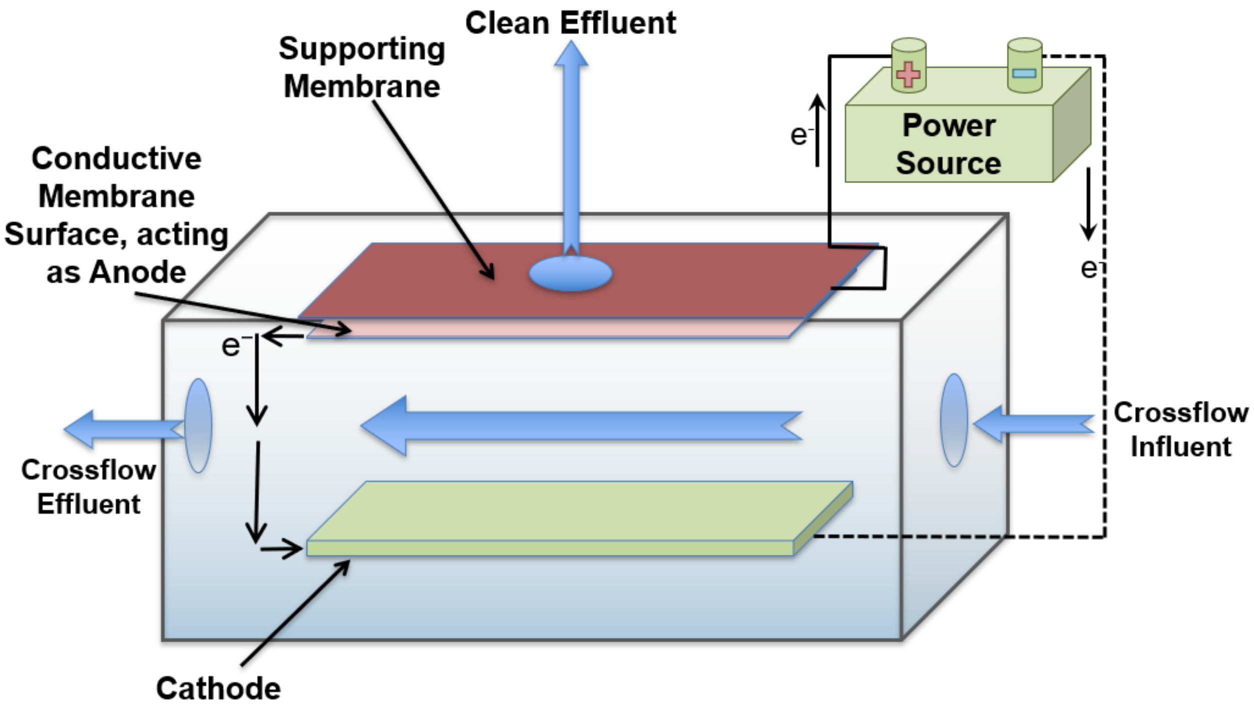

Figure 3 Electro-Filtration process where a conductive membrane is covering a supporting membrane surface

Conductive membranes have been researched for their potential for some time, but many surface coatings suffer from physical deficiencies such as brittleness and very rough surfaces[40]. The brittleness unfortunately disqualifies this method for wastewater treatment as it would always break, and surface roughness leads to adsorption into the membrane introducing a gateway for foulants to latch onto membrane surfaces[40,41]. Inorganic conductive membranes have also been investigated, but they are very expensive to manufacture, difficult to produce, and cannot be sized to typical membrane filtration units[40]. However, with the introduction of the easy to make, inexpensive, and conductive carbon nanotubes (CNT), multiwalled carbon nanotube (MWNT) sheets can be used as either a membrane or a membrane surfactant for EF processes [14].

2.5.4 Electro-Coagulation

The use of inorganic metal coagulants, such as aluminium sulphate and ferrous sulphate, can be effectively used as a primary coagulant[32]. Electrocoagulation (EC) takes advantages of this by generating similar coagulants via electrically dissolving aluminum (Al) or iron (Fe) from electrodes.

These metal cations dissolve at the anode according to the following equations:

$$Fe_{(s)} \rightarrow Fe^{n+}_{(aq)} + ne^{-} \qquad [3\text{-}1]$$

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-} \qquad [3\text{-}2]$$

These coagulants are produced through the dissolution of the Al/Fe electrodes when a charge is placed on the electrode plates. This Al/Fe coagulant encourages the pollutants to floc together, making them more readily available to be removed[38]. The traditional set up of EC is shown in Figure 4.

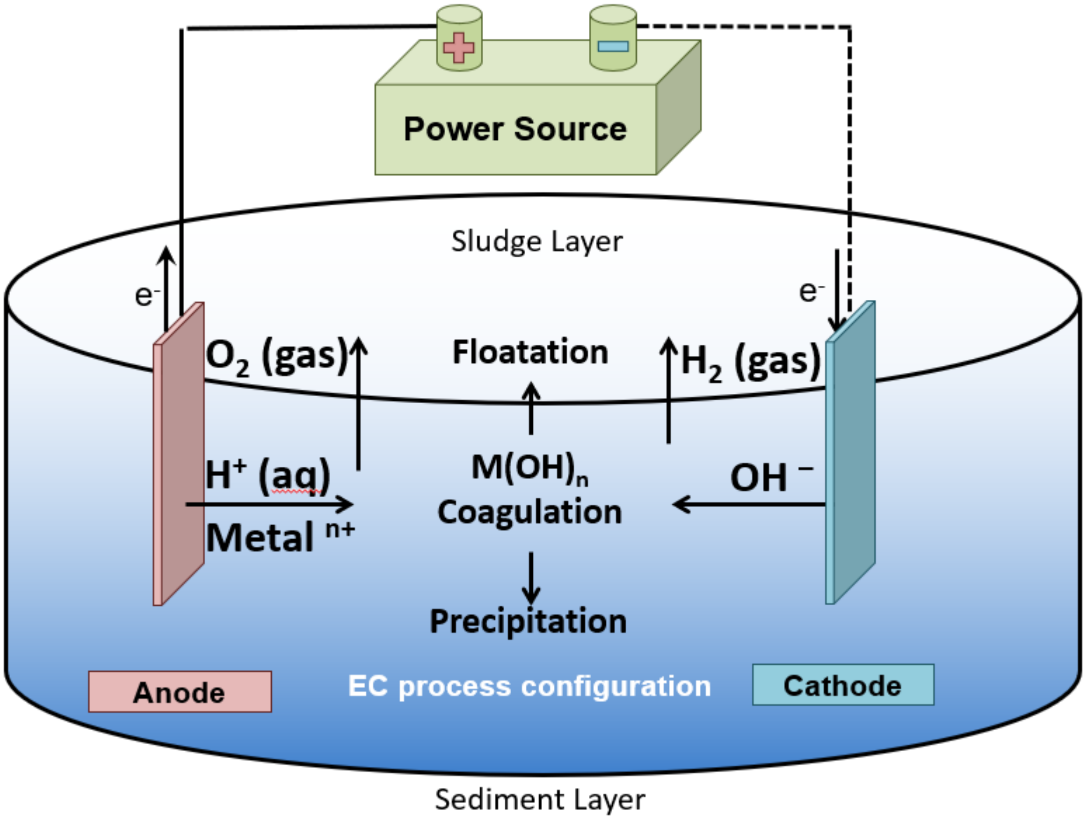

Figure 4 Electro-Coagulation process configuration

A novel application of EC is through charge induction, as opposed to the traditional set up shown in Figure 4. In charge induction, one charged object is brought close to a neutral yet conductive object without touching it. The neutral object will be induced to demonstrate an imbalance of electrons, and the electrons will be moved. This movement of electrons leaves an imbalance of charge on opposite sides of the neutral conductor. Refer to Figure 5 for an example.

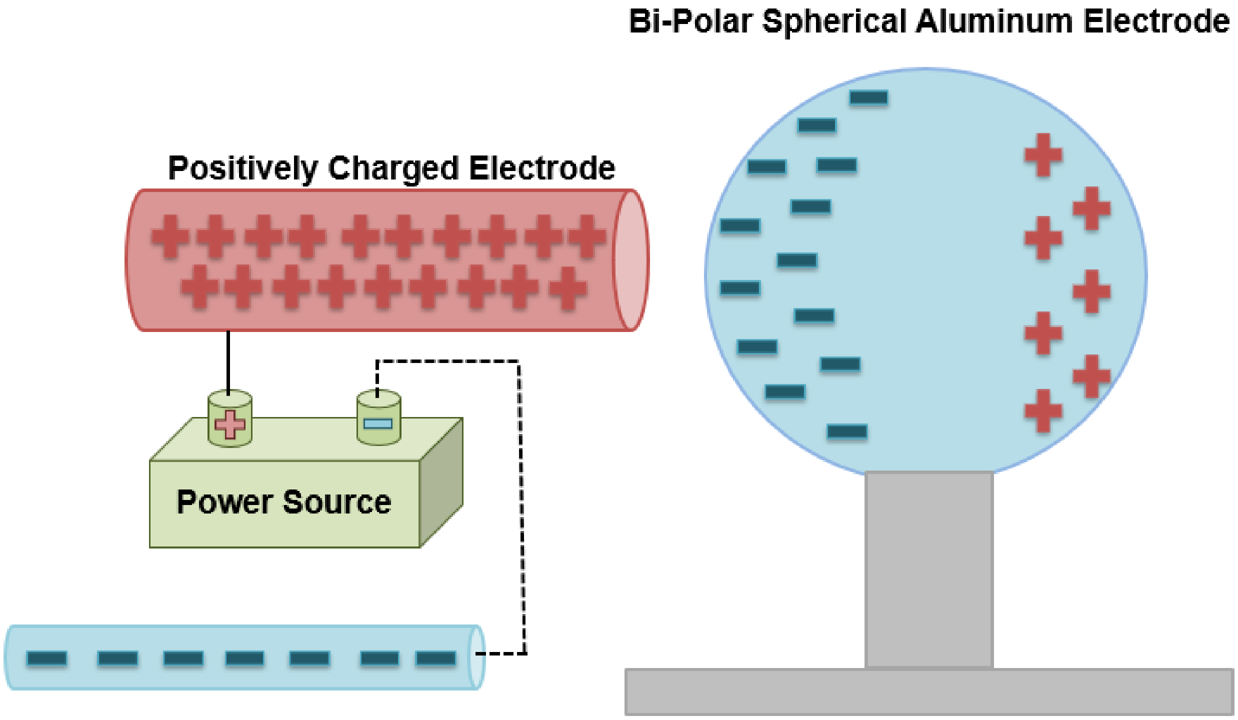

Figure 5 Example of charge induction

In the EF process, an electric field is created between the negatively charged anode and the positively charged cathode. If the charged placed on the Al/Fe electrode is through a charge induction from the existing EF electric field, there is theoretically no additional power consumption required if EC is paired with EF.

The general advantage of the EC method is that this technique generates the coagulants in-situ, meaning it does not require any chemical transport or handling. Furthermore, research shows other advantages over chemical coagulation processes such as there is no chemical addition needed, EC produces flocs over a wider pH range, a reduction in sludge volume, and flocs are produced at a more rapid rate[33]. All of these advantages come with an increase power consumption for inducing a charge on the electrode. However, as noted earlier, if using a charge induction process, there is theoretically no additional power consumption if paired with an EO process.

2.6. Combined electrochemical treatment

At first glance, it seems there are many wastewater treatments using combined electrochemical systems. Researchers have noticed the optimal and positive treatment capacity of combined electrochemical techniques and have challenged the boundaries of these techniques. Projects have been published using EC, Electro-fenton, EF, or EO (or a combination of these) for a myriad of different wastewaters, including wastewaters containing electroplating effluents[12], trace emerging contaminants[13], bacteria[14], dyes[15-22], pharmaceuticals[23], industrial effluents[24], and agriculture effluents[25] among others. However, many research papers use these processes in a sequential, or step wise, functions instead of a combined single reactor. For example, research in "combined electrochemical treatment" may use electrocoagulation as a single first step, and in the second step, ozonation[12]. Or, research could use EO as an initial treatment to be followed by gamma-irridiation[17.] Not only are these separate sequential processes (with the space requirements or footprint for two processes), but not all the processes are even electrochemical wastewater treatment methods. Electrochemical processes can be used in a pre-treatment, post-treatment, and/or a fully integrated treatment[43]. Many different combined configurations can be used, with a few examples shown in Figure 6 to Figure 8. Removal capacities for electrochemical and combined electrochemical treatment can be shown in Table 2 and Table 3.

Electrochemical processes can replace more traditional wastewater treatments if advantageous enough, such as electrocoagulation in lieu of chemical coagulation[32,33,36] (as mentioned earlier in Chapter 2.5.4). For example, electrocoagulation may be more advantageous over chemical coagulation if the treatment prioritizes no chemical handling and a decrease in sludge volume while using a wastewater that will respond well to electrochemical coagulants, all while being able to facilitate increased power consumption through applying an electrical current to the Al/Fe electrode for the dissolution of coagulants[38]. The advantages and disadvantages of the electrochemical treatment techniques are included in their respective sections in Chapter 2.

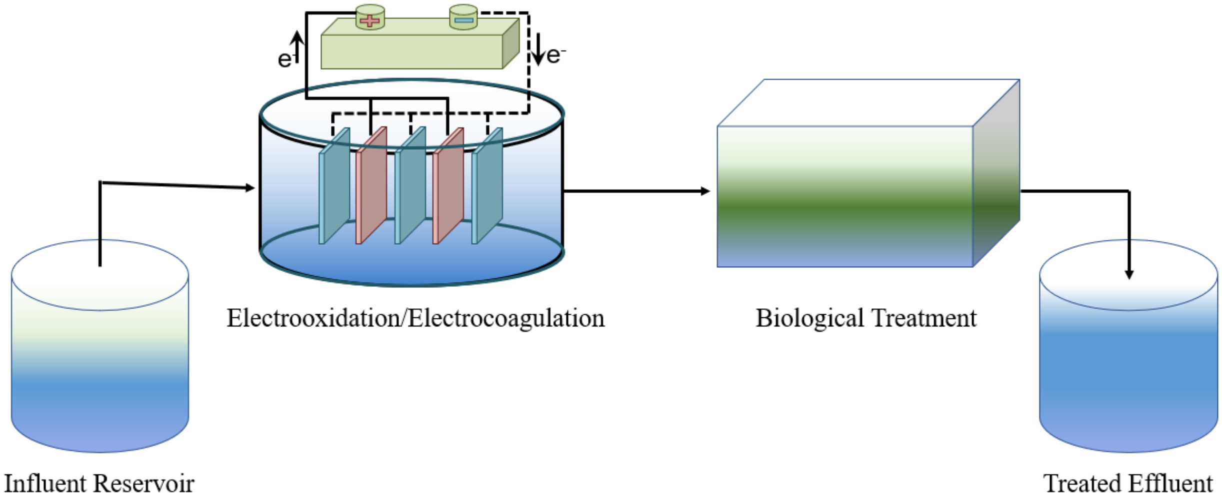

Figure 6 Combined Electrochemical Treatment process with the electrochemical operations being pre-treatment or initial treatment

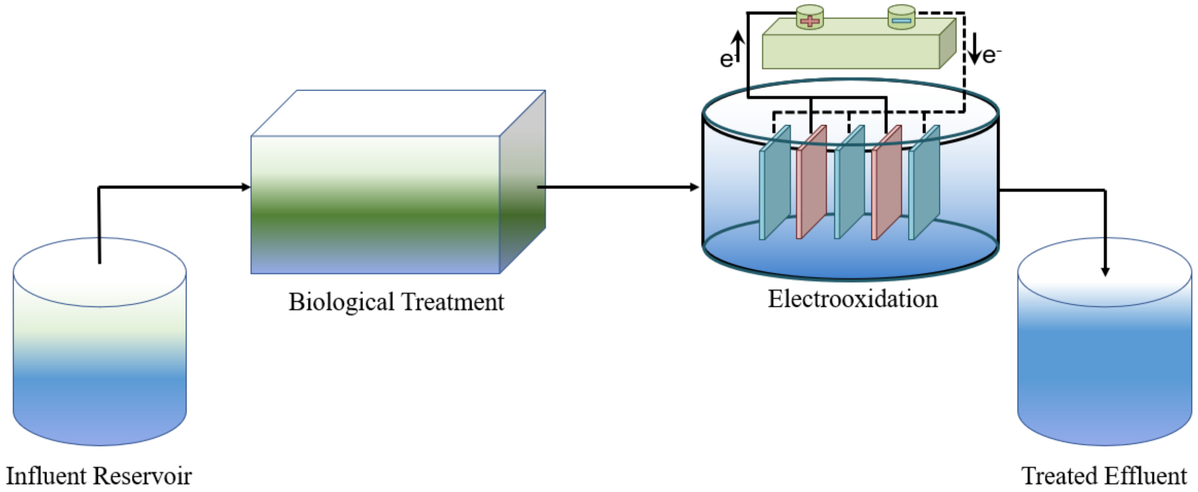

Figure 7 Combined Electrochemical Treatment process with the electrochemical operation being post-treatment or secondary treatment

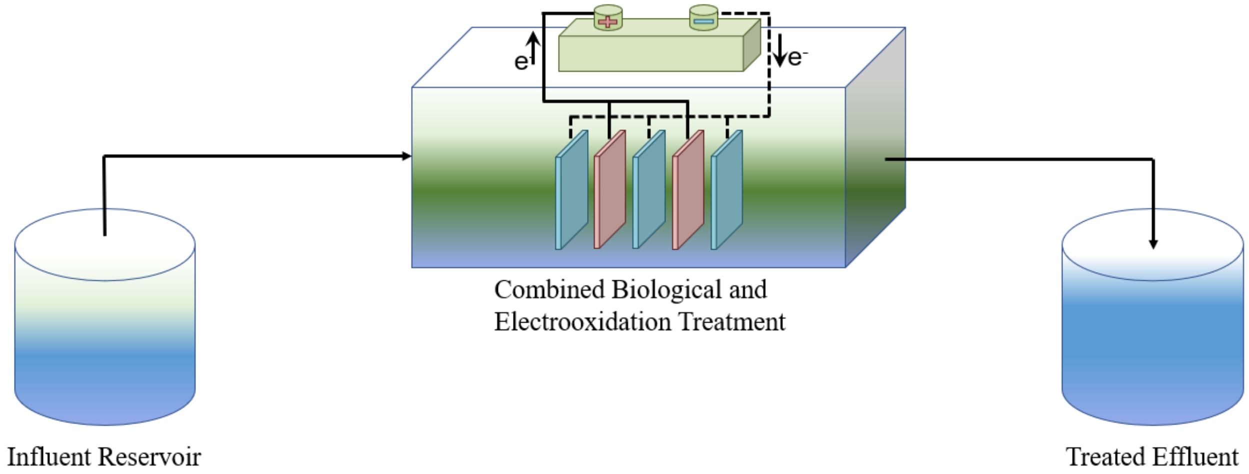

Figure 8 Combined Electrochemical Treatment process with a single process step combined into one reactor

2.6.1. Advantages of Combined Electrochemical Treatment

While replacing more traditional methods (such as chemical coagulation for electrocoagulation) with electrochemical treatment methods could produce similar results in a more efficient or environmentally friendly way[33,38], using a combined treatment that is not exclusively electrochemical may miss out on some benefits of a fully electrochemical wastewater treatment module. These benefits include the inherent modular characteristic of a single reactor. A modular system has everything needed for operation self-contained and is therefore scalable by design, easily shipped anywhere in the world. If there is a need for increased capacity, others can be added as needed to address need for increased capacity. This is especially boosted if all the techniques are electrochemical that essentially only require an applied charge for overall functionality[1,2,44-46]. If you can simply plug in a modular and all-in-one electrochemical wastewater reactor, it will be able to clean wastewater. In addition to the modular designs, the footprint that would typically be needed for separate treatment processes is decreased as there is only one step of treatment needed. Finally, there is inherent simplicity in using electrochemical wastewater treatment as there is no chemical handling or chemical additions necessary (in EC, EF, or EO).

2.7. Recorded Removal Efficiency by Standalone and Combined Electrochemical Wastewater Treatment Research

Table 2 and Table 3 are a representative selection of EAOPs and their capabilities in COD and color removal abilities. These tables confirm the ability of EAOP processes to remove color and COD in wastewater streams.

Table 2 shows the results of previous EO treatment research, mainly showing complete or adequate color removal and various COD removal capacities. Note that removal capacities rely on anode materials, residence time, electrode spacing, and applied charge, among other criteria[19-22,59,60]. Many of these results were introduced through a review paper[43].

Table 2 Recorded COD and Color Removal Abilities for Electro-Oxidation Wastewater Treatment

$[C]_0$ Influent	Anode Material	% COD Removal	% Color Removal	Time	Ref.
404 mg/L COD	$Ti/TaIrPt_{alloy}$	10	85	180 min	21
404 mg/L COD with catalyst	$Ti/TaIrPt_{alloy}$	60	100	180 min	21
135 mg/L COD	Ti/Pt	50	100	240 min	19
550 mg/L COD	Ti-Pt/ β-PbO_2	78	100	60 min	22
650 mg/L COD	Si/BDD	100	100	1080 min	20
60 mg/L methylene orange	$(Co/Ni)/TiO_2$	-	90	10 min	59
Real Textile Wastewater	Graphite Felt/Pt	56.3	67.9	210 min	60

Table 3 shows the results of previous combined electrochemical treatment research, again mainly showing the COD and color removal. The electrochemical treatment portion relies on anode materials, residence time, electrode spacing, and applied charge, among others, while overall removal capacities also depend on the combined treatment option. As electrochemical treatment can be used a pre-treatment, post-treatment, or a combined reactor, these results are less representative of the functionality of EAOPs, but more a confirmation that electrochemical processes can be combined with many different treatment scenarios.

Table 3 Recorded COD and Color Removal Abilities for Combined Electrochemical Wastewater Treatment Systems

$[C]_0$ Influent	**Combined System Identification**	**% COD Removal**	**% Color Removal**	**Time**	**Ref**
400 mg/L Methylene Orange	**EO+Chemical** Electro-oxidation plus Chemical addition – Kaolin as an adsorbent	89.6	95	60 min	18
3400 mg/L COD 3750 Pt/Co color	**EC+EO+Radiation** Electrocoagulation, Electrooxidation, then gamma-irradiation	95	90	95 min	17
100 mg/L Methylene Blue	**EO+Chemical** Electrooxidation, then Fly Ash adsorbent	84	99	120 min	15
760 mg/L COD	**EO+Chemical+Sonication** Electrooxidation, Peroxide oxidation, then Ultrasonication	92	-	Unclear	16

3. Research Methodology

3.1. Reactor Design Considerations

This research introduces the designs and validations of a novel EO-EC-EF reactor. As such, the disadvantages of each EAOP had to be addressed to be able to create a functional reactor.

The main disadvantage of the EO process is diffusion limitations of constituents in wastewater[9,17]. Direct EO is an adsorption process where organic material needs to touch the anode for anything to happen. To address this, a cross-flow reactor set up was used to ensure a constant cycle of wastewater in contact with the anode.

A main disadvantage for the EF process is the brittleness, the rough surface of these membrane materials, and the costly nature of these membrane or membrane coating material[39,42]. To address these issues, MWNT Buckypaper was used as an affordable conductive membrane coating on top of a structural UF membrane, allowing the promising results of EF while addressing the cost and brittleness drawbacks.

EC is rarely used within the same reactor as a membrane process as the coagulation process creates large solid flocs that will directly foul the membrane[38]. To address this issue, EF was used to deter all foulants away from the membrane surface. Furthermore, the typical organic foulants that would create a biofilm are potentially oxidized through the direct EO process taking place on the membrane coating[61]. Additionally, the cross-flow reactor design also has anti-fouling properties[34,40].

Taking all these potential disadvantages in mind, the design considerations were understood, and the reactor was created. The first design consideration was to move away from single cell reactors, or batch reactors, towards a cross-flow and continuous process, as most electro-chemical wastewater treatment research does not use a cross-flow reactor. The cross-flow set up adds anti-fouling properties to the membrane function, while also addressing the diffusion limitations for direct oxidation. The conductive membrane is the second design consideration, as it adds further anti-fouling properties to the membrane in addition to functioning as the anode in the powerful electro-oxidation reaction. The third design consideration is to implement both electro-coagulation with electro-oxidation within the same reactor. An aluminum electrode is placed between the anodic filter and cathodic SS electrode, promoting a bi-polar charge portfolio due to the induced charges from the anode and cathode. The induced positive side of the aluminum electrode produces the aluminum coagulants within the system. While the main intention is to use the clean effluent after being passed through the conductive membrane, the residual effect of the electro-oxidation and electro-coagulation still benefits the rest of the water within the closed system through each cycle. A visual is shown in Figure 9, as well as photos of the lab set up in the Appendix.

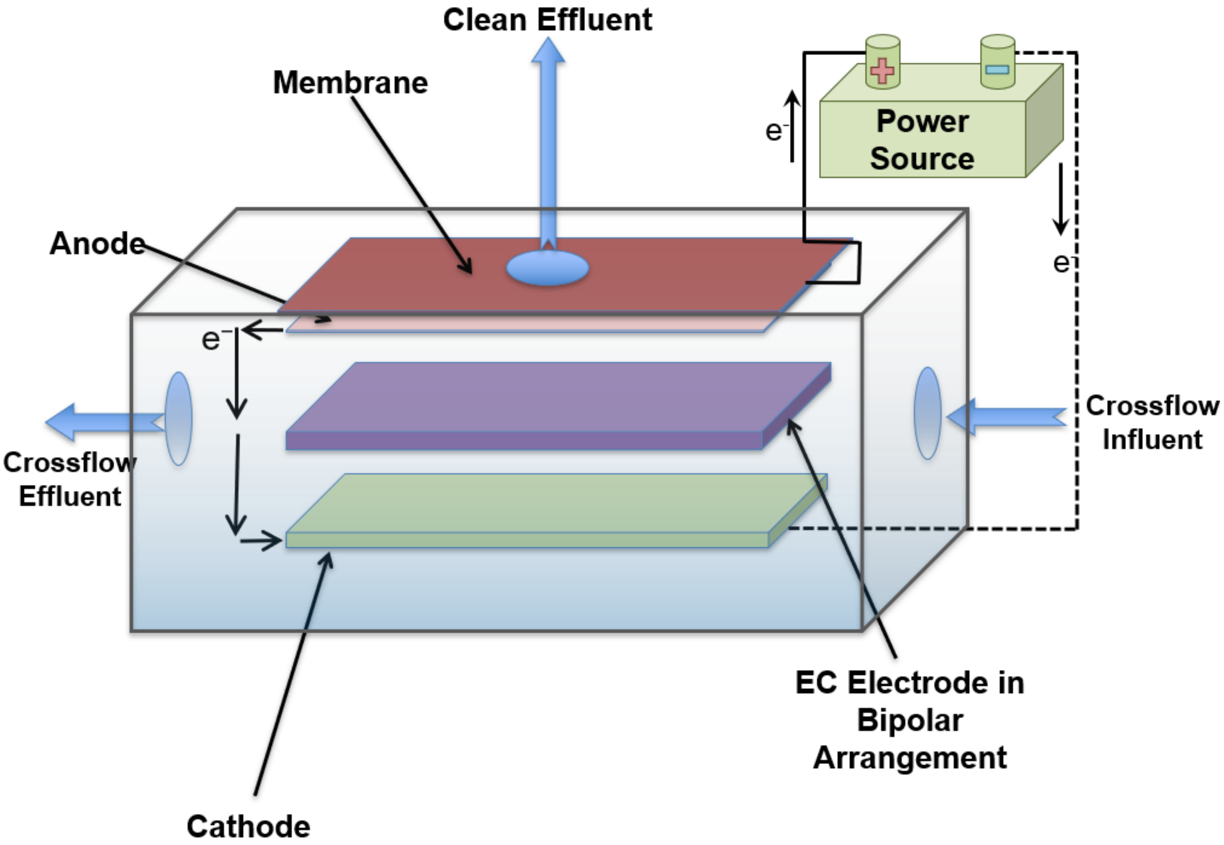

Figure 9 Reactor Visual Representation

3.2. Reactor Materials

The main reactor design is the cross-flow unit, which houses three electrodes for the implementation of electrochemical techniques. The entire reactor measures 10cm x 14.8cm x 10cm, while the active membrane surface measures 4.6cm by 10.8cm. The electrodes run parallel to the direction of the water flow, ensuring no significant flow obstructions. The "bottom" electrode (see Figure 4 for reference) is the cathode, which is made from stainless-steel (SS) material, sourced by McMaster Carr (Elmhurst, Illinois, USA). The charge is introduced to this electrode through a conductive metal rod, which is in contact with both the SS electrode and the power supply to ensure a negative charge is maintained (see Figure 12 in the appendix). The anode for this reactor is a surface on the membrane unit. The conductive membrane material, a High Conductivity MWNT Blend Buckypaper from NanoTechLabs Inc (Yadkinville, NC, USA), with a porosity around 100 kDa and the standalone MWNTs demonstrating a Zeta potential around 3.5 mV, has been overlapped onto the ultrafiltration membrane, a chemically stable, rigid, and relatively costly 20 kDa hydrophilic PES membrane from Synder Filtration (Vacaville, CA, USA). Synder Filtration recommends PES for the resistance to oxidizing agents and the robust chemical and temperature resistance. The active membrane surface area is ~50cm^2 with the Buckypaper and the conductive material comes in first contact with the influent. This allows a charged surface of the membrane (for anti-fouling properties) while maintaining the structural integrity of the commercially available UF PES membrane unit. The Buckypaper has a charge implemented onto the surface through conductive tape, which is placed both on the Buckypaper and on the positive end of the power supply. The membrane is backed by a perforated plastic sheet as a structural support layer. Finally, sandwiched between the anode and cathode is a perforated bi-polar aluminum electrode, sourced by McMaster Carr (Elmhurst, Illinois, USA). The positive side of the aluminum plate thus electrically dissolves, producing the aluminum coagulant via induced charge.

3.3. Analysis Equipment

To be able to induce a charge on the conductive membrane, a Keysight E3620A Dual Output DC Power Supply (Santa Rosa, CA, USA) was used. This particular power supply can maintain either a constant voltage output (V) or constant ampere (amp). Since the electrolytes in the solution are consumed in electrochemical processes, a steady decrease in amperage was witnessed throughout the trials. Therefore, a constant voltage has been used across all trials at 4 volts, as opposed to a constant ampere rating which would increase the voltage output over time. This low voltage has been used in previous research projects at Concordia while also validated in the literature[14,40]. In comparison with other electro-chemical treatment studies in literature, 4 V is lower than the typical voltage used[15-22], notably reducing energy requirements.

To measure the effluent flux, a Sartorius Quintix 5102-1S (Göttingen, Germany) scale was used. This scale has the capability to output results at consistent and short time intervals, which was utilized to give constant by-minute mass readings. The change of mass over time measured by this scale was used to calculate effluent flux.

The Cary 8454 UV-Vis Diode Array System from Agilent (Santa Clara, CA, USA) is a spectrophotometer using a photodiode array to measure the ultra-violet and visible light spectrum to identify the purity of liquid samples. After determining the wavelength of methylene blue, initial influent water was sampled to confirm initial methylene blue dye concentrations, which was then compared to hourly effluent samples to validate removal capacity.

Chemical Oxygen Demand (COD) was measured in the same validation steps (initial sample to effluent sample) as with the methylene blue, to validate the removal capacity of the reactor. Hach TNT 821 COD vials tests (Loveland, CO, USA) were used to calculate the COD concentration in liquid samples. These vials were placed in the Hach DRB 200 thermostat reactor (Loveland, CO, USA) to be heated to 150 ˚C after the sample was added, to then have the COD concentration measured in the Hach DR 2800 Spectrophotometer (Loveland, CO, USA).

To address the pressure requirements for membrane usage (30 psi), a Sterlitech Hydracell pump was used (Kent, WA, USA).

3.4. System Materials

Water was circulated with customized PVC pipe, guided through different tube fittings. The PVC piping was customized in the shop to proper lengths and thread counts. Crossflow was measured using a flowmeter for water, and the flowrate was controlled using precision flow-adjustment valves. Cross-membrane pressure was measured using a pressure gauge. All pressure and flow gauges, PVC piping, pipe fittings, flow adjustment valves, and clamps were sourced from McMaster Carr (Elmhurst, Illinois, USA).

3.5. System Methodology

The spacing of the electrodes has a direct effect on the productivity of the electrochemical processes. The rate of formation for •OH radicals increases as the electrodes come nearer to each other, directly increasing the oxidation performance. However, as the electrodes come close to each other, it directly reduces the mass transfer within the reactor (thereby reducing the direct oxidation effectiveness). An optimized electrode distance of 20 mm is constant throughout all the trials, found through research projects from previous lab members and validated in literature[12].

Current density has a straightforward effect on both treatment efficiency and power consumption; increased current density means greater treatment efficiency with a greater power consumption. The connection between treatment efficiency and power consumption is not linear (if power consumption is doubled, treatment efficiency is not always doubled), showing that there is an optimization point to be found[62]. The voltage has been set at a constant low voltage, 4 V, for all trials in this research. As noted previously, this low voltage has been used in previous research projects at Concordia while also validated in the literature[14,40]. In comparison with other electro-chemical treatment studies in literature, 4 V is lower than the typical voltage used[15-22] notably reducing energy requirements.

Temperature, transmembrane pressure, and reactor crossflow were monitored throughout the experiment. The temperature was consistent through all the different trials, remaining between 29˚C and 32˚C. The temperature increase is likely caused by the pump, which has a high operating temperature that influences the temperature of the water. The transmembrane pressure was measured using the precision pressure gauge, used to ensure a consistent 30 psi pressure rating is placed upon the membrane. As more fouling occurred over time on the membrane surface, the transmembrane pressure slowly decreased, requiring an increase of input pressure in response. The pressure gauges and pump controls were used to increase the pressure, as needed, to maintain the 30 psi rating. Effluent flux was constantly measured and noted on a per-minute basis.

Samples of the clean effluent and the cycling influent are taken every hour for testing. The cycling influent has consistent concentrations for each trial, and less than 10 L is cycled for every experiment.

3.6. System Validation

To represent inorganic solid foulants, 200nm and 500nm non-functionalized colloidal silica nanospheres (at 10mg/ml) were purchased from Alpha Nanotech (Vancouver, BC, Canada). These sizes of 200nm and 500nm were chosen to ensure removal by the filtration membrane (and to guarantee inorganic membrane fouling) as the silica nanospheres are larger than the pore size in the ultrafiltration membrane (20 kDa). These colloidal silica nanospheres from Alpha Nanotech have a zeta potential of -33.5 mV, a 0.0611 mS/cm conductivity rating, consistent size distribution, and are prepared by the sol-gel process. Suwanee River Natural Organic Matter (SRNOM) was purchased from the International Humic Substances Society (IHSS) (St. Paul, MN, USA) to represent organic matter and organic foulants. SRNOM from the IHSS is a popular reference material for NOM in wastewater treatment research used to represent organic content typically found in natural water sources. This was chosen to represent natural water systems to validate this reactor on a water type similar rural community applications. Methylene blue solution at a 1.5% concentration was ordered from Sigma-Aldrich (Oakville, ON, Canada) as a cationic (charged) stain substance to measure aesthetic pollution removal while contributing to the organic content. Methylene blue has measurable light absorption properties, allowing the UV-Vis Diode Array System to measure concentrations in the influent and effluent streams. Sodium chloride (≥99%) was purchased from Sigma-Aldrich (Oakville, ON, Canada). Deionized water was created in-situ using the Milli-Q purification systems from Millipore (Burlington, MA, USA).

For each trial, pure deionized water is initially cycled through the reactor for membrane compression. Dependant on the trial, different samples were prepared. While several different samples were prepared and investigated for removal capacities, the concentrations of each constituent added stayed consistent throughout all trials. For example, the concentration of methylene blue (1mg/L) used in the sample with only methylene blue and NaCl (Wastewater A), is identical to the concentration of the sample with methylene blue (1mg/L), NaCl, silica beads, and SWNOM (Wastewater D). Table 4 has the concentrations of each constituent if added for a trial. The composition of the four manufactured wastewaters are discussed in Table 5.

Table 4 Constituent Concentration for Sample Preparation

Constituent	Concentration
Methylene Blue	1 mg/L (±0.05 mg/L)
NaCl	2.8 g/L (±0.14 g/L)
SWNOM	4 mg/L (±0.2 mg/L)
Colloidal Silica Nanospheres (200nm)	1.67 mg/L (±0.1 mg/L)
Colloidal Silica Nanospheres (500nm)	1.67 mg/L (±0.1 mg/L)

All solutions were prepared in deionized (DI) water. Each constituent was added to DI water over a magnetic stirrer, briefly mixing for 5 minutes total.

There were several types of wastewater prepared and used: Wastewater A contained only methylene blue, Wastewater B contained methylene blue and SWNOM, Wastewater C contained methylene blue and two sizes of silica nanospheres, and Wastewater D contained methylene blue, SWNOM, as well as two sizes of silica nanospheres. Electrolytes were added to all types of wastewaters to ensure the electrochemical processes can take place. Table 5 highlights each wastewater characteristics. The experiment was set up to be able to measure the effect of different types of foulants (SWNOM represents organic fouling, Silica Nanospheres represents inorganic fouling, Methylene Blue produces organic and aesthetic) on each reactor configuration (UF, EO-EF, and EO-EC-EF). All wastewaters also contained NaCl at a concentration of 2.8 g/L.

Table 5 Wastewater Characteristics

Constituent	Wastewater A	Wastewater B	Wastewater C	Wastewater D
Methylene Blue	X	X	X	X
SWNOM		X		X
Silica Nanospheres			X	X
NaCl	X	X	X	X

The following steps were consistent for every trial completed:

- After reaching flux stabilization for membrane compression using DI water, each experiment was run for six hours,
- There was a constant trans-membrane pressure held at 30 psi, and
- Temperature was maintained between 29 degrees Celsius and 32 degrees Celsius.

A baseline experiment was created using just an UF membrane (EF membrane without an induced charge) and measuring the methylene blue removal, the COD removal, and the flux decrease over time (due to fouling). This baseline experiment was then compared to each additional stage of the reactor.

The next phase of experiments followed the identical set up with the addition of electro-oxidation. As the membrane used is conductive, the anti-fouling properties should be apparent, while also directly oxidizing the organic materials (methylene blue and SWNOM). Through the comparison between the UF and EO-EF results, the benefits of the electrochemical techniques for each specific foulant will appear.

With the addition of electro-coagulation in the same reactor, the final phase of experiments take place. This experiment should increase the removal capacity through the addition of electro-coagulation via the creation of flocs from the contaminants to settle out. This introduces more solids, thus, increasing the fouling potential. A balance must be found between increased removal capacity at the expense of increased fouling.

Although some electrochemical wastewater treatment research in literature has trials only 45 minutes long[43], this research is conducted for 6 hours to offer a more realistic approach if used in industrial applications. Laboratory photos for the set-up and used conductive membrane surface photos are provided in the Appendix.

Due to the COVID-19 pandemic, lab closures at Concordia University forced this research to be cut short before all trials could be completed. In cases where results are unavailable, they were extrapolated from similar trials, which will be indicated hollowed points on charts and through the footnotes through the result sections. Table 6 delineates what reactor and wastewater combinations were completed prior to the lab closures.

Table 6 Laboratory Results Confirmation by Sample Type, Reactor Set Up, and Wastewater

Reactor Set Up	**Wastewater A**	**Wastewater B**	**Wastewater C**	**Wastewater D**
Laboratory Results: Flux				
UF	X	X	X	N/A
EO-EF	X	X	X	X
EO-EC-EF	X	X	X	N/A
Laboratory Results: Methylene Blue Removal				
UF	N/A	X	N/A	N/A
EO-EF	X	X	X	X
EO-EC-EF	X	X	X	N/A
Laboratory Results: COD Removal				
UF	N/A	X	N/A	N/A
EO-EF	N/A	N/A	N/A	N/A
EO-EC-EF	N/A	X	N/A	N/A

4 Results and Discussion

4.1 Anti-Fouling membrane properties by introducing EO-EF measured through flux

Anti-fouling properties for membrane operations has received a great deal of interest in wastewater treatment research recently[34-36]. In this study, EF was implemented to measure the anti-fouling capabilities on different typical types of foulants found in wastewater. A common mode to measure anti-fouling is to monitor the permeate flux rates and to measure the propensity in which flux decreases over time[13,23]. The permeate flux rate has been measured in this study and the results of UF compared to EO-EF are shown in Table 6 and through Figure 10 to Figure 13. Table 6 represents the flux data for each type of wastewater and the corresponding decrease in flux for each reactor set up. The anti-fouling propensity can be substantiated by comparing the flux decrease from the standalone UF membrane to the reactor set-up using EO-EF. The flux was measured through constantly measuring the volume of the effluent over time.

Table 7 Flux Decrease (%) for Reactor Set up UF and Reactor Set up EO-EF for Wastewaters A to D

Wastewater Identification	Flux Decrease with Reactor Set up UF [$100*(J_0-J)/J_0$]	Flux Decrease with Reactor Set up EO-EF [$100*(J_0-J)/J_0$]
A	10.1%	3.5%
B	31.2%	8.0%
C	9.5%	3.8%
D	31.2%[a]	24.8%

Increased flux was achieved through the introduction of EO-EF in every wastewater type due to the anti-fouling capabilities of EF. Experiments carried out with EO-EF, when compared to a non-conductive membrane, clearly show the benefits of utilizing a conductive surface in membrane technologies. Referring to both Table 7 and Figure 11, regarding Wastewater B, which contains the problematic organic foulant (SWNOM), there is a flux decrease of 31.2% when using the non-conductive membrane as compared to an 8.0% flux decrease when using the conductive membrane. This sample suggests a close to a four-fold increase of efficiency when referring to only flux and organic foulants. A similar outcome is shown using Wastewater A.

Interestingly, the inorganic foulants were seemingly unaffected by introducing EF. The only difference between Wastewater A and Wastewater C, is that Wastewater C has incorporated the silica nanospheres (representing the inorganic foulant). Therefore, the impact EF has on inorganic

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[a] The flux values for the UF reactor set up for Wastewater D are extrapolated from the most similar trial, the UF reactor set up for Wastewater B (the only difference is the addition of Silica Nanospheres, which have shown to have little significance on flux values). This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University.

fouling could be investigated by comparing the flux results between Wastewater A and Wastewater C. Referring to Table 7 and Figure 10, flux performance was improved from a 10.1% flux decrease when using the UF set up, to a 3.5% flux decrease using the EO-EF set up in Wastewater A. Similarly, referring to Table 7 and Figure 12, flux performance improved from a 9.5% flux decrease when using the UF set up, to a 3.8% flux decrease using the EO-EF set up in Wastewater C. Comparing the flux data from Wastewater A to Wastewater C shows very little change through the UF and EO-EF trials (<0.75% for both UF and EO-EF reactor set ups), suggesting some inorganic foulants are less affected by conductive membranes than organic foulants.

Overall, there was an average two-fold increase of efficiency in terms of flux when using EO-EF as compared to UF, from an average 20.5% flux decrease using UF to an average 10% flux decrease using EO-EF.

4.2 Membrane Fouling when incorporating EC within a membrane reactor

Coagulation/flocculation processes and membrane processes have long been separated due to the significant fouling suspended solids cause to membrane processes[32,34,38,40]. The general question to be asked when adding EC to a membrane process is; is the removal capacity added through incorporating EC to this reactor worth the increased fouling EC introduces?

This question can be answered through the permeate flux readings. As mentioned earlier, a common mode to measure fouling is to monitor the permeate flux rates and to measure the propensity in which flux decreases over time[13,23]. The permeate flux rate has been measured in this study and the results of EO-EC-EF compared to UF and EO-EF are shown through Table 8, as well as through Figure 10 to Figure 13. The fouling effect can be investigated by the flux drop of the EO-EC-EF reactor set up compared to the UF or EO-EF set up for each wastewater.

Table 8 Flux Decrease with Reactor Set ups UF, EO-EF, and EO-EC-EF for Wastewaters A to D

Wastewater Identification	**Flux Decrease with Reactor Set up UF [100*(J_0-J)/ J_0]**	**Flux Decrease with Reactor Set up EO-EF [100*(J_0-J)/ J_0]**	**Flux Decrease with Reactor Set up EO-EC-EF [100*(J_0-J)/ J_0]**
A	10.1%	3.5%	29.3%
B	31.2%	8%	33.4%
C	9.5%	3.8%	5.2%
D	31.2%[b]	24.8%	33.4%[b]

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[b] The flux values for the UF and EO-EC-EF reactor set ups for Wastewater D are extrapolated from their most similar trial, the UF and EO-EC-EF reactor set ups for Wastewater B (the only difference is the addition of Silica Nanospheres, which have shown to have little significance on flux values). This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University.

As expected, introducing coagulation within the same cell as a membrane increased the fouling on the membrane in certain wastewaters. The fouling propensity was increased with the introduction of EO-EC-EF in most experiments, sometimes drastically, due to the addition of the larger flocs caused by coagulation. As shown in Table 8 and Figure 10, for Wastewater A, the EO-EC-EF reactor set up had a flux reduction of 29.3%, compared to a flux reduction of 10.1% using UF. The addition of coagulation seems even more moot when compared to the EO-EF reactor set up for Wastewater A, which only had a 3.5% reduction in flux.

However, when considering Wastewater B, C, and D, the addition of coagulation in the EO-EC-EF reactor set up is not deemed an unsuitable treatment when considering flux, especially when compared to UF. With Wastewater B (Methylene Blue, SWNOM), the normalized flux decrease using an UF membrane was 31.2%, as compared to a normalized flux decrease of 33.4% for an EO-EC-EF reactor set up. While the flux is indeed worse in the EO-EC-EF, it is unexpected that coagulation can be added in a membrane process and produce similar flux results to a standalone filtration process. With the combined anti-fouling properties of a conductive membrane and cross-flow reactor, flux was relatively unchanged when comparing an UF membrane process to a EO-EC-EF process. If the decolorization and COD removal is increased with EO-EC-EF, but the flux decrease is similar between UF and EO-EC-EF, this combined coagulation step could be reasonably implemented. It should be noted that the flux rating for every EO-EF set up was more efficient than the EO-EC-EF set up.

Across a few different trials, there was a common occurrence where flux suddenly decreased around the minute 200 mark after remaining relatively steady up until that point. The only parameters changing over time in this experiment are fouling and pH, both of which increase over time. Potentially, the membrane could be uniformly fouled after 200 minutes, making no pathway for the constituents to get through the membrane easy. Future laboratory testing would need to confirm the uniformity of fouling before and after the 200-minute mark to validate this theory.

Overall, there was an average 1.24 fold decrease in flux efficiency when utilising the EO-EC-EF reactor as compared to UF, from an average 25.3% flux decrease with EO-EC-EF to an average 20.5% flux decrease when using UF, while not considering the increased removal capacities of EO-EC-EF.

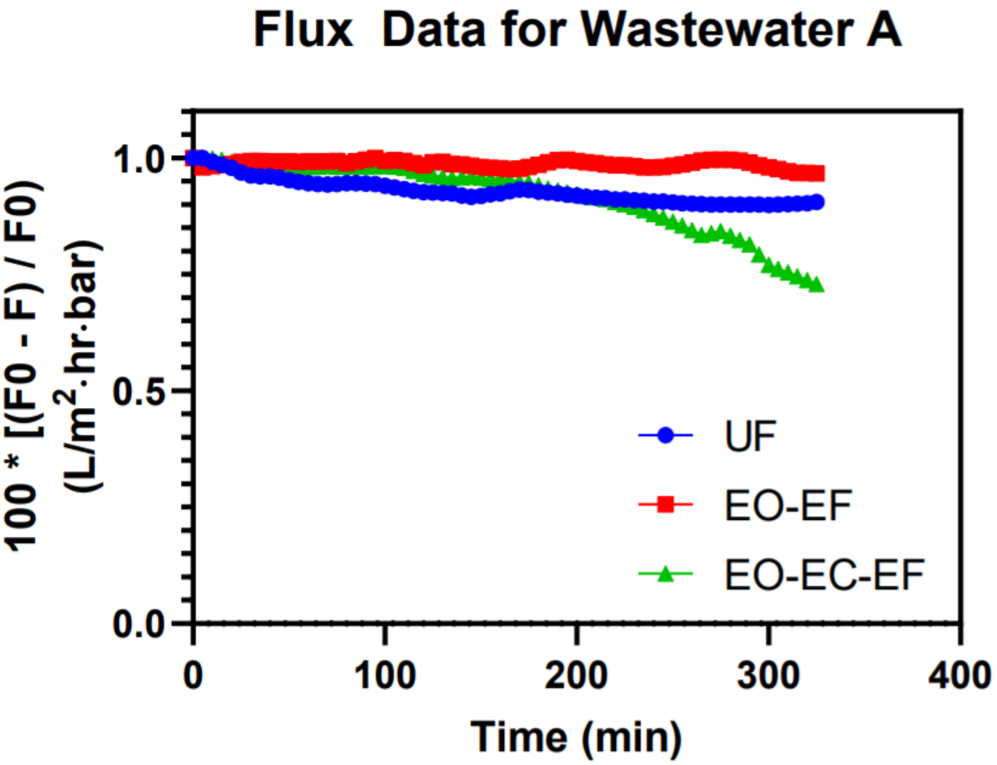

Figure 10 Normalized flux data measured for Wastewater A (Methylene Blue) for the UF, EO-EF, and EO-EC-EF reactor configurations

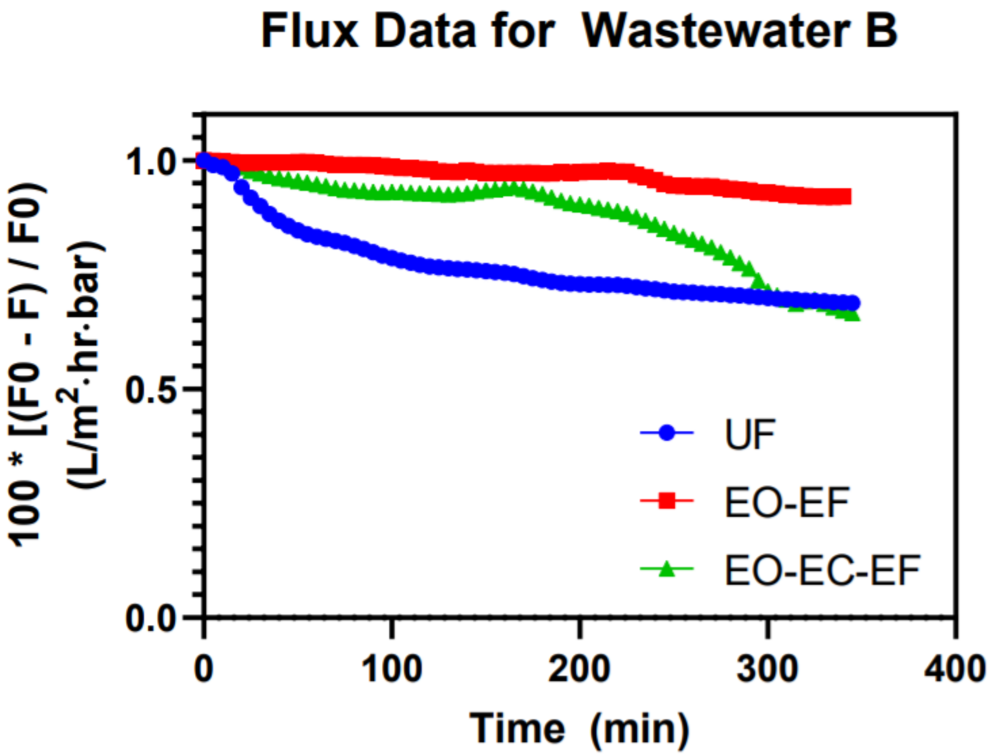

Figure 11 Normalized flux data measured for Wastewater B (Methylene Blue, SWNOM) for the UF, EO-EF, and EO-EC-EF Reactor Configuration.

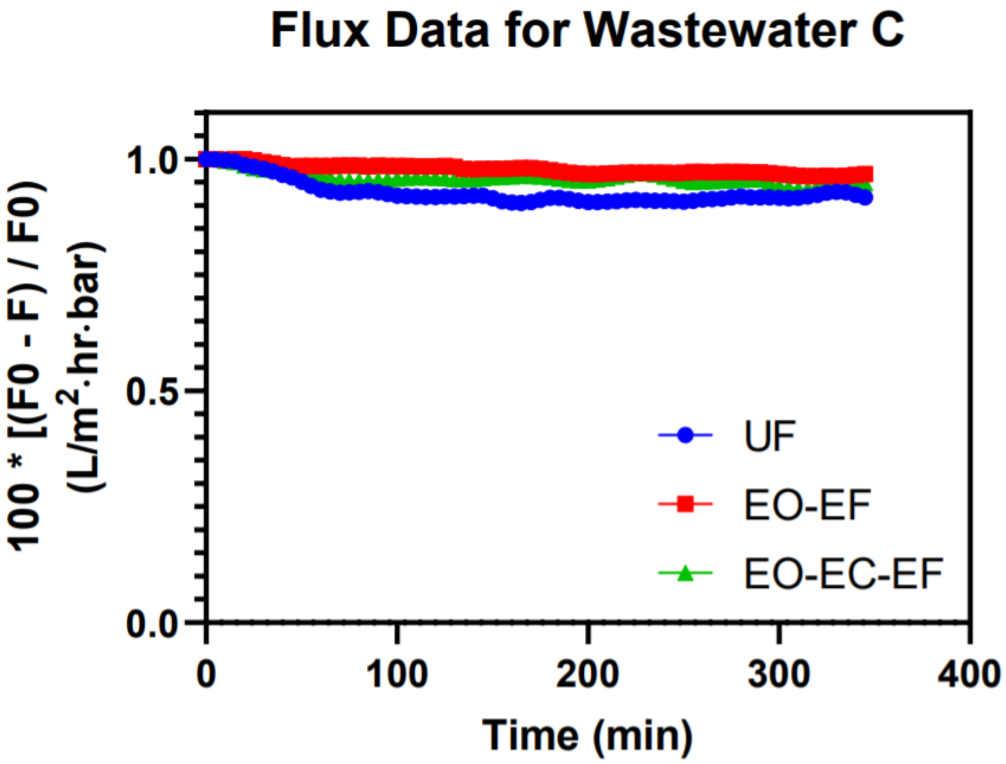

Figure 12 Normalized flux data measured for Wastewater C (Methylene Blue, Silica Nanospheres) for the UF, EO-EF, and EO-EC-EF reactor configurations

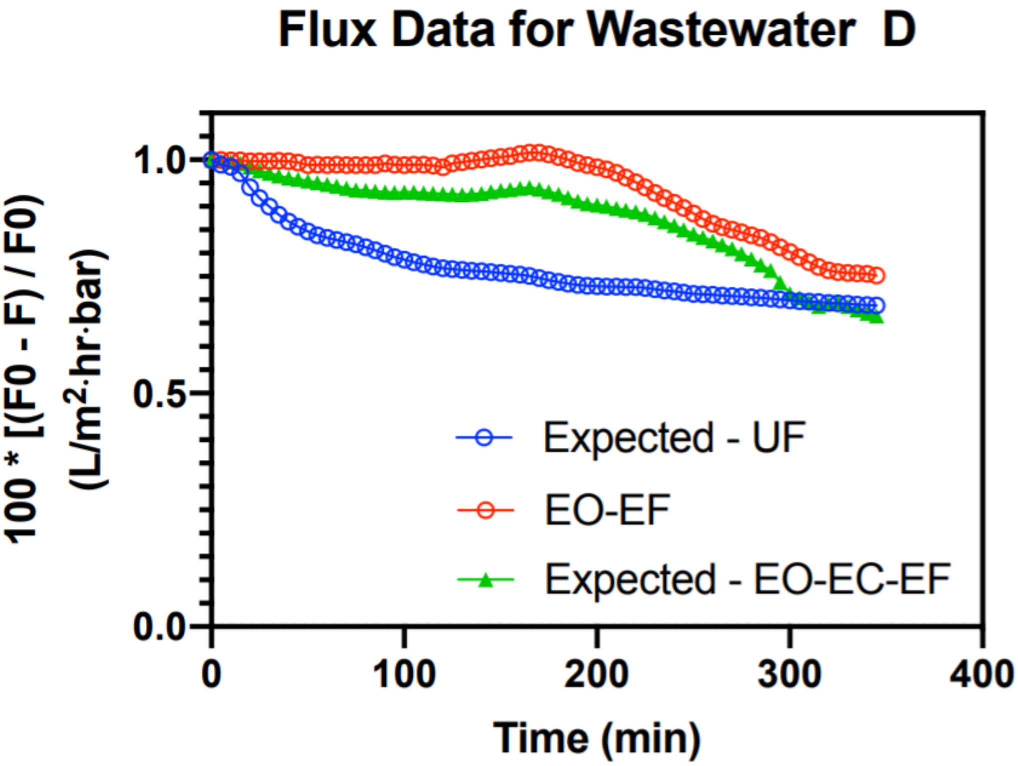

Figure 13 Normalized flux data measured for Wastewater D (Methylene Blue, Silica Nanospheres, SWNOM) for the UF, EO-EF, and EO-EC-EF reactor configurations. The flux values for the UF and EO-EC-EF reactor set ups for Wastewater D are extrapolated from their most similar trial, the UF and EO-EC-EF reactor set ups for Wastewater B (the only difference is the addition of Silica Nanospheres, which have shown to have little significance on flux values). This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University.

4.3 Methylene blue removal propensity with electrochemical techniques

Standalone and combined EAOPs have been successful in plainly removing dye materials from wastewater[12-25,41,59]. The expectation is therefore the ability to remove methylene blue for all the reactor set ups that have incorporated electrochemical techniques. The most straightforward method to investigate removal capacity is to measure the dye content in the influent wastewater and compare it to the dye content in the clean permeate water after treatment. The methylene blue removal capacity is shown in Figure 14 for each reactor design and for each wastewater. As noted in the previous section, the UV-Vis Diode Array System from Agilent is used to measure the ultra-violet and visible light spectrum to identify the purity of liquid samples. After determining the wavelength of methylene blue, the influent water was sampled hourly to confirm the methylene blue dye concentrations, which was then compared to the corresponding hourly effluent samples to validate removal capacity. The difference of concentration between each hourly influent and effluent samples is noted as the removal capabilities for the reactor.

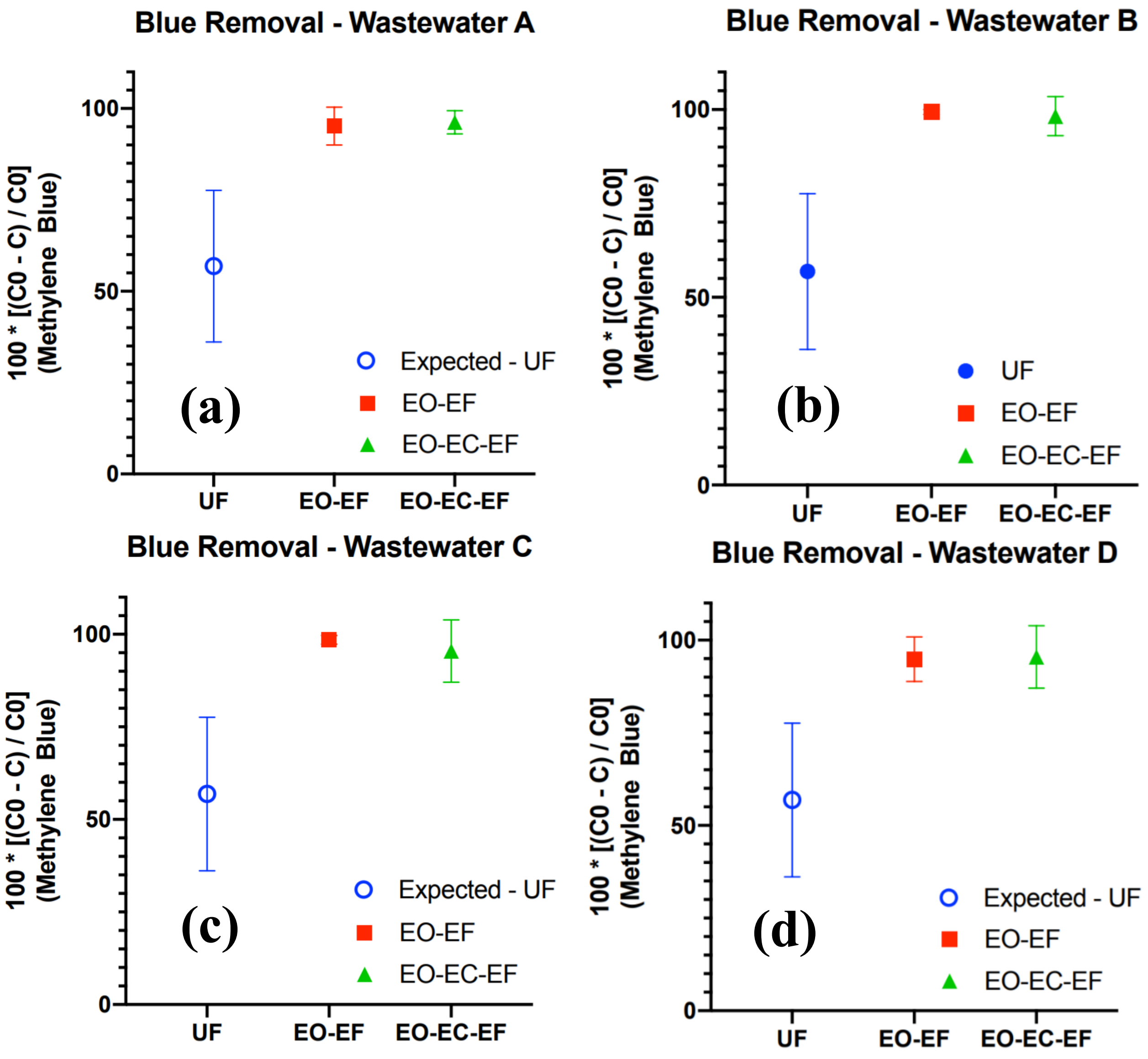

Figure 14 Normalized Methylene Blue removal capacity by each reactor configuration (UF, EO-EF, and EO-EC-EF) for Wastewater A (a), Wastewater B (b), Wastewater C (c), and Wastewater D (d). The blue removal for Wastewater A, Wastewater C, and Wastewater D are extrapolated from the Blue Removal – Wastewater B trial. This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia

Electrochemical wastewater treatment techniques plainly removed methylene blue for all tested wastewaters and with all the reactor configurations. A baseline methylene blue removal capacity was around 33%[c] after 6 hours when using only the membrane, whereas all reactor configuration incorporating electrochemical treatment had a removal capacity of at least 95% for methylene blue, with a maximum 100% removal found for each reactor set up as well, as shown in Figure 14. These results are expected as previously published research shows near complete to complete removal of dye materials in wastewater when using EAOPs[12-25,41,59]. This shows a very clear benefit for using electrochemical techniques for the removal of methylene blue dye.

At the end of six hours, the standalone UF reactor set up had a removal capacity of 33% for the final sample, which was more effective than expected for methylene blue removal as literature notes UF membranes at 20 kDa as inadequate for methylene blue removal[63]. Due to the (non-charged) conductive MWNT Buckypaper being paired on the surface of the UF membrane, a more effective removal capacity was demonstrated due to there being effectively two membranes. Membrane adsorption for the early portion of the trial may have contributed to the methylene blue removal as well, due to the high surface area, or surface roughness, of the Buckypaper[41]. It is expected that removal capacity of the Buckypaper and UF membrane for methylene blue would continue decreasing over time beyond the 6-hour threshold of this experiment.

There was an expectation that the introduction of different foulants may deter the methylene blue removal capacity for EO-EF and EO-EC-EF trials due to fouling, preferential oxidation, or a combination of both. However, EO seemingly oxidized the methylene blue at a steady rate without preference with the other foulants within the wastewater. Even with the introduction of SWNOM to methylene blue (wastewater C), methylene blue removal in the EO-EF reactor maintained a removal capacity of over 97%.

The additional flocs produced by EC also did not impose any complications in terms of blue removal capacity for the membrane, shown by very successful removal capacity trials which utilize EC. The average removal rate for the reactor configuration using EO-EF is 97.3%, as compared to an average removal rate of 96.8% for the reactor configuration using EO-EC-EF. However, even though EO-EC-EF is very effective at removing methylene blue, it is slightly less efficient than EO-EF processes while also exhibiting a much less impressive flux rate. In terms of flux and methylene blue removal, EO-EF is clearly more effective than EO-EC-EF.

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[c] The removal capacity of UF for all reactor set-ups was extrapolated from data from using a UF reactor set up with only Wastewater B. This is necessary due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University. Literature suggests an even lower removal capacity for methylene blue using more difficult wastewaters, such as Wastewater D, but for consistency sake, it will remain at 33% for all the Blue Removal capacity results.

4.3.1 Adsorption Propensity with the Buckypaper Membrane

Figure 14 shows the UF blue removal readings as an average reading to remain consistent with the EO-EF and EO-EC-EF trials, but the removal capacity decreased steadily over time. Figure 15 demonstrates the hourly removal capacity for a standalone UF membrane, based upon a UF Reactor set-up for Wastewater B. A second trial (only five hours) was completed to further clarify the methylene blue removal tendencies, which shows that over time, the UF membrane becomes less capable of removing methylene blue. This may indicate that the Buckypaper is continuously adsorbing the methylene blue over time onto its surface until it reaches a capacity where it is no longer able to adsorb additional methylene, called the equilibrium point[64]. At this point, the methylene blue is more freely able to pass through the membrane, shown through the decreasing removal capacity over time. The adsorption capabilities may be due to the rough surface of the Buckypaper, as the surface roughness increases the surface area of the membrane[64]. The higher the surface area, the more surface of the membrane that is susceptible to fouling and adsorption. As noted in Chapter 5, additional tests validating the adsorption capabilities of Buckypaper is required to confirm this theory.

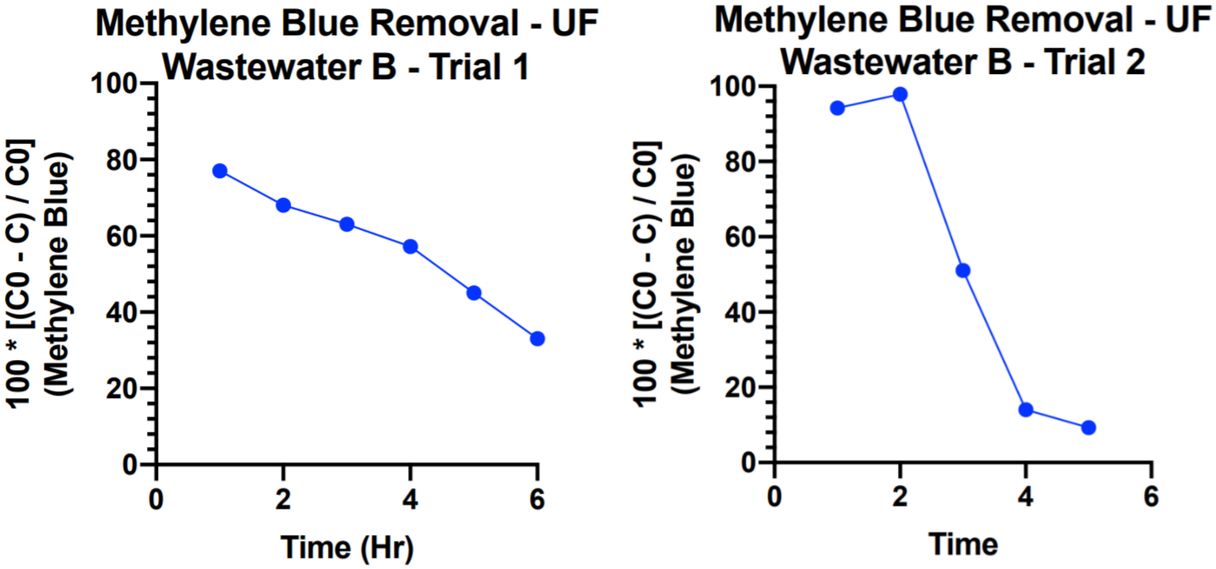

Figure 15 Methylene Blue Removal for a UF Reactor Set-Up using Wastewater B over Time

4.4 COD removal propensity with electrochemical processes

EAOPs have been recorded to have some ability in COD removal in the literature, ranging from <5% removal to a complete 100% removal[12-25]. The expectation of this reactor is to get close to complete COD removal when utilising both EAOPs with the filtration module. The process to measure COD removal is simple, where you measure the COD of the influent wastewater and compare it to the clean permeate COD. Unfortunately, lab closures prevented testing all variables. The normalized removal capacity for available data is shown in Figure 16.

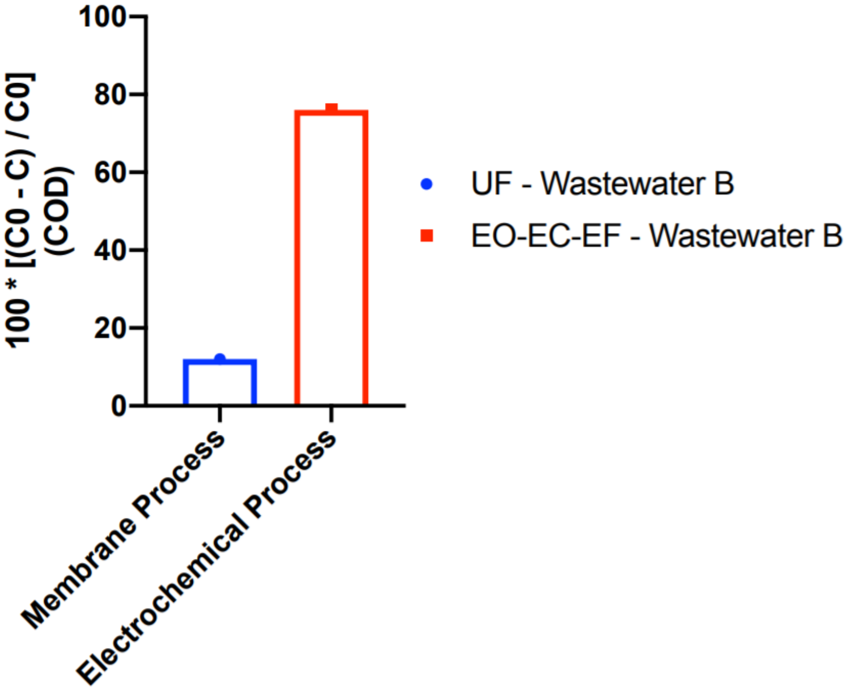

Figure 16 Normalized COD removal performance for a standalone membrane process compared to the COD removal capacity for an electrochemical process.

The removal capacity of electrochemical processes is much more effective than standalone membrane separation processes. The average removal rate of COD when using electrochemical processes was nearly 77%[d], whereas membrane processes removed nearly 12%[e]. The removal rate was measured as a comparison between influent and effluent COD concentration.

Electrochemical processes were able to readily oxidize organic material, which greatly improved removal capacity when compared membrane processes. It was expected to be more effective in terms of removal capacity but flocculated organic particles or organic matter may have been able to pass through the membrane prior to being fully oxidized. This is likely a disadvantage of a continuous process as opposed to batch or static processes, as there may be less contact time between electrodes and organic materials.

The membrane processes are simply outmatched, and the removal capacity numbers show this. Some literature demonstrates even worse removal capacities for COD using UF processes, including no removal at all[65].

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[d] Removal capacity number comes from an EO-EC-EF trial for Wastewater B as no other data regarding the removal capacity of COD from electrochemical processes is available. This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University.

[e] Removal capacity results come from a UF Trial for Wastewater B as no other data is available demonstrating the removal capacity of COD using only membrane processes. This is due to the COVID-19 Pandemic and its restrictions on lab access at Concordia University.

5. Conclusion and Future Perspectives

In this study, a reactor was designed and constructed to facilitate the novel combination of electro-oxidation, electro-coagulation, and electro-filtration. This newly designed reactor addressed the shortcomings of each electrochemical treatment method while creating a mobile, simple, and effective reactor demonstration anti-fouling and comprehensive removal capabilities. The anti-fouling capacity of electro-filtration was validated through flux measurements, while the purification capacity of the reactor was validated through the removal efficiencies of methylene blue and COD. This research could be used as a steppingstone to address the issue of low to trace concentration contaminations for municipalities, industries, and independent communities alike, while further substantiating electro-filtration as an anti-fouling technique.

To address different potential foulants on the filtration process, several constituents representing organic, inorganic, and aesthetic water pollution were added in low to trace concentrations to be tested by several reactor designs. Overall, this work investigates using standalone membrane processes and compares them electrochemical techniques. In terms of fouling effecting the flux, utilizing a conductive membrane improved performance from an average 20.51% normalized flux decrease using a standalone UF reactor, to an average 9.99% flux decrease using a combined EO-EF reactor. This increase in efficiency shows the anti-fouling properties of an induced charged on the membrane surface. Interestingly, even when adding EC (and the associated increase in larger solids) within the same reactor, similar flux results to membrane filtration was found. Overall, there was an average normalized flux decrease of 25.34% when incorporating coagulation to the reactor compared to an average normalized flux decrease of 20.51% using standalone UF reactor designs, which demonstrates a similar flux rating while also adding the benefits of coagulation to a membrane reactor.

In terms of removal capacity, incorporating electro-chemical techniques within the reactor demonstrated an average removal rate of around 97% for methylene blue, a nearly 65% increase compared the final 33% removal rate demonstrated by the standalone filtration membrane. These results correspond well with literature, showing similar complete dye removal capabilities[12-25]. Furthermore, the average COD removal when using electrochemical processes was 77% when compared to the 12% removal when using the standalone UF process, which demonstrates a solid removal performance when compared to published EAOP results showcasing removal capacities between <5% to 100%.

Clearly, the flux and removal capabilities are similar to other combined electrochemical treatment studies found in literature. However, the removal results from this research are more significant as they are obtained using a standalone reactor, which has much less of a footprint, follows a facile plug-and-play directive, and has an inherent modular design. With further validation steps, this standalone reactor can have applications in wastewater treatment is rural areas where the infrastructure for a large facility may not be practical, as well as a clarification step in current treatment facilities for trace contaminations.

While the novel electrochemical reactor demonstrated satisfactory results, this study encountered limitations during the experiments. Conductive membrane surfaces are very brittle and are prone to tear when not fully immersed in liquid. Furthermore, removal capacities for COD did not reach over 80%, which would have been preferred for absolute recommendation of this electrochemical processes.

This research was also ultimately cut short due to the COVID-19 pandemic and the corresponding lab closures at Concordia University. The following tasks were unable to be completed at the time of submission and may be addressed at a later or safer time;

- The UF and EO-EC-EF trials using Wastewater D.
- Complete the remaining COD sampling for further validation.
- SEM imaging on all membranes used in trials to validate the fouling portfolios.
- Compare the removal efficiencies of COD for each reactor design in terms of energy consumption per volume of removal.

Based on the completed work, the following recommendations can be made for future studies;

- Comprehensive measurements for the concentrations of •OH radicals, coagulant addition, pH levels, and the toxicity of potential intermediate products of the pollutants and electro-chemical processes.
- Investigations of influential wastewater parameters, such as temperature, pressure, pH, and concentration of select constituents on the results.
- Quantify methylene blue adsorption of the Buckypaper over time to determine its contribution in the removal of methylene blue of the UF process.
- Investigate the zeta potential to describe the reactions between membranes, electric fields, and different constituents used.
- Determine oxidation potential of the Buckypaper material, and compare the production of hydroxyl radicals to oxygen over different applied voltages.
- Measure the UV-Vis spectrum of the other constituents present in the wastewater to verify they do not interfere with the methylene blue wavelengths.
- Pilot-scale experiments should be completed to confirm the scalability of the reactor.
- Application of this reactor on real wastewaters from different sources to measure the effectiveness.
- Improvements on the robustness of the conductive membrane to improve rigidity and performance.
- Energy consumption portfolio of each reactor set up, and their comparison to traditional wastewater treatments.

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7 Appendix

This chapter consists of laboratory photos to introduce a visual for different parts of the research, including the entire system set up, several sample photos, and the conductive membrane surface.

Figure 17 Aerial view of the entire set up. Visual in this photo is the connection to the reactor with all precision flow meters, pressure meter, and flowmeter. The clean effluent comes through the top of the reactor.

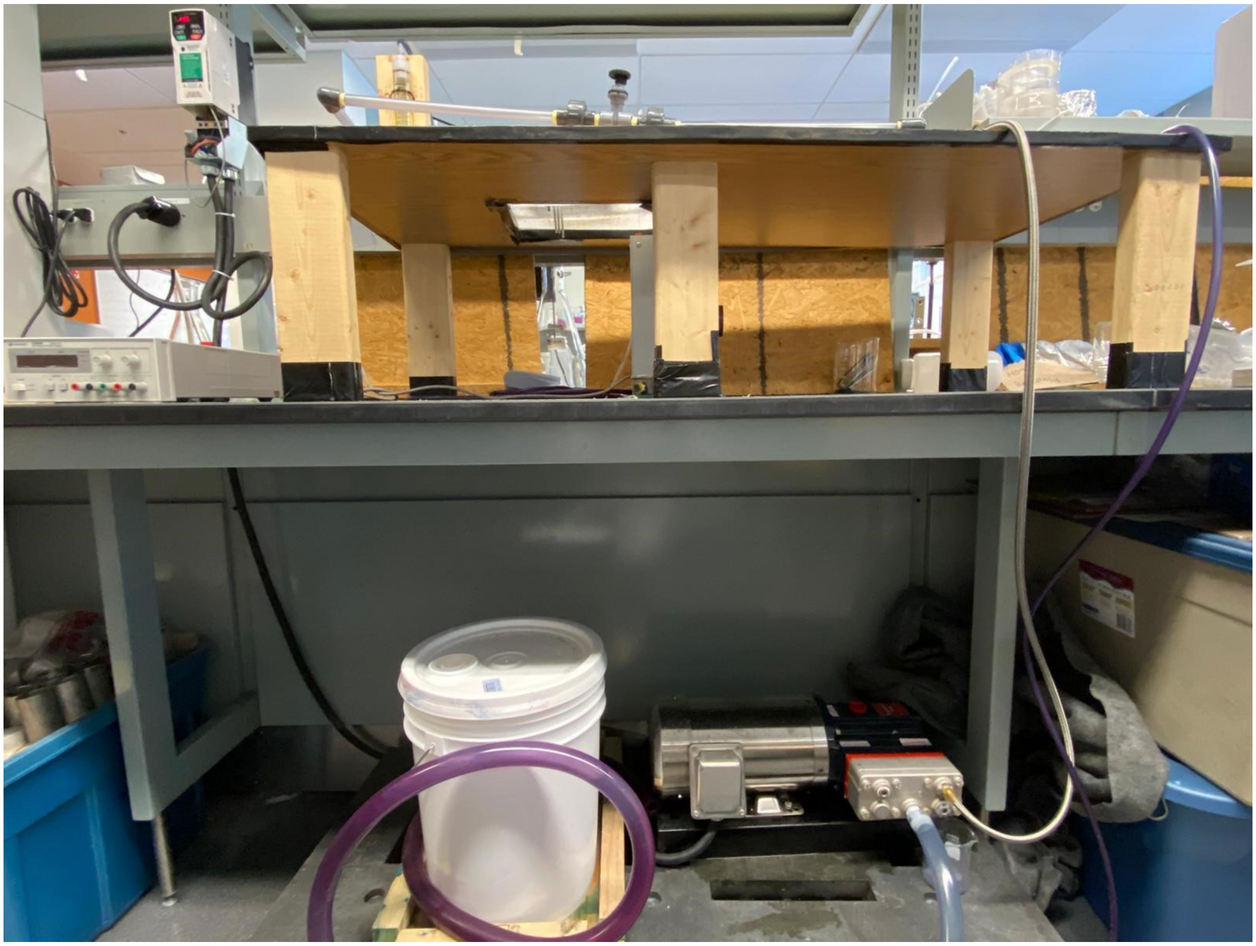

Figure 18 Horizontal view of the entire system. The pump placed on the floor produces the pressure requirements for the entire system. The three metal rods protruding from the elevated surface are the conductive connections from the voltmeter to the reactor.

Figure 19 Collection of wastewater samples at 1-hour intervals for one trial, showing consistent colour throughout

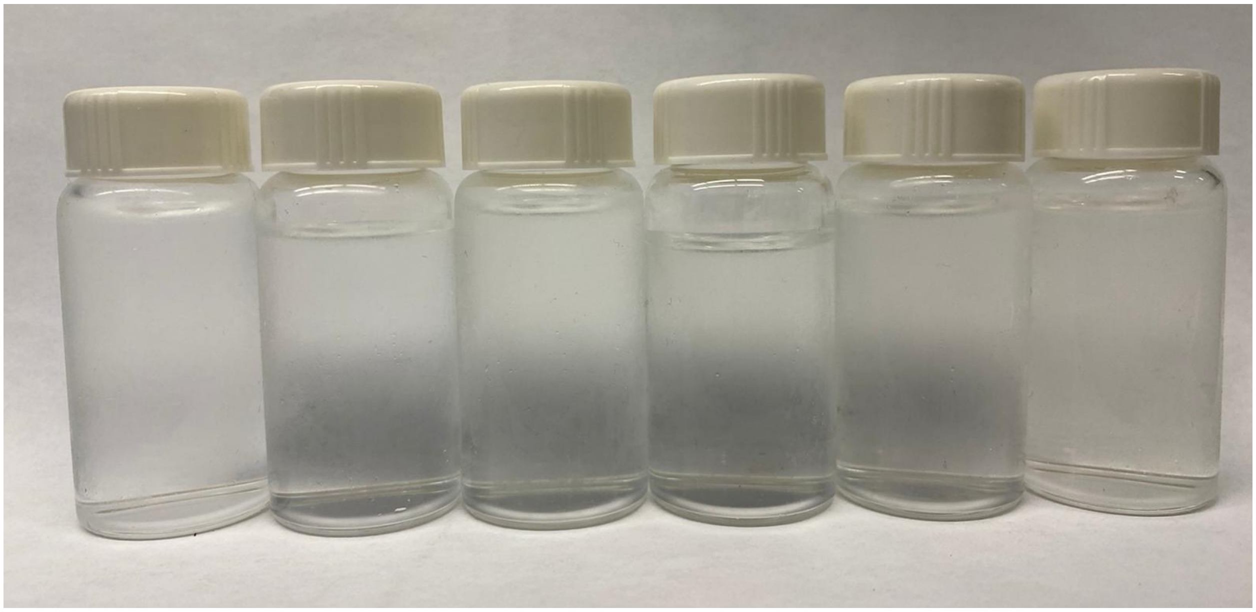

Figure 20 Collection of clean permeate samples collected at 1-hour intervals, showcasing the effluents removal capacity for aesthetic pollution

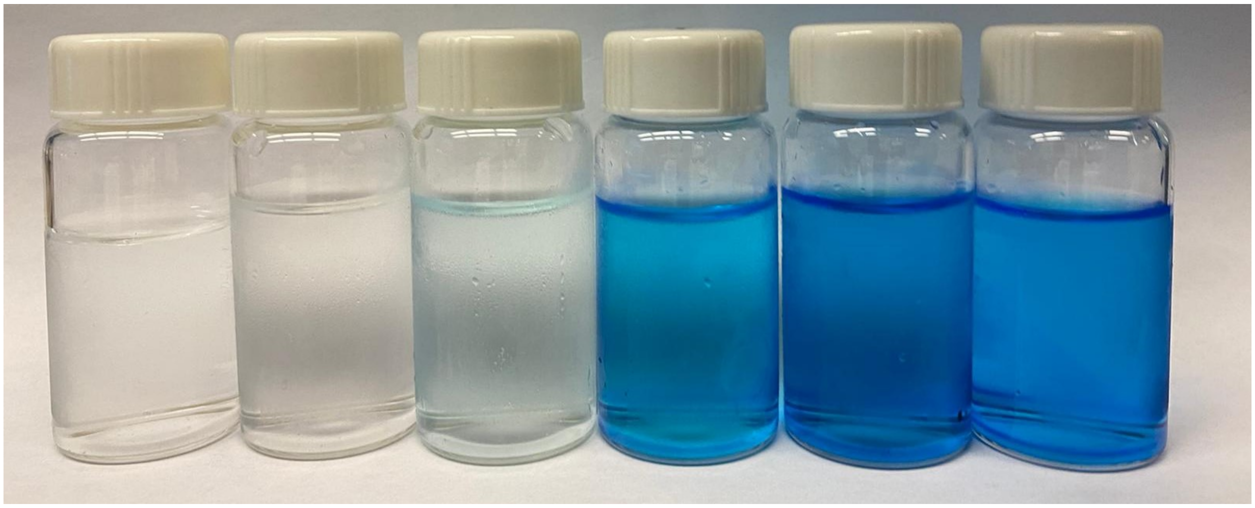

Figure 21 Blue removal capacity of UF Membranes shown through methylene blue aesthetic pollution

Figure 22 Photo of the conductive membrane surface. Note the markings left by the compressed seal around the outer edges of the membrane surface, indicating no water losses. This MWNT Carbon Buckypaper was backed by the Ultrafiltration membrane. This conductive surface came in direct contact with the wastewater and acted as the anode in electrochemical processes