Active Anti-fouling and Defouling of Membranes using Electrochemical Methods

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Abstract

Industrial wastewater treatment from cattle slaughterhouses traditionally use dissolved air floatation (DAF) to remove the high organic content of fat, oil and grease (FOG) from wastewaters and recover them for producing other products, including tallow, gelatine and food additives. Dissolved air floatation presents several operating difficulties including the large size, high energy use and odour issues resulting in increased operation costs and decreased efficiency. Replacing a DAF unit with microfiltration or ultrafiltration membranes to recover FOG and protein could reduce operating costs and space, increase product quality through fractionation of various valuable nutrients and reduce or eliminate the smell. However, membranes have rarely been considered for such applications due to the high fouling propensity of the feed and the inability of conventional methods and membranes to effectively deal with this. One relatively unexplored fouling mitigation/cleaning technique involves electrochemistry to either prevent fouling through charge repulsion or remove fouling via electrochemical reactions. The key target of this work therefore is to investigate the suitability of conductive stainless steel membranes for filtration of a FOG / protein stream utilising electrochemical cleaning methods.

In theory, in-situ membrane antifouling (the inhibition of fouling) and defouling (the removal of fouling) can be achieved by varying the applied potential on an electrochemically active and conductive membrane. Oils and organic matter tend to carry a negative charge in aqueous solutions at neutral pH and increase in negative charge density with alkali pH. For antifouling, maintaining a negative charge on a membrane surface repulses negatively charged molecules in solution, which in turn, both inhibits adsorption and/or induces them to migrate away from the electrode/membrane surface. The major finding here was that reductive potentials, at or below the hydrogen evolution reaction were successful in minimising fouling on an electrode and also succeeded in mitigating fouling by 67% in a full membrane setup. There is an ideal operating window for negative potential to achieve antifouling, enough to induce repulsion but not negative enough to initiate redox reactions at the membrane surface between -0.4 V to -1.2 V. However, to achieve the best performance antifouling probably requires constant operation at potentials negative enough to initiate the hydrogen evolution reaction or reductive desorption. The commercial implications of this are likely to be power requirements, on the order of 10W/m². Or to put it another way, this translates to an energy requirement of 1 kWh/kL of permeate flux through the membrane, which for treating a stick water stream in typical abattoir.

Defouling by contrast uses electrochemical reactions to either oxidise the organic foulants or produce gas bubbles which can lift off foulants through physical shear forces. The major finding
here is that, when operated as anodic electrodes, membranes which have oxidative potentials applied, demonstrate some defouling. However, there is also polymerisation of organics into a gel layer which frequently remains attached to the membrane as well as some bulk polymerization. Further there is corrosion of the membrane surface. For reductive potential, there is an ideal operating window to achieve defouling, enough to produce hydrogen bubbles to remove fouling but not enough to initiate extensive base catalysed polymerization reactions in the bulk between -2 V to -3 V. For the full membrane setup the mitigation of fouling was not as successful as antifouling and resulted in mitigating fouling by only 3%. The membrane fouled very quickly and was unable to recover its performance effectively using electrochemical means. This suggests that long-term antifouling is a more suitable choice for effective fouling mitigation in abattoir waste water streams.

This is the first known application of reactive electrochemical membranes to abattoir wastewater treatment. The ultimate aim here would be to clean the membrane without damaging the recovered products, without requiring cost inhibitive chemicals, whilst simultaneously reducing, and possibly eliminating, back washing time. Future areas of research include continuous operation under both anti-fouling and defouling protocols to see the long term impacts on both the membrane and fats, oils and proteins. It is anticipated that this study can be a worthwhile entry point for more sophisticated electrochemical engineering membrane fouling mitigation studies.
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Significant contributors included Dr Simon Smart and Dr Eric McFarland for the conception and design of the project; analysis and interpretation of research data; critically revising and editing the work in an advisory capacity. Significant contributors included Rongzhi Chen for non-routine technical work.

Statement of parts of the thesis submitted to qualify for the award of another degree

None
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List of Abbreviations

FOG: fat, oil, grease
DAF: dissolved air floatation
HER: hydrogen evolution reaction
OER: oxygen evolution reaction
EMF: electromotive force
BSA: bovine serum albumin
LMH: unit L/m²/h
SEM: scanning electron microscopy
SHE: standard hydrogen electrode
CV: cyclic voltammogram
UV-Vis: ultra violet – visual
HOMO: highest occupied molecular orbital
LUMO: lowest unoccupied molecular orbital
E: electrochemical potential, measured in volts
V: volts
A: Amps
1 Introduction

1.1 Background

Cattle slaughterhouses generate large volumes of organic rich wastewater, including high concentrations of proteins and fat, oil and grease (FOG). These wastewater by-products are useful for creating other products, including tallow, gelatine and food additives. Currently, most abattoirs recover their FOG using dissolved air floatation (DAF) in large vats and then treat the remaining organics with anaerobic digestion, in either anaerobic lagoons or anaerobic membrane bioreactors. Dissolved air floatation presents several operating difficulties including the large size, high energy use to produce bubbles, and skimming of the FOG, which creates a smell that is difficult to control. The layer of floating FOG that caps the DAF tank keeps the heat inside. Regulating the temperature of the DAF is important to maintain operation as it impacts on both the nature of the fat emulsion and the solubility of air. The melting point of fats vary from subcutaneous (29 °C) to intestinal and tallow (46 °C). The melting point of the fats changes the FOG particle size. Poor air solubility makes DAF units ineffective above 40 °C. The uncontrolled temperature of the wastewater entering the DAF is between 35-45 °C, but can be lowered by cooling in a holding tank, however this increases the DAF footprint. In fact, recently Australian abattoirs faced with rising water costs and uncertain water supply have stopped cooling the influent, to the detriment of DAF operation. A lack of dissolved air and reduced FOG particle size means DAF recoveries have been reduced, leading to a high FOG in the effluent, which in turn inhibits the anaerobic digestion.

The idea here is to test the use of membranes to replace either replace the DAF or reduce the content of FOG and protein entering the DAF by filtering the stick water stream from the tallow rendering plant. The stick water stream has perhaps the highest concentration of FOG and proteins across an abattoir waste water facility. The use of membranes might allow greater recovery of organics, for use as tallow, however fouling can add significant cost to the operation and as yet their use has been limited. Electrochemical membranes have been used successfully in wastewater purification where the concentration of organics is low and initial fouling has been reduced during continuous operation only, however high concentrations of organics have not been within the scope of that work. Electrochemical techniques have been successfully used in industry to purify, separate and recover food industry products including proteins, colloids, and some oil emulsions. The application of these techniques to abattoir wastewaters is expected to produce a body of knowledge useful for the cost effective active defouling and antifouling of membranes in high concentration organics recovery.
1.2 Problem Summary
The complex nature of abattoir wastewater limits the use of membrane separation due to high rates of fouling by colloids such as proteins, FOG, starches/sugars and cellulose. Previous attempts at using microfiltration and ultrafiltration membranes were hampered by severe cake fouling. Further this could not be minimized by the traditional practices of increasing membrane porosity, reducing transmembrane pressure or increasing cross flow velocity. Product recovery, purification, operating down-time and operating cost are all negatively affected by the use of cleaning agents and/or chemicals.

Electrochemistry offers a new set of parameters and techniques to control or eliminate fouling. For example, we can place a charge on the membrane surface and repel the charged foulants, minimizing cake formation. We have termed this approach active antifouling and it bears similar characteristics to electrofiltration which has been successful in the dairy industry for protein separation, but not in abattoir wastewaters. Successful application of active antifouling to the separation of proteins and fats in abattoir wastewater would allow for the replacement of DAF, as well as provide a versatile technology for the removal of nutrients before anaerobic digestion.

The second approach is to use electrochemistry to remove existing fouling either through direct oxidation of fouling on the membrane surface, formation of oxidising species at the membrane surface or formation of nanobubbles which remove fouling through shear forces. We have termed this approach defouling. Successful application of electrochemical defouling could be applied at much shorter time scales to conventional chemical cleaning of membranes and could potentially improve membrane performance and reduce demand for cleaning chemicals.

1.3 Objective
The objective of this work is to demonstrate anti-fouling and defouling of membranes for use in the food processing industry, specifically for abattoir wastewater purification and product recovery. The use of stainless steel membranes were chosen for their low material cost, relative durability and electrical conductivity. The primary research questions are:

1. What are the physical and electrochemical mechanisms associated with antifouling and defouling?
2. How effective is antifouling at maintaining membrane flux with a high organic content feed water?
3. How effective is defouling at restoring membrane flux on a heavily fouled membrane?
1.4 Contribution to the field of knowledge
The first major finding of the thesis is that antifouling at or below the hydrogen evolution reaction were successful in minimising fouling on an electrode and also succeeded in mitigating fouling by 67% in a full membrane setup. There is an ideal operating window for negative potential to achieve antifouling, enough to induce repulsion but not negative enough to initiate redox reactions at the membrane surface between -0.4 V to -1.2 V. However, to achieve the best performance antifouling probably requires constant operation at potentials negative enough to initiate the hydrogen evolution reaction or reductive desorption.

The second major finding of the thesis is that electrochemical defouling is not an effective technique for recovering membrane flux. When operated anodically there is some defouling but predominately polymerisation of organics into a gel layer which frequently remains attached to the membrane, further there is significant corrosion of the membrane surface. Operated cathodically there is a theoretical window to achieve defouling through reductive desorption and hydrogen evolution but practically this is not sufficient to defoul a membrane in situ.

The main contribution of this work is to the field of resource recovery and membrane separations by demonstrating a new technology (antifouling) for the operational cleaning of membranes in-situ, thereby expanding the range of operating life time and materials that can be successfully and continuously separated with membranes.

1.5 Structure of thesis
This thesis provides a comprehensive literature review on membrane separations and electrochemical separations in the food processing industry and wastewater treatment industry in Chapter 2. This is followed by the electrochemical and membrane testing methods in Chapter 3. Chapter 4 details the fundamental demonstration of antifouling for both membranes as electrodes and the full membrane setup. Chapter 5 demonstrates of the physical removal of the abattoir organics (i.e. defouling) from the membrane electrode surface and proposed mechanisms. Chapter 6 summarises the conclusions of the thesis and makes several recommendations.
2 Literature Review

2.1 Introduction
This chapter provides a summary of existing literature on organic fouling of membranes and electrochemical defouling techniques. The basics of membrane operation including the various membrane types and their application in food related industries is covered in Section 2.2. An overview of membrane fouling is covered in Section 2.3 which is followed by the current state of the art in defouling (Section 2.4), and anti-fouling (Section 2.5). The literature review finishes by summarising the current understanding and challenges in electrochemical membranes in Section 2.7.

2.2 Membrane fundamentals for wastewater treatment in food industries
A membrane is a semi-permeable barrier that separates fluids and entrained solids based on molecular size, physicochemical properties and specific interactions between the membrane and the feed [1]. The process advantages of membranes over several traditional separation technologies are that they operate without a phase change (reducing energy demand), have no moving parts (reducing complexity) and do not require complex process modelling or control schemes [2]. Membranes can be polymeric, ceramic, metallic or combinations of these. Polymeric membranes are commonly used in industry due to cost, where they dominate the desalination and water treatment sectors, and have applications in natural gas processing and the food industry [3, 4]. Ceramic and metallic membranes are more costly and have found application in niche markets where polymeric membranes are unsuitable such as the food industry [5], where the high fouling, extreme cleaning and sterilization regimes, and elevated operating temperatures are necessary [4-8]. Membranes offer concentration and separation ability with the advantage of increasing product quality by maintaining the nutrition and flavour of the product, while reducing contamination and spoilage risk. Traditional food industry concentration and separation processes are thermal concentration (boiling down), dissolved air floatation (slaughterhouse/abattoir industry), decantation, filtration, and centrifugation. Membranes are more economical than traditional high energy processes and flexible in the range of applications within the process train [5, 9]. Specific examples of membrane application in the food industry include [10]:

- Fruit juice beverage industry for pulp removal from fruit juice and as a non-thermal means of concentrating the desired product [11, 12].
- Beer and wine industry for clarification at low temperature to preserve flavour [13, 14].
- Dairy industry for milk fractionation, whey processing, cheese production, cold pasteurization and the reuse of process wastewater [15, 16].
• Fish and poultry industry for protein recovery, the concentration of specific molecular weight peptides to increase bioactivity and processing of wastewater [17]. Gelatine (protein) purification by UF, as opposed to ion-exchange columns, is particularly important for cost savings [18, 19].

• Slaughterhouse/abattoir industry for byproduct fat, oil, grease (FOG) and protein recovery by UF and RO, which while successful (≥90%) required intense chemical cleaning [20-22].

The fundamental property of a membrane is its ability to selectively allow the permeation of certain species and membrane performance is principally characterised by flux and selectivity. Net flux is achieved if the driving force is greatest from the feed to the permeate side and typical driving forces used for membrane separation include pressure and concentration gradients [23]. Membranes are classified by pore size selectivity for particle range, with the most commonly used membrane types in the food industry being: Microfiltration (MF) where particle cut off ranges from 10-1.0 µm, and ultrafiltration (UF) where particle size cut offs range from 0.1µm–5nm. More recently nanofiltration (NF) membranes with pore sizes <5nm have found application in processing feed streams with low total dissolved solids where they are effective at polyvalent cation removal and partial rejection of solvated ions based on size. In the case of MF and UF membranes, pressure is used to force liquids (water) and some dissolved solids to overcome concentration gradients and move from the feed to the permeate side, concentrating the feed side. The last commercially important category for the food industry includes reverse osmosis (RO) and forward osmosis (FO) membranes, where only water molecules are able to pass. Membrane performance is optimized for the feed type as membranes with smaller pores have greater selectivity but lower fluxes and vice-versa for membranes with larger pores. [24]

A membrane operation unit includes the membrane, housed in a module, in connection with pumps, valves and control systems. Membrane operations are typically designed for constant flux to improve downstream operability, and flux is controlled through pressure variation. As the membrane fouls and ages the flux decreases and the pressure must be raised to maintain flux. As the primary operating cost associated with membrane separation is pumping energy, membrane fouling represents the greatest challenge to all membrane technologies. Strategies designed to control membrane fouling, such as reducing the transmembrane flux or backwashing, inherently reduce the productivity of the membrane unit operation. More aggressive cleaning techniques such as chemical cleaning frequently reduce membrane lifetime and represent additional costs to the process. [25]

Membrane modules currently come in four types: tubular, spiral wound, plate and frame, and hollow fibre. The primary advantage of tubular membranes is their tolerance of very high suspended solids and fibres and their ability to operate with high turbulence cross-flow velocity to
minimize possible oil wetting of the membrane [5, 26], otherwise spiral wound membranes (hydrophilic polymer) can be more cost effective for clean, stable oil emulsions [5]. This makes them ideal for abattoir wastewater processing, where an array of suspended solids including proteins, fats, flies, and animal hairs must be separated from the liquids. The main drawback is that they have a small surface area to volume ratio thereby taking up more space and being more expensive than other designs. Spiral wound membranes are more commonly used in industry based on sales than tubular membranes [27]. Hollow fibres represent a compromise between the solids handling capabilities of tubular membranes and the high surface area to volume ratio of spiral wound membranes. They are frequently used in UF applications. The ability to easily dismantle and reassemble plate and frame membranes has ensured they have found application in high fouling processes like the food industry where sterilization of the equipment is a requirement. Polymeric membranes have achieved commercial success for oily wastewaters with 97% of the UF/MF installations over inorganic membranes; however, they suffer from fouling and degradation with use, especially with natural fats and oils, and are ideal for clean emulsified and synthetic oil recovery at low temperature (<cloud point of membrane) [5]. Oilfield and fracking wastewater, with low total dissolved solids, prefer ceramic MF, UF and NF membranes due to higher tolerance to temperature, high oil content, foulants and cleaning agents [8, 28-32], similar to food oils [33, 34]. Tubular membranes are the best choice for slaughterhouse wastewater, where effluents have very high suspended solids and they provide ease of cleaning [5]. Additionally, metal and ceramic tubular membranes can be sterilized by high temperatures, a necessity in slaughterhouses.

2.3 Membrane Fouling

Fouling is the formation of a material layer on the surface of the membrane that creates resistance to permeate flux and feed flow. The formation of the fouling layer can be by attachment, accumulation or adsorption of materials on the surface and/or within the pores [35]. Fouling is a complex process that is highly dependent on both the operation of the membrane unit and the characteristics of the feed waters. Factors that contribute to fouling include (but are not limited to): surface chemistry, surface roughness, surface hydrophobicity/hydrophilicity, hydrodynamic conditions and the solute concentration, ionic strength and zeta potential [36]. Initial fouling research focused on the mechanisms of fouling and the best processes and chemicals to defoul (clean) membranes. It has progressed to operational considerations such as hydrodynamic optimization to avoid fouling (antifouling), and most recently onto membrane modifications such as altering the surface hydrophilicity/hydrophobicity to avoid irreversible fouling.

Measuring fouling is difficult and has generated a substantial amount of literature. Fouling measurement is most frequently done indirectly through monitoring flux decline and
transmembrane pressure increase, although more recently ultrasound and impedance measurements have been used to measure cake thickness. Direct fouling observation is avoided as a frequent technique, being reserved for membrane autopsy as it requires microscope, microprobe and atomic force analysis of the membrane after it has failed. [37]

Different processes and feed waters foul in different ways [38] and hence require different strategies to overcome [36]. The main types of fouling mechanisms are listed below [10] and illustrated schematically in Figure 1:

- Adsorption of solute on the membrane surface around and in the membrane pores (ex. proteins) causing pore size reduction and blockage (Figure 1, a, b).
- Adsorption of solute on the membrane surface for cake fouling, which is where inorganic & organic colloids form an initial deposition layer over open pores. These layers build up over time to completely close off the pores. Cake formation does not include crosslinking of the deposited materials, meaning cake fouling is often reversible. The compressibility of the cake is of particular interest as highly compressible cakes can densify rather than increase their flux when the transmembrane pressure is increased. Sand is designated as the ideal, incompressible cake whereas cakes formed from fats and proteins are highly compressible. The intermolecular forces and hydrodynamics affect the fouling rate before a cake is compacted. After the cake is compacted, the different foulants have similar flux decline rates [39] (Figure 1, c).
- Biofouling is the formation of a complete, dense biofilm, which is initiated by the adsorption of extracellular polymeric substances (EPS) to the membrane surface, thereby forming an attractive attachment site for bacteria or other cells. These biofilms can cover the entire membrane surface and reduce flux to zero. The difference between cake formation and biofilm formation is the absence of cells, whose crosslinking ability often makes biofilm fouling irreversible.
- Aggregate fouling appears to be a result of a high concentration of particles (proteins) above the pore mouth due to convective flow resulting in protein precipitation. This reduces flux according to the Hagen-Poiseuille equation and demonstrates that the deposition of a small amount (mono-layers) of protein reduces the pore radius which in turn dramatically reduces flux (as flux \( \alpha \) radius\(^4\)). Therefore the start-up of membrane based protein separation should be done at low initial flux [40] (Figure 1, d).
- Concentration polarization (CP), which is more of a transport phenomenon than typical fouling. CP occurs when the flux across the membrane is significantly greater than the cross-flow velocity and a large boundary layer builds up at the membrane surface. It is not
fouling in the truest sense but gradual changes to the polarized layer can lead to gel formation or cake consolidation [36] (Figure 1, e).

![Diagram of various pore fouling mechanisms]

**Figure 1: Schematic of various pore fouling mechanisms. Adapted from [10]**

Different types of membranes are prone to different types of fouling [41]. MF membranes foul primarily by pore blocking with colloids and macromolecules [42], whereas UF [43] and NF [44] membranes foul primarily by cake/gel layer formation. Hydrophilic membranes are preferred to hydrophobic to avoid protein and most other organic fouling [5, 10], as the membrane attracts water instead of organics. A limited number of organics can prefer hydrophobic membranes [45]. Regardless, once the initial fouling layer forms the membrane type matters little as the foulants interact with each other (physico-chemical interactions) and fouling continues according to foulant type and operating conditions.

Likewise different types of foulants are prone to different types of fouling [46]. Fat and protein fouling are similarly prone to pore blockage (different from pore fouling) and cake/gel formation [35, 47]. Protein fouling occurs by three mechanisms: (1) Concentration polarization, where macromolecules being filtered accumulated at the surface, followed by gel formation, (2) Adsorption of proteins on the surface and in the pores (cake formation) and (3) Protein aggregate formation, followed by deposition and pore blocking [36]. Poultry rendering plants, which have high fat, oil, grease (FOG) and protein content, have recently explored the use of UF membranes instead of dissolved air floatation (DAF) [48]. The initial fouling mechanism was particle deposition (not adsorption) and internal and intermediate pore blocking followed by cake formation. Once a cake layer was formed, additional layers formed at the same rate regardless of the membrane type, meaning that the membrane type they chose only mattered for initial cake layer formation. The cake formed was highly compressible, although this was reversible if the transmembrane flux/pressure was reduced. Their conclusion was that increasing pore density would
not enhance flux, instead fouling should be controlled through process operation which was best at just below the threshold flux of 15 L/m²/d, with no more than 5 bar transmembrane pressure.

In a study of the adsorption of proteins to terminal functional groups [49], proteins initial adsorption kinetics were fastest on –COOH > -CH₃ > -OPh > –NH₂ > -OH > -CONH₂ and was controlled by hydrogen bond formation and electrostatic attraction. The presence of Ca²⁺ caused BSA adsorption to change depending on the surface functional group. Proteins packed tighter, initially fouled quicker, and enhanced the fouling of polysaccharides for all surface functional groups. They suggest surface chemistry is more important than bulk properties, such as zeta potential and non-specific electrostatic repulsions, in adsorption and irreversible (protein) fouling. [49]

2.4 Membrane Defouling
Membrane defouling, cleaning, can be done by physical (hydrodynamic) or chemical methods to remove reversible and irreversible fouling, respectively. Chemical defouling can damage membranes, especially polymeric ones, so minimal cleaning is preferred. Physical defouling by rubbing or scraping off the fouling layer is avoided generally because it can force the foulants deeper into the membrane’s pores. Physical defouling methods remove reversible fouling and are highly effective and commonly used, including bubble cleaning and backwashing. Once irreversible fouling has caused the maximum operating transmembrane pressure or the minimum flux/flow to be reached, then chemical membrane cleaning is required to return to the initial flux operation.

Chemical cleaning is the standard method for both in-situ Cleaning-In-Place (CIP) and ex-situ cleaning, which is less common. CIP is usually performed by flushing (often sequentially) industrial cleaning solutions of bases, acids, disinfectants, surfactants and enzymes past the membrane surface. Acids, bases, surfactants and disinfectants hydrolyse and solubilise organic fouling, reducing adhesion and killing active biofilms. Adhesion reduction is most effective when the chemical can access the base of the fouling layer, otherwise the chemical is effective only on the top layers resulting in excessive use. Surfactants make micelles from organics, allowing them to be washed away [50]. Enzymes lyse the organics and are the gentlest on membranes, however the most expensive. Milk proteins removal has been optimized for inorganic membranes (zirconium oxide) [51], without lysing them into detectable peptides and avoiding enzyme deposition onto the membrane [52].

Cleaning solution effectiveness is dependent upon the foulant, the membrane type, the feed pH, concentration, temperature (reaction rates, mass transfer rates and solubility), hydrodynamic conditions, cleaning frequency and residence time [25, 50]. Slaughterhouse wastewater requires the fats recovered be used in food grade products. Therefore, high doses of acids, bases and surfactants (including chlorine) are not the best choice because they will make the fats unusable (spoil) before
they detach the fouling layer resulting in a polluted wastewater that is difficult to deal with. Enzymes do not justify their cost. Hence, there is no satisfactory chemical for cleaning membranes used for slaughterhouse wastewater. Electrochemical defouling can target adhesion reduction at the base of the fouling layer without spoiling (degrading) the remaining fat layers allowing them to be recovered and the resulting wastewater will not be further polluted. Electrochemical defouling targets only the adsorbed layer, eliminating excess chemical use and cost. Electrochemical membrane techniques to avoid the formation of a fouling layer on membranes include molecular repulsion techniques and oxidation of low concentration organics during continuous operation.

2.4.1 Chemical Oxidation for Defouling
Defouling chemicals include oxidants. Most oxidants can be used to clean membranes, given they do not damage the membrane. Organic molecules can be oxidized with oxidizing agents by simple oxidation from organic molecules (BOD) to simple end products (CO₂, H₂O etc.) in wastewater treatment. A positive reaction potential, E⁰reaction, calculated using the half reaction potentials, determines simply if the reaction will happen. However, the reaction rates are usually too slow to be used for general wastewater treatment [53] (p.524). Increasing the reaction rate of the chemical oxidation of organics usually requires one or more catalysts, such as transition metal cations, enzymes and pH adjustments.

In standard wastewater treatment, chemical oxidation is typically performed after biological treatment on low-molecular weight polar organic compounds and complex organics with benzene rings that were not easily degradable (recalcitrant). Oxidizing agents are used for reducing the concentration of organics, odor control, disinfection (killing bacteria and viruses), neutralization (pH), scale control (precipitation) on membranes, ion stabilization to avoid pipe corrosion, and to take out the inhibitory and/or toxic effect of organic or inorganic molecules to microbes and aquatic flora. The oxidation of ammonia with chlorine was done in the past, however the build-up of acid, total dissolved solids and undesired chloro-organics discontinued this practice [53] (p.524). Advanced oxidation processes, AOP, oxidize complex organics, usually with hydroxyl radicals, which cannot be oxidized by ozone or chlorine. Oxidizing agents and/or disinfectants include ozone (O₃), hydrogen peroxide (H₂O₂), permanganate (MnO₄⁻), chlorine (Cl₂ or HClO), oxygen (O₂), and halogens bromine (Br₂) and iodine (I₂). The typical dose of ozone for secondary effluent is 6 kg/kg destroyed organics [53] (p.524) see p.1293 for calculations and ozone dose table of various wastewater types.

2.4.2 Electrochemical Oxidation for Defouling
Electrochemical defouling includes the production of chemicals (usually oxidants) at the electrode surface, such as hydrogen peroxide at the cathode, which is an effective biocide [54] and reactive...
oxygen species at the anode (O\textsubscript{2}, O\textsuperscript{2−}, O\textsubscript{3}, OH radicals). Defouling of inorganic scaling can be achieved when potential is applied without pressure to increase cross flow velocity and shear removal efficiency of scaling [55]. Electrochemical defouling was shown on composite conductive carbon nanotube and polyamine membrane for scaling (CaSO\textsubscript{4} and CaCO\textsubscript{3}) on RO membranes anodes, where H\textsuperscript{+} ions resulting from OER ionized and dissolved the scale [55]. The majority of electrochemical defouling methods using intermediates (chemical oxidants) focus on anodic oxidation or cathodic production of oxidants. A thorough discussion of electrofiltration operation methods is in the antifouling literature review.

Electrochemical advanced oxidation processes, EAOP, typically focus on oxidation of the complex organics and inorganics addressed in advanced oxidation processes at low concentration using electrodes and chemical oxidants as intermediates. Electrochemical oxidation of wastewater, EAOP, is usually done by cross flow through electrode banks. It has been explored for porous membranes including Ebonex Ti\textsubscript{4}O\textsubscript{7} anodes [56] and ceramic dimensionally stable anodes (DSA), for example for oily wastewater [32]. Electrochemical advanced oxidation processes are able to oxidize a wider range and concentration of persistent micropollutants, nitrogen species and microorganisms than traditional advanced oxidation processes [57, 58]. The reactive oxygen species, ozone, hydrogen peroxide and hydroxyl radicals, are ideal for wastewater treatment with electrodes as they do not produce dissolved solids unlike chlorination of organics [53] and intermediate hydroxyl radicals non-selectively oxidize most organics. The rate limiting step at steady state in most cross flow EAOP is diffusion of the hydroxyl radicals and organics [59]. Reaction density increases with flow-through porous anodes [60]. Their defouling ability is limited to the avoidance of a fouling layer by continuously oxidizing the low concentration organics as they pass through the electrochemically reactive membrane. If we apply EAOP to removing adsorbed organic filtration cakes by hydroxyl radicals, the rate limiting step is likely to be the production of hydroxyl radicals at the surface of the electrode and base of the fouling layer, which is a function of water availability at the surface and can be enhanced by back flushing with water.

Electrochemical defouling can include high strength electric pulses to attempt to delaminate the cake (defouling) or disrupt the concentration polarization (antifouling) [61]. Materials deposited on membrane surfaces will retain a surface charge (in general filtration and especially in electrofiltration), so high strength pulses combined with increased cross flow velocity can successfully defoul some cakes from the surface of the membrane [62] depending on the foulant. Colloidal silica cakes can be successfully defouled with high voltage electric pulses at close to 100% (defouling) and BSA cakes at around 96% (antifouling), however the mechanism remains unclear [62]. Generally short pulses (7.5 sec) at high voltage (100 V) are most successful, although the pulsing effectiveness depends on all the parameters affecting the electrochemistry of the solutes.
in solutions [62]. In addition to pulses, brief polarity reversals using high shear can also be successful at avoiding adsorption and/or electrodeposition of materials [63].

Another electrochemical process worth mentioning in contrast is electro-coagulation or enhanced organics recovery in food processing to collect food particles. An electric field induces a charge on the food particles, causing them to coagulate and migrate towards an electrode with a membrane before the electrode of attraction. The food particles can be collected without altering their structure and/or function [64].

Electrochemical defouling of reactive electrochemical membranes to recover the fat fouling from slaughterhouse wastewater and restore membrane operation will require an electrode that either desorbs fats readily at a given potential or produces a reactive oxygen species in sufficient current density to non-selectively oxidize the adsorbed fouling layer allowing its removal.

Electrochemical membranes [56, 65-69] are currently used primarily in packed bed electrodes and/or flow through membranes for wastewater treatment of low concentration chemicals that are not otherwise degradable by anaerobic digestion, primarily in labwork, to replace high hydrogen peroxide use. In industrial practice, membrane filtration with electric fields often isolates the electrodes to eliminate fouling and places multiple layers of ion exchange or filtration membranes between the electrodes in cross flow patterns, to increase the working membrane area acted upon by the electric field and allow the electric field induced by the moving ions to reinforce the EMF created by the electrodes, thus reducing the total power needed for operation [23]. Few studies have focused on reductive reactions until recently and have applied the production of hydrogen peroxide production to membrane bioreactors to defoul wastewater biofouling [70, 71]. Defouling in the reductive range has focused primarily on hydrogen bubble production on metal surfaces.

A review of electrochemical wastewater oxidation including packed beds operating with flow through conditions details the successful oxidation of multiple organics, including carboxylic acids, and recommends removing (cathode) scaling by polarity reversal [72]. Electrochemical membranes that are defouling by oxidation during continuous flow through operation for wastewater treatment include TiO$_2$ coated carbon for oily wastewater [65, 66]; and BDD coated Titanium for of blue dye in dye wastewater [67], which further determined oxidizing graphite electrodes leads to increased pore size and increased membrane flux [67].

The electrooxidation of olive mill wastewater was investigated to decrease the organic load before anaerobic digestion, as oils retard anaerobic digestion [73-78]. EAOP materials were found to be effective at reducing the organic load and improving anaerobic digestion rates, however operating costs were often prohibitive for the large volumes of wastewater.
Electrochemical membranes where shown to defoul using hydrogen nano-bubbles for yeast cell biofoul on carbon cathode nano tubes, coated on PVDF [69]. Cathode electrodes (not membranes) were shown to defoul using hydrogen nano-bubbles for proteins (BSA) on stainless steel. Highly oriented pyrolytic graphite (HOPG) was also tested, however degradation led to carbon-protein clusters remaining at the surface [68]. Nano bubble defouling was evidenced by hollows in the BSA film coverage under AFM. The defouling mechanism was proposed to be physical migration of the BSA at the solid-liquid interface to the vapour-liquid interface caused by bubble growth. No electrochemical reduction mechanisms were investigated.

2.5 Antifouling
Antifouling can include physical, chemical and electrochemical processes and technologies. Physical antifouling techniques include engineered membrane materials to deter adsorption and feed-back control methods during operation. Operational control is perhaps the most common anti-fouling measure across all industries and typically involves backflushing at regular intervals to remove adsorbed species. The frequency and duration of the back pulse is experimentally determined for effectiveness. Importantly, the backwash pressure must be higher than the operating pressure [79] and can be ineffective if the fouling is strongly adsorbed or in the pores [25]. Hydrodynamic control of the transmembrane pressure and permeate flux allows the membrane module to maintain continuous operation below the critical flux point. The critical flux is defined as being the maximum flux at which fouling is reversible. The critical flux point is not fixed and can be increased by manipulating the solute concentration, the cross-flow velocity (measured by Reynold’s number and/or shear stress), transmembrane pressure, temperature (as it affects viscosity and mass transfer coefficients), and the pore size and pore surface density. Hydrodynamic control to limit fouling has been studied extensively for milk fat & proteins [16, 80], and fruit juice polysaccharides & pectin [11].

Other physical anti-fouling methods include bubble cleaning where gas is sparged over the membrane to create turbulence and disrupt the polarization layer. Bubble cleaning is common for stainless steel filters and can be used for vertical tubular and hollow fibre membranes. Gas sparging has been studied extensively, including in separations involving milk fats and proteins [81]; however it is not suitable for either. Milk proteins denature and precipitate, or sometimes lyse into peptides, in sparged membrane unit operations, whilst milk fats foam, reducing membrane efficacy. This is suggestive that sparging would be equally unsuitable for use in abattoir waters for similar reasons. Further, sparging is not compatible with electrochemical anti-fouling or defouling methods as bubble resistance on the surface of the membrane causes increased electrical resistance. Lastly, mechanically induced shear stress from ultrasonication or vibration of the membrane module have
been shown to reduce fouling for milk protein concentration [82] as well as bovine serum albumin and lysozyme mixtures [83].

2.5.1 Physio-chemical Antifouling

Chemical antifouling is primarily focused on adding biocides before filtration to minimize biofouling and anti-scaling chemicals to minimize scaling. Researchers have also focused significant attention on physical antifouling, designing membrane surfaces that are less likely to foul by deterring adsorption. For example biofouling can be reduced by adding silver nanoparticles to the membrane structure [84]. Likewise, making hydrophobic polymeric membrane surfaces hydrophilic, by adding a charged functional group, can improve electrostatic interactions between the membrane surface and the charged molecules such as proteins [85] [86], collagen [87], and BSA [88]. In addition, decreasing the hydrophobicity of a membrane surface attracts more water into the boundary layer and can serve to reduce both concentration polarisation and fouling [89]. For non-polymeric membranes like ceramics the use of photoactive materials like zinc oxide and titanium dioxide as a way of reducing or controlling fouling have gained research prominence, although as yet have not seen industrial application.

2.5.2 Electrochemical Antifouling

Electrochemical antifouling depends upon the electromagnetic repulsion of charged foulants away from the membrane to reduce cake concentration profiles and particle deposition [90, 91] and is commonly referred to as electrofiltration. The electric field created between two electrodes of opposite charge depends on distance between electrodes and difference in potential between the two electrodes (voltage). The electromotive force (EMF) induces charges (electrons and electrons on molecules) to move in an electric field (migration). The mobility of the molecules in the electric field is determined by their charge. The order of magnitude of the forces is convection > migration > diffusion. Increasing the net charge, zeta potential, on a molecule will increase the migration rate in an electric field. The migration force is uniform on the solution and background electrolyte for migration, resulting in wasted electromotive force in highly ionic solutions. Ideal migration efficiency requires highly charged molecules in low electrolyte concentrations. Diffusion constants affect migration accordingly, with the exception of hydrogen ions and hydronium ions, which can travel faster (~10x) by channelling. Electrofiltration, or antifouling, is ideal for low background ionic strength solutions and/or systems with shear sensitive particles, such as foods [62].

Electrofiltration assemblies commonly place the cathode behind the membrane [62] to avoid electrode fouling and may electrically connect the electrode to the surface of the membrane to enhance the repulsive antifouling effect on the polymeric membrane surface [54]. Electrofiltration is used for both particle repulsion and attraction. Electrofiltration was first applied to dead-end
filtration, to enhance particle deposition, increasing filter cake growth rates and permeate flux [92, 93], known as ‘electroosmotic dewatering’, including for proteins and polysaccharides [94, 95]. Cross-flow electrofiltration was developed to reduce particle deposition and the concentration polarization that developed [90, 91] and is sometimes called electrophoresis. Cross-flow electrofiltration is used to enhance hydrodynamic antifouling methods. The electromagnetic force is balanced against the pressurized fluid force moving the foulants towards the membrane. By increasing the electromagnetic field, the cake of charged foulants can be dispersed and minimized by the cross flow shear. With less cake, the voltage required to disrupt the cake formation lessens, allowing the cross flow velocity and voltage to be gradually lowered as a part of start-up in continuous operation [63]. Briefly reversing the polarity and/or using high shear [63] can also enhance antifouling by disruption of the polarization profile that develops in continuous operation. Operating parameters are optimized to balance the voltage field strength versus the Reynolds number (cross flow velocity) for minimum cake thickness, for example for oil and kaolin clay emulsions in water [63]. A limiting voltage exists, called the critical voltage, where no cake layer forms and particles remain a non-discrete cloud above the membrane, after which an increase in cross-flow velocity (fluid shear) decreases particle filtration rates. Hence, operation should be performed below the critical voltage, where filtration rate increases with increasing Reynolds number.

Cross-flow electrofiltration can be applied to biological materials that are shear sensitive, including proteins (gelatin) [96]. The zeta potential and shape of biological materials, such as proteins, are highly pH sensitive and in electrofiltration the isoelectric point has the minimum flux [47], as the molecules have a net neutral charge. Transport modeling for electrochemical membranes allows calculation of the membrane’s zeta potential, without reactions [97]. Cross flow electro-ultrafiltration of proteins (BSA) is able to minimize cake formation based the concentration, zeta potential and pH [98] and can be enhanced in combination with electric pulses [61, 99]. Electro-ultrafiltration of industrial enzymes is successful for high concentration at low cross flow [100].

Electrochemical antifouling was shown on composite conductive carbon nanotube and polyamine membrane cathodes for alginate proteins on ultrafiltration membrane cathodes at -1.5 to -3.4 V at 100 minutes [101]; and for biofilm growth and cell deposition on NF membrane, using both DC current as a cathode and AC current to disrupt deposition [102]. Electrochemical antifouling was shown for biofouling EPS proteins and polysaccharides in continuous flow membrane bio-reactors (MBR) for laminated (polyvinylidene fluoride, PVDF) MF membranes with an embedded stainless steel mesh as a cathode at 2 V/cm [54]. Although they claim H2O2 could be made and well detail the possible antifouling mechanism, they did not actually test for H2O2. Further, the stainless steel mesh was fully embedded inside the polymer membrane so any H2O2 produced inside the
membrane would have travel out the pores to the surface was assumed to antifoul by reacting with proteins and increasing their (negative) zeta potential, not defouling the surface as in AEOP [54]. Electrochemical antifouling was shown for polyester membranes coated in graphene at 1 V/cm [103]; for stainless steel cathodes, which achieved simultaneous defouling and wastewater treatment by producing H₂O₂ at 18.5 A/m³ [70]; for stainless steel cathodes in an upflow design combined with a microbial fuel cell anode and air gas sparge below the cathode, which successfully removed COD and ammonia by producing H₂O₂ [71]; and has become a recent publication point in MBR operation.

Antifouling has previously been proven for the model foulants present in abattoir and slaughterhouse wastewater, including bovine serum albumin (BSA) protein, sodium alginate (SA) polysaccharide, humic acid (HA) and silicon dioxide (SiO₂) [54], as well as for oils in charged electrolyte. In general, the use of electrically conductive membranes for combined defouling and antifouling has received far less attention and appears to be an emerging publication field [56, 70, 71].

2.6 Electrochemical membrane materials
The electrode material and operating conditions determine the oxidation/reduction reaction mechanism, reactant selectivity, overvoltage, kinetics and process performance for an electrochemical reaction. Reactions occur in steps, usually electrochemical, chemical, electrochemical. Any chemical intermediates therefore must be reacted to proceed. If intermediates do not desorb, then the electrode lose surface sites to regenerate and the reaction cannot be completed, i.e. poisoning. Adsorption and desorption, and poisoning, depend on the adsorption kinetics of the electrode material for any given reaction. Intermediates may include radicals. Radicals do not have an electric charge; however, they can carry one. To perform electrochemical reactions successfully, the electrode materials will require (1) corrosion stability at the potential range of organics oxidation, ~1.5 to 2.3 V vs SHE, (2) the ability to perform oxygen transfer reactions, or alternately hydrogenation reactions, (3) non-toxic, (4) sufficient electrical conductivity, (5) selective electrocatalytic activity for the desired reactions, and (6) high overvoltages for undesired reactions.

High ionic strength can reduce the ohmic resistance of electrochemical wastewater treatment methods, thus reducing the power requirement during operation. Adding salt or using chlorine bleach in the abattor is not recommended however, despite increasing the ionic strength of the wastewater. The presence of chlorine can create chlorinated organics from both natural and industrial organics, all of which are toxic.
A review of suitable electrode materials for electro-oxidation determined AEOP materials were best suited for organics oxidation. The oxidizing power of an anode is determined by the anode overpotential for the oxygen evolution reaction and the adsorption enthalpy of the OH radicals created [104, 105]. By-products result from incomplete oxidation due to the selectivity of the electrode material (direct) or the intermediate (indirect). Direct oxidation mechanisms at a sufficient anode potential result in the most by-products due to limited selectivity. Indirect oxidation by intermediates includes oxygen, halides such as chlorine species, and hydroxyl radicals, which are the least selective. Anodic defouling in Electrochemical Advanced Oxidation Processes has focused on the production of hydroxyl radicals for the indirect oxidation of organics in wastewaters, primarily to clean the wastewater electrochemically and defoul the electrodes secondarily [57]. The four most effective inactive electrode materials for Electrochemical Advanced Oxidation Processes, EAOP, are doped SnO$_2$, PbO$_2$ [106], BDD [60, 107-110] and sub-stoichiometric and doped TiO$_2$. Anodes that can combust organics include graphite felt with palladium nanoparticles [110], and mixed metal oxides [111, 112] including Ti/SnO$_2$-Sb and Ti/PbO$_2$ [106]. Sub-stoichiometric TiO$_2$ produces hydroxyl radicals at a reaction rate lower than BDD, however they are stable and already commercially available, as a product called Ebonex. Sub-stoichiometric TiO$_2$ has a porous structure and has even been used in an electrochemical reactive membrane recently [60].

Platinum has corrosion stability over a large potential and pH range. Platinum and its oxides are sufficiently electrically conductive, perform oxygen transfer reactions, and have the lowest overvoltage for hydrogen and oxygen evolution reactions of the pure metals. Platinum metal cathodes are catalysts for hydrogenation reactions as well.

Nickel anodes corrode at pH 6 until ~1.3 V vs SHE. At more alkaline pH, Ni(III)OOH forms and is stable for oxygen evolution reactions. Nickel cathodes in alkaline solution have a low hydrogen overvoltage and are good hydrogenation electrocatalysts. Raney nickel can be electrodeposited to a surface and used [113].

Graphite and glassy carbon are suitable for most organic electrochemistry in organic media. However, carbon anodes in aqueous solution at oxygen evolution potentials will eventually corrode to CO$_2$ [56] [67]. Carbon cathodes have a high overvoltage for hydrogen and a low catalytic activity for hydrogenation reactions. Carbon’s conductivity is about 100 times less than metals, which increases the energy consumption during operation. Carbon is a common support material for catalyst layers [114] and would be appropriate as a cathode catalyst support.

Titanium is a commonly used as a support metal for catalyst it is corrosion resistant over a wide range of pH in aqueous media up to ~2 V vs SHE. However, titanium oxide, TiO$_2$, is only semiconducting and inhibits oxidation reactions, called a passivating layer or valve metal. Titanium
is protected by the oxide layer during CVs. Long term operation of a titanium cathode for hydrogen evolution at high current density lead to hydrogen embrittlement. Catalysts coated on the titanium will reduce the overvoltage required for the reaction. For oxidation, platinum, BDD or Ebonex powder, a mixture of sub-stoichiometric titanium oxides, coated on titanium coated will provide catalysis. Ebonex is a ceramic oxide mixture of sub-stoichiometric titanium oxides that is corrosion resistant and electrically conductive. It has a high overvoltage for oxygen and hydrogen evolution. It usually comes in powder form. For reduction reactions, catalysts such as nickel, platinum or palladium could be coated on.

Gold is a stable anode at pH 6 at $\leq -0.65$ V vs SHE, after which it begins to oxidize. Gold is a noble metal useful for mechanism studies in organic electrochemistry as a low potential range material, particularly in organic media.

Aluminium forms a passivated oxide, $\text{Al}_2\text{O}_3$, at pH 6 at $\sim -2$ to 2.5 V vs SHE. Aluminium acts as a cathode at pH 6 starting at $\sim -2$ V vs SHE. Aluminium is passivated until it reaches $\leq -2$ V vs SHE, where it is subject to hydrogen embrittlement and corrosion during long term operation.

Molybdenum forms a passivated oxide, $\text{MoO}_2$, at pH 6 at $\sim -0.6$ to 0 V vs SHE. Molybdenum acts as a cathode at pH 6 starting at $\leq \sim -0.6$ V vs SHE and is used as a dopant for hydrogenation.

Stainless steel and iron cathodes have a relatively low hydrogen overvoltage suitable for commercial use. Stainless steel anodes corrode quickly and are suitable only as sacrificial anodes. Iron corrosion is used for fat collection in electro-coagulation where the iron migrates under the electric field to the cathode and removes fat particles from solution in the process by coagulation. The porosity of the iron electrode is important as more porous electrodes have less even coverage of the passivating oxide layer, limiting protection and leading to corrosion. The presence of iron in solution with oxygen during cathodic production of hydrogen can lead to the production of $\text{H}_2\text{O}_2$, which accelerates organics oxidation, as detailed previously in electro-fenton processes in water [115]. The iron from blood in the stick water is unlikely to be in high enough concentration to affect the stainless steel cathodes. Iron corrosion from steel pipes or rendering cookware could cause membrane fouling as it coagulates fat and Fe ions are attracted to the negative cathode.

Iron is a stable cathode at $\leq -0.8$ V SHE and forms a passive oxide layer from $\sim 0.2$ to 1.4 V SHE at pH 6 according to the E vs pH diagrams. Pourbaix shows the lower limit of passivation potential on iron at pH 6 is $\sim -0.11$ V SHE. Below pH 8, the presence of oxygen in solution limits the formation of the passivation layer and increases the corrosion rate of iron. Above pH 8, oxygen promotes the formation of the passivation layer and iron is protected against corrosion in solutions without chloride. Passive stainless steel means the chromium oxide layer is present and protecting the surface from corrosion. The chromium oxide layer can only re-oxidize when attacked, meaning
repair itself, if sufficient oxygen is present. This means once corrosion is initiated, it can continue without access to oxygen, such as when covered by organics. Organic oxidation occurs at higher anodic potentials than those that provide anodic protection of the stainless steel, resulting in corrosion. The polarization curve of 304 stainless steel shows the passivation region at 0.341 to 1.041 V vs SHE [116], which is below the potential range for organics oxidation. Oxidizing organics will occur simultaneous to stainless steel corrosion at the given potentials of 1.5 to 2.3 V SHE. The rate of organic oxidation and the rate of corrosion will be dependent on the reaction kinetics.

2.7 Current understanding, Challenges and Research Gaps
Electrochemical anti-fouling and defouling research began in the 1920s and has had a research revival approximately every decade spurred by advances in membrane separation science. Our current understanding of electrochemical membrane separations including defouling and antifouling and the challenges for its application to abattoir wastewaters is therefore a combination of well-established knowledge of electrofiltration from other industries (dairy and wastewater), the electrofiltration of the same basic (smaller) biochemicals as abattoir wastes (proteins and fats), and previous attempts at the filtration of abattoir wastes. As such, the use of electrochemical methods for anti-fouling is ideal for high concentration foulants which are shear sensitive and need to be filtered at low cross flow velocity. The electric field can interact best with the charged particles at high concentration, so the voltage necessary to repel the cake is strongly related to the foulant concentration. A pulsed electric field can be used too, which uses less energy [117, 118]. Electrochemical anti-fouling techniques are therefore ideally suited to abattoir wastes due to their high concentration, high conductivity, and need to be pumped at low cross flow velocity to avoid pipe plugging. This thesis seeks to address the apparent gap in the field for abattoir waste waters, but more importantly it also seeks to extend the electrochemical techniques to defouling mechanisms as well, which is a more neglected topic as seen in Section 2.4.1.

The challenges of electrochemical separations are balancing long term stable operation with cost. Long term stable operation can include ensuring an electric field does not interfere with biological function, as in the peptide activity of dairy proteins separated by electrofiltration or the production of toxic intermediates, such as those produced by incomplete mediated oxidation in wastewater treatment. The costs of electrofiltration are often limiting when compared to other methods. Minimal power use on readily available, cheap electrodes increases the economic applications of electrofiltration. Therefore, an appropriate value proposition for the electrofiltration process will take the form of a series of operational envelopes (for example in Figure 2) where the rate of
fouling (based on the foulant and hydrodynamic regime) is correlated with the required power to either effectively defoul or antifoul. There will also be a region where electrochemical methods are not suitable which is hypothesized to be when the rate of fouling and required power is too high to be economically attractive. The series of operational envelopes presented in Figure 2 has not yet been developed, particularly for working with abattoir waters and this thesis seeks to address that theoretical gap.

![Figure 2 - Theory of fouling mechanisms and rate versus applied power (for antifouling and defouling)](image)

This thesis is the first known examination of electrofiltration, either electrochemical antifouling and/or defouling of abattoir and slaughterhouse wastewater, other than electrocoagulation.
3 Experimental Methods
This chapter is concerned with the details of the experimental aspects of this research. It begins with a description of the synthetic stick water solution used throughout the experiment. This was diluted at times (as specified in Chapters 4 and 5). Then a description of the stainless steel membranes used is given, followed by an outline of the experimental membrane testing module. The chapter ends with a description of the relevant characterisation techniques used in the thesis.

3.1 Synthetic Stick Water Solution
A literature review of abattoir wastewater [119-121] resulted in the formulation a synthetic stick water model (Table 1). The electrolyte was balanced to be pH neutral, so as not to bias the antifouling or defouling results. The amount of chloride was kept at low levels to balance only the sodium and potassium counter-ions because chlorine is not commonly reported in the abattoir wastewater literature. Excess chlorine, from chlorine bleach washing or in this case as the counter-ion from the electrolyte salts, may result in chlorinated organic by-products which are carcinogenic. Further, chlorine is known to attack and degrade stainless steel and would likely increase corrosion. An analysis of proteins resulted in the selection of gelatine, which is the most abundant protein in the body, common in rendering wastewaters and a suitable analogue for other proteins like bovine serum albumin (BSA). An analysis of fats resulted in the selection of oleic acid as it represents the largest single fraction of fatty acids, with palmitic and stearic acids being the next most common. The salt concentrations represent the average of those reported in literature. The pH was kept at 7. The temperature of rendering wastewater is 40±5 °C. The wastewater was raised to 40 °C for two hours with mixing to emulsify the gelatine and oleic acid, which remained suspended in solution for several days, but not longer than a week. The temperature of the solution during membrane testing was kept at a constant 22 °C.
Table 1: Synthetic Stick Water Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Concentration</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>mol/L</td>
</tr>
<tr>
<td>Fats, Oils and Grease (FOG)</td>
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<td></td>
</tr>
<tr>
<td>Oleic acid</td>
<td>10000</td>
<td>0.01664</td>
</tr>
<tr>
<td>Protein</td>
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<td></td>
</tr>
<tr>
<td>Gelatine</td>
<td>6000</td>
<td></td>
</tr>
<tr>
<td><strong>Organic nutrients / Electrolyte salts</strong></td>
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<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Organic P</td>
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<td></td>
</tr>
<tr>
<td>NH&lt;sup&gt;4&lt;/sup&gt;Cl&lt;sup&gt;-&lt;/sup&gt;</td>
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<td>0.001722</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;HPO&lt;sub&gt;4&lt;/sub&gt;</td>
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<td>0.000213</td>
</tr>
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</tr>
<tr>
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<td>0.000125</td>
</tr>
<tr>
<td>MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>15.7</td>
<td>0.000165</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>12.0</td>
<td>0.000125</td>
</tr>
<tr>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>4.18E-05</td>
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<td>NaHCO&lt;sub&gt;3&lt;/sub&gt;</td>
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<tr>
<td>KCl</td>
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</tr>
<tr>
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</tr>
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<td>1.28E-05</td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>1E-07</td>
</tr>
</tbody>
</table>

3.2 Membranes
Stainless steel electrode membranes were chosen as the electrochemically active membrane material for this work. Stainless steel is known to be corrosion resistant without applied anodic potential and corrosion resistant in the cathodic range. Stainless steel also has ~ 10 to 14 % nickel content, a known catalyst for hydrogenation reactions.

Stainless steel hollow fibres were used primarily for the cyclic voltammetry and potentiostatic testing and imaging under scanning electron microscopy. These membranes acted solely as electrodes and were chosen for their small size and ease of testing. They were prepared as detailed in [122].
For the membrane module testing as outlined in Section 3.3 commercially available AccuSep 316L stainless steel membranes from Pall Corp were used. These membranes were 10cm in total length with an effective membrane length (i.e. the porous section) of 4.5cm and an external diameter of 1cm. The membrane pore size is characterised at 2µm according to the manufacturer. The ends of the membrane were welded, solid 316L stainless steel.

3.3 Membrane Testing Module

The design for the testing rig to evaluate the anti-fouling and defouling capabilities of commercially available AccuSep stainless steel membranes was designed for constant pressure and variable flow is shown in Figure 3. The equipment included a custom made glass membrane reactor module, a Nord GmbH & Co SK200E370 peristaltic pump for the feed, which operated at 1.09 L/min; a JAVAC MY632-2B5 vacuum pump for the permeate, which had a vacuum of ~10kPa; a BioLogic SP200 potentiostat operating the standard EC-Lab software; TPS LabChem pH and conductivity meter with pH probe, ionode IJ44C pH and k10 conductivity probe; and Basi 3M Silver-Silver Chlorine reference electrode at 2 cm length to withstand pressure. The feed flow rate of 1.09 L/min yields a cross flow velocity of 2.8 cm/s and a Reynold’s number of ~210 which is in the laminar regime.

![Figure 3 - Experimental rig for testing electrochemical based anti- and defouling methods](image)

To minimize potential differences down the length of the membrane, the reference electrode was placed at the opposite end of the electrical connection. The counter electrode was a platinum cylindrical sheet wrapped around the working electrode at a distance of 0.5 cm and the reference
A electrode was placed 2 cm down the length of the membrane ~0.3 cm from the non-porous area. The reference electrode was not affected by the EMF field of the counter electrode because the counter electrode was placed further up the membrane.

A drip was placed in the liquid line to ensure the pH meter was not affected by the potentiostat operation. The wires connecting the potentiostat to the membrane and counter electrode were single copper wires with silver loaded epoxy, covered in acid resistant, insulating resin.

Membrane flux was determined by applying measuring the mass collected in the trap over a set period of time (typically 2.5 or 5 minutes). The flux was then converted to units of L/m²/h (LMH) in the common parlance of the membrane field. In a typical run the membrane would be tested for MilliQ water, electrolyte (i.e. the synthetic stick water solution without gelatine or oleic acid) and the synthetic stick water solution at 10% or 50% concentration, which was diluted with standard electrolyte to maintain the electrolyte concentration. Between each test the membrane was washed in 1M sulphuric acid at 50 °C for 20 minutes and dried under vacuum. Permeate was collected and analysed via UV-Vis (details).

3.3.1 Antifouling Procedure
For antifouling testing it was important to ensure the membrane was charged and/or electrochemically active prior to the introduction of the synthetic stick water solution. To do this the membrane was first exposed to electrolyte (i.e. the synthetic stick water solution without gelatine or oleic acid) and the potentiostat was turned on at the desired applied potential. Then the electrolyte feed was switched to the synthetic stick water solution (often diluted) and recorded as time zero. The solution took approximately 10 seconds to fill the membrane module.

3.3.2 Defouling Procedure
For the defouling testing it was important to ensure the membrane was already fouled before the defouling potential was applied. Typically, this involved exposing the membrane to the synthetic stick water solution (often diluted) for sufficient time to see that the flux had declined as a result of fouling. This was typically after 5 or 10 minutes or two sampling intervals. Then the potentiostat was turned on at the applied potential. In some instances, the potential was left on for the remainder of the test whilst in others cycling of the potential was attempted. Cycling typically took the form of 2 sampling intervals on and 2 sampling intervals off.

3.4 Characterization
3.4.1 Scanning Electron Microscopy
Hollow fibre membrane characterization was performed by scanning electron microscopy (SEM) to determine antifouling and defouling. SEM samples were prepared by drying either over night or in a
desiccator. Drying by vacuum was found to damage the soft organics on the surface. Samples were imaged in a NeoScope SEM at 10 eV to 15 eV. Higher power was found to charge and/or melt the organic surface, resulting in blurred images. Imaging was performed down the length of the membrane at 50x resolution and the images were divided into 10 squares and assessed for organic fouling, resulting in an organic defouling percentage. The SEM images were also examined at 150x, 500x and 1000x and greater when required, to ensure defouling had occurred. Close up examination was performed as standard practice on defouled samples to ensure thin layered fouling was accurately assessed. Control SEM images of fouling with gelatine, oleic acid, the emulsion, corrosion in electrolyte and corrosion in emulsion were used for comparison to ensure accuracy of visual assessment. In order to obtain accurate SEM images, the membranes were removed immediately after testing and dried for SEM.

3.4.2 Electrochemical Characterisation

Membrane resistance was measured to ensure the surfaces were sufficiently conductive and non-corroded before use. Membranes were characterized electrochemically by cyclic voltammogram in electrolyte. Electrochemical characterization could result in irreversible corrosion onset in the oxidative range. As a result, in order to take triplicates or duplicates, a single hollow fibre membrane was cut into three pieces and each of the three pieces was operated once. In the reductive range, membranes were found to be undamaged by operation and could be operated repeatedly, as long as they remained only in the reductive range during both cyclic voltammogram and potentiostatic operation.

Fouling for lightly fouled hollow fibre tests was performed by leaving membranes in fully emulsified solution for a minimum of 1 hour. Tests were run immediately after. Fouling for heavily fouled hollow fibre tests was performed by manually applying congealed emulsion precipitate, which occurred at ~1 week, to completely cover the surface of the membrane at ~1 mm thick. The congealed organic remained rigidly applied without external force and deemed adsorbed.

Electrochemical characterization tests included cyclic voltammagrams in oxidative and reductive ranges, potentiostatic operation (constant applied potential) and galvanostatic operation (constant applied current). The electrode potential range chosen for the reductive range on the hollow fibre stainless steel membranes was -0.2 to -1.5 V SHE. The potential range for the pall membrane was between -0.25 and -0.85. The power of the potentiostat limited the negative potential range available for testing on the AccuSep membrane. The presence of anodic current density on initial cyclic voltammagrams could result from corrosion and not oxidation of reduced species on the surface of the membrane. Therefore, initial cyclic voltammagram scoping tests led to minor adjustments of the cyclic voltammagram range to avoid anodic current, as it could cause corrosion.
A literature review of food industry electrochemistry resulted in estimating the electrochemical parameters for reductive desorption of gelatine using the reductive desorption of oligonucleotide sulphur bonds in phosphate buffer as -0.4 V on gold [123]. As the reductive desorption mechanism was a hydrogenation, it was hypothesized that on stainless steel the potential would be near or above stainless steels hydrogen evolution point, which are greater than those on gold (-1.2 V for pall Acusep membranes). The electrocatalytic hydrogenation of various types of organics was investigated on iron electrodes with deposited nickel, which is similar to stainless steel surfaces, and showed the hydrogenation of similar long chain conjugated olefins, between 30 to 60% [124]. The cell voltage of the system increased over time, indicating the incomplete HER resulting in minor fouling. Chemisorbed oleic acid is similarly desorbed by hydrogenation of the double bond at the HER potential on catalysts, including nickel [125, 126]. Iron produced hydrogen when water is available, however is not a commonly used catalyst for hydrogenation of organics. The reduction potential of stainless steel shows passivation by anodic current at potentials more positive than -0.2 V, so this was the upper limit for cyclic voltammograms in the reductive range.

The oxidation of oleic acid, and stearic acid, was shown to follow the OER of catalytic materials by Kolbe decarboxylation in protic solvents at ~1.4 V [127]. Review literature places Kolbe decarboxylation in organic solvents between 2.1 and 2.8 V regardless of carboxylic acid chain length [126]. Literature for stainless steel corrosion showed a passivation layer from 0.3 to 1.04 V [116] and corrosion at 0.4 V when corroded by abrasion to remove the passivated layer [128], at 1.5 with fresh oxide passivated layer [128], and at 0.94 V (in acidic and chlorinated media) when the passivating layer was removed by oxidizing current at ≥1.34 V [129]. Cyclic voltammogram scoping tests showed the corrosion of stainless steel at ~ 0.7 V when the passivating layer was removed and the OER of new membranes at ~1.3 V. The passivating layer was between ~0.2 and 1.3 (OER) while the oxide layer was present. This led to the test range for organic cyclic voltammograms to be from the onset of -0.2 to 2.2 V. Based on the cyclic voltammograms, the oxidation test range chosen was between 2.0 to 2.4 V. The scoping cyclic voltammograms showed (see results section) (1) the oxidation of organics with the onset of OER and (2) the increase of current density starting at 1.6 V, with a significant current density difference by 2.0 V. This indicated a steady organic oxidation was occurring by 2.0 V at increased current density, separate from corrosion. The electrooxidation of gelatine was not researched extensively as it was shown to respond positively to oxidation with hydrogen peroxide and hydroxyl radicals, which are produced at potentials far above 2.0 V. Scoping tests showed gelatine oxidation in solution also occurred with the onset of OER, however the complete oxidation of adsorbed gelatine would likely require stronger oxidants at higher potentials. Emulsions showed oxidation at OER and a current density between that of gelatine and oleic acid.
The potentiostatic and galvanostatic operation tests were conducted over 2 hours, with a platinum counter electrode and a reference electrode placed in an equilateral triangle position to ensure the EMF between the working and counter electrode did not affect the reference electrode potential measurement. The reference electrode was placed within 1 cm of the working electrode. The cyclic voltammagrams on platinum were operated with stirring. The potentiostatic tests and cyclic voltammagrams on membranes were operated without stirring as the rotation of the stirring magnet was found to affect readings and the small square containers used for potentiostatic tests were too small to comfortably accommodate even the smallest stir bar purchased, without hitting the electrodes. Therefore, pH profiles were expected to develop during the 2 hours. All tests were run at constant room temperature.

Cyclic voltammagrams were conducted before and after potentiostatic tests as standard operation to ensure electrode activity had not, or had, changed accordingly. The range of potentiostatic tests was selected using the reaction information provided by the cyclic voltammagrams. Control cyclic voltammagrams were taken for electrolyte and increasing organics concentrations on platinum, 316L stainless steel bar, the stainless steel hollow fibres and the AccuSep stainless steel membranes.
4 Antifouling

4.1 Introduction

This chapter demonstrates the concept of membrane antifouling, where fouling from organics such as oils and proteins, can be prevented or at least minimised by using a conductive membrane as a negatively charged cathode. Oils and organic matter tend to have negatively charged density in aqueous solution [63] at neutral pH and increase in negative charge density with alkali pH [96]. For example, gelatine is negatively charged in aqueous solutions with a pH larger than 4.7 [96]. Maintaining a negative charge on the membrane surface repulses negatively charged molecules in solution, which in turn, both inhibits adsorption and/or induces them to migrate away from the electrode / membrane surface. There is an ideal operating window for negative potential, enough to induce repulsion but not negative enough to initiate redox reactions at the membrane surface. To avoid redox reaction scenarios, including hydrogen evolution and the associated alkali pH increase, this operating window is likely to be between -0.4 V to -1.2 V, to ensure repulsive rather than reactive scenarios. Increasing the solution temperature will reduce the overpotential of a hydrogen evolution reaction, whilst increasing the pressure would require a more negative potential for a hydrogen evolution reaction, based on the Nernst equation. It therefore makes sense from an electrochemical reaction scenario to repulse organics at high pressure with negative potentials that avoid reduction reactions. Similar research has shown antifouling to be successful for negatively charged electrodes for oils [63, 130] and proteins [96, 117]. The approach for this chapter is to examine the potential for effective antifouling using applied potentials between -0.2 and -1.8 V. Membranes were first examined as electrodes using cyclic voltammetry, potentiostatic testing and imaging via scanning electron microscopy. Full membrane tests, where the membrane electrode was operated as a membrane, examined the flux and rejection performance at applied antifouling potentials of -0.8 V and -1.3V.

4.2 Results

4.2.1 Cyclic Voltammetry

Porous stainless steel hollow fibres were characterised using cyclic voltammetry in both an electrolyte control solution and the synthetic stick water described in Chapter 3. In house made porous stainless steel hollow fibres [122] were a proxy for the commercial AccuSep membranes from Pall due to ease of testing. The cyclic voltammagrams (Figure 4) show cathodic current and negative capacitive polarization begins at -0.41 V (Figure 4, inset). Prolonged operation at potentials more positive than -0.41 V could result in organic adsorption and iron corrosion (Fe||Fe$^{2+}$ at -0.41 at all pH). Capacitance continues until ~ -1.0 V in the electrolyte control, where the
hydrogen evolution reaction (HER) begins, indicating an overpotential of ~ -0.6 V. Hydrogen bubbles (visible HER) are observed in the electrolyte control at -1.3 V. The synthetic stick water solution (containing organics) shows an increased capacitance compared to the electrolyte control. In contrast to the control, capacitance continues in the synthetic stick water until ~ -1.2 V, where HER (bubbles were unobservable) likely begins, as capacitance stops and the single line of hydrogen evolution begins. Decreased faradic current begins ~ -1.0 V in organic solution, indicating hydrogen evolution is preferential if the electrode surface is clear of organics. The region between -1.0 and -1.2 V is the shift of the hydrogen tail due to hydrogenation of organics [131] and the onset of reductive desorption of remaining organics. Hydrogen bubbles are directly observable in the synthetic stick water solution at potentials more negative than -1.5 V, provided the current density was high enough (≥ ~ 1 mA/cm²).

![Figure 4: Cyclic voltammagrams with organics at standard concentration (blue) and without organics, i.e. electrolyte, (red dash) showing capacitive polarization increases for organic solution from -0.2 to -1.2 V and decreased faradic current in the organic solution starting at -1 V. Cyclic voltammograms from -0.2 to -0.6 V show onset of negative capacitive polarization at -0.41 V is greater for electrolyte (red dash) than 1-10th organic solution (blue). The scan rate was 1 mV/s.](image)

The change in faradic current gave varying results with increasingly negative potential. In most instances the faradic current decreased with increasingly negative potential, due to the indirect hydrogenation of adsorbed organics and reductive desorption of chemisorbed organics. Proteins are zwitterions and their ionization induces additional capacitive current around the hydrogen evolution point [123] (see section 4.3 for further discussion). However, occasionally some hollow fibre membrane samples showed increased current for the synthetic stick water solution at the hydrogen...
evolution point (not shown). In this case it seems organic reduction is preferential to water reduction and may be a result of increased nickel content (an electrocatalyst for hydrogenation of organics [125]) and/or catalyst activation at the membrane surface [132].

Figure 5: Cyclic voltammagrams with increasing organic concentration using electrolyte (red dash), 1-10th concentrated solution (light blue), and standard concentration solution (dark blue). Showing increased organic concentration leads to decreased current density. The scan rate was 20mV/s. The arrow shows the decrease in current density with increasing organic concentration.

Ultimately, three phenomena are evident in the cyclic voltammograms (Figure 4 and Figure 5): capacitance increases with increased organic concentration, competitive reduction reactions to hydrogen evolution occur in the synthetic stick water solution, and the lack of reduction peaks (reactions) beyond the hydrogen evolution point demonstrates indirect hydrogenation of organics. These three phenomena are examined in detail within the following sections.

4.2.2 Scanning Electron Microscopy

Cyclic voltammetry demonstrated the preferred operational window for antifouling stainless steel hollow fibre membranes; however, it did not provide any information about the impact of the negative potential on the level of fouling, or the longer-term performance of the electrode. Hence, the stainless steel hollow fibre membranes were deliberately fouled in the synthetic stick water solution, operated at constant potential (-0.5, -0.8, -1.0, -1.2, -1.3, -1.5, and -1.8 V) for two hours and then the fouling was characterised via scanning electron microscopy (SEM) as outlined in Chapter 3. Control tests (without applied potential) for the electrolyte solution and synthetic stick water solution are shown in Figure 6 and Figure 7 respectively. Some mild corrosion is evident for the electrolyte control (Figure 6).
Figure 6: Control membrane left in electrolyte solution overnight at 50x (a) and 1000x (b) magnification.

The adsorption of the gelatine and oil emulsion is clearly observable in Figure 7 as darkened areas overlaying the lighter membrane and as speckled white spots on the hollow fibre surface respectively. The speckled white spots are chunks of emulsified organic held further from the surface, where they become increasing charged by the electron beam of the SEM. Control images of a membrane fouled individually with either oleic acid (Figure A1 (a) and (b)) or gelatine (Figure A1 (c) and (d)) can be found in Appendix A, where the different appearance is eminently noticeable. Oleic acid (oil) adsorption appears as a smooth, dark, opaque pool homogenously filling the crevices of the membrane surface. Gelatine adsorption appears as a dark, semi-transparent, gelatinous coating, speckled over the membrane surface. The emulsion appears differently than either control, but is identifiable as a combination of the two. The adsorption of the emulsion appears speckled homogenously across the surface like the gelatine, however is smoother, more opaque, and spreads farther, with a cake batter like quality, which is the result of the oleic acid bound with the gelatine. The lack of emulsification can be identified by observing both gelatine and oil adsorption separately on a membrane, not shown.
Figure 7: Control membrane left in synthetic stick water solution overnight at 50x (a) and 1000x (b) magnification. Darkened and/or smoother areas are emulsified oil and gelatine adsorbed to the membrane surface. White arrow indicates emulsified oil and gelatine protruding from the surface and being charged by the electron beam of the SEM (appearing white).

Anti-fouling tests demonstrated desorption and repulsion of the (ionized) species from the membrane surface (Figure 8 and Figure 9 compared to Figure 7), which can happen simultaneously on the reactive membrane surface. SEM images in Figure 8 show the effectiveness of increasingly negative capacitive polarization to prevent organics from adsorbing to the surface and/or more effectively desorb them from the surface at increasingly negative potentials. Each membrane surface in figure 8 is visibly cleaner compared to the cake batter-like membrane coverage in figure 7. Organic spots ≥ 20 µm remained on the surface at -0.5, -0.8, and -1.0 V (Figure 8 a,b,c). These spots appeared to be primarily gelatine, based on their color and semi-transparent nature. The organic spot size reduced slightly at -1.2 V and reduced further to appear only in crevices of the membrane at -1.5 V. Oleic acid, the fat component of the synthetic stick water is effectively prevented from adsorbing at potentials more negative than -0.5 V. No corrosion was observed during these potentiostatic tests.

Figure 8: Antifouling membranes at -0.5 (a), -0.8 (b), -1.0 (c), -1.2 (d), -1.5 V (e) at 1000x magnification. White scale bar = 20µm. Gelatine remains adsorbed (dark amorphous areas) at -0.5, -0.8, -1.0 and -1.2 V; trace gelatine in membrane crevices at -1.5 V.
Residual spots of gelatine (as determined by comparison with Fig. A1 (c) and (d) in Appendix A) remain adsorbed at -0.5 to -1.2 V as can be seen in Figure 9. The darker areas are gelatine spots or clusters of gelatine spots remaining adsorbed to the surface. The frequency of gelatine spots increases at -1.0 V. The spot size and frequency diminishes in later tests with increasingly negative potential, resulting in a maxima of gelatine coverage at -1.0 V, compared to -0.5 V and -0.8 V. The reason for the maxima was determined to be protein ionization and unfolding near the surface (Figure 9). The gelatine spot size and frequency is minimal by -1.5 V (Figure 9 e).

Figure 9: Antifouling membranes at -0.5 (a), -0.8 (b), -1.0 (c), -1.2 (d), -1.5 V (e) at 50x magnification. White scale bar = 500 µm. Comparative slight increase in gelatine coverage at -1.0 V

The repulsion effect increases down the length of the membrane to the bottom tip, where the reference electrode was located and the potential was set (Figure 10).

Figure 10: Antifouling membrane at -1.0 V, image is taken at the bottom of the electrode (a) closest to reference electrode and top of the electrode (b) furtherest from reference electrode at 30x magnification, demonstrating that repulsion is a function of distance from the set potential.

The region where the hydrogen evolution reaction begins (but before bubbles are observable) shows some altered behaviour where desorption and electrochemical reactions begin to play a role and mark the transition between antifouling and defouling. At -1.2 V the gelatine spot size remained the same, gelatine pieces could be seen appearing to detach (Figure 11(a) and (c)), and the surface was lightly scattered with small rolled up bits of organic matter close to the surface. The gelatine spot
size reduces significantly to small amounts in membrane crevices at -1.5 V, indicating reductive desorption (Figure 11(b)). The surface at -1.5 V is otherwise clean, indicating reductive desorption is complete and repulsion is effective. The small pieces of organic matter that appear briefly on the surface at -1.2 V could be either (1) organics from the bulk being reacted at the membrane surface before desorption and repulsion or (2) base catalysed polymerization caused by a small localized pH effect due to the onset of hydrogen evolution.

![Figure 11](image)

**Figure 11:** Comparison of antifouling at -1.2 (a) and -1.5 V (b) at 1000x magnification. Close inspection (4000x magnification) -1.2 V (c) shows what appears to be organic delaminating from the surface.

### 4.2.3 Potentiostatic Tests

The antifouling tests showed increased cathode current density with increasingly negative potential (Figure 12). For low negative potentials (-0.5 to -1.2 V) there is a start-up capacitance that levels off to a steady current density which ranges from near zero for -0.5 V to ~ -0.25 mA/cm² for -1.2 V. Both the capacitance and the time taken to reach the steady current increases with increasingly negative potential. The increased capacitance is maintenance of repulsion, whilst the increased current density indicates reaction. The shape of the potentiostatic graph changes between -1.2 V and -1.3 V, indicating a change in reaction type. Capacitance is no longer observed, rather a steady current is seen from the outset indicating a steady hydrogen evolution reaction. Visible hydrogen bubbles occurred at potentials equal to or more negative than -1.5 V (dark blue) and the scallop shapes to the lines at -1.8 V (magenta) are hydrogen bubbles being released. The shape of the curve is different at -1.5 V, visible hydrogen bubbles appeared after 4 minutes but coated the surface, rather than bubble vigorously as per the -1.8 V test. The potentiostatic information fits closely with cyclic voltammetry in that capacitance occurs until -1.2 V, then a steady reaction occurs after, specifically hydrogenation of organics and/or HER. Once hydrogen bubbles are formed, they do not hydrogenate organics without the presence of a catalyst surface, meaning observed hydrogen bubbles signify the potential is too negative for hydrogenation reactions to occur at high efficiency.
Figure 12: Antifouling potentiostatic tests at -0.5 (grey), -0.8 (blue), -1.0 (red), -1.2 (brown), -1.3 (green), -1.5 (dark blue), and -1.8 (magenta) in 1-10th synthetic stick water solution for 2 hours to determine the point of continuous hydrogen evolution instead of repulsion, which occurs at -1.5 to -1.8 V.

In repeated potentiostatic tests at -1.0 V (Figure 13), start-up capacitive current increased, followed by the current levelling off to the same near zero value for the first two cycles. This indicates no reactions are occurring and the set potential is maintaining electrode polarization and repulsion. Repulsion after desorption is evidenced by the increase in start-up capacitance, since desorption of physisorbed materials leaves a greater surface area exposed and this leads to increased start-up capacitive current, but not additional polarization current to maintain repulsion. The third cycle showed even greater start-up capacitance indicating repulsion and then settled at an increased current density (~ -0.15 mA/cm²) indicating a surface reaction (red line in Figure 13) rather than the polarization as seen in the first two cycles. For comparison, operation at -1.2 V is shown, which produced more current to maintain both polarization and reaction (yellow line in Figure 13). Interestingly, the third test at -1 V has the same start-up capacitance profile as the -1.2 V test, indicating repulsion, yet the steady current density is about 40% less, indicating reaction at the limiting current density of -1 V. A fourth test at -1.0 V (black line in Figure 13) was operated with applied potential prior to testing to avoid start-up capacitance and mimic long-term operation to see what the highest current density possible was at this potential. It overlapped well with the current density from the 3rd test suggesting this is the limiting current density for -1.0 V. This series of tests
demonstrated that reductive desorption is possible at sufficiently long time scales at lower potential and may require a pulsing potential technique.

Figure 13: Potentiostatic tests at -1.0 V (1st orange, 2nd blue, 3rd red, and 4th black), and -1.2 V (yellow). Increasingly negative potential results in greater cathodic current. Operation at -1.0V showed increased start-up capacitance from desorption and then repulsion. Increased current is possibly due to protein ionization. Operation at -1.2V showed continued ionization and repulsion.

The corresponding cyclic voltammagrams after the antifouling potentiostatic tests (to test membrane surface stability) show no reaction peaks developing other than HER (Figure 14). The minor increase in the current density of the hydrogen tail indicates a slight reduction of the nickel on the metal surface during prolonged operation (i.e. catalyst activation) at potentials near or greater than nickel reduction, which is expected. Nickel reduction (Ni^{2+}) in organic-aqueous solvents have been shown to occur at -1.08 V SHE [133]. The lack of electroactive reaction peaks developing means only HER or reactions between the adsorbed hydrogen and adsorbed organics (hydrogenation) are occurring. Organic reactions occurring with the adsorbed hydrogen can shift HER to more negative potentials. The most likely reactions are varying degrees of reductive desorption and hydrogenation (protonation), given that at -1.0 V we observe capacitance, ionization and repulsion and at -1.5 V we observe reductive desorption, repulsion and possibly hydrogenation.
Membrane tests were conducted for antifouling as described in Chapter 3. Briefly the membrane module was first flushed with electrolyte solution so that it was permeating and then the potentiostat was turned on at an applied voltage of -1.3 V SHE (Figure 15 and Figure 17). Then the electrolyte feed was switched to the synthetic stick water solution (50% of real stick water example). This was considered time zero, although it took approximately 10 seconds for the synthetic stick water to fill the membrane module. For comparison, MilliQ water, electrolyte (with and without applied potential) and the synthetic stick water solution (without applied potential) were run. Between each test the membrane was acid washed and dried under vacuum pump for at least 20 minutes.

The antifouling concept clearly had an impact in mitigating fouling at potentials concurrent with the hydrogen evolution reaction. Figure 15 clearly shows that the synthetic stick water fouls the membrane to such an extent that there is almost zero flux after 10 minutes and no recordable flux after 20 minutes. By contrast with -1.3 V SHE potential applied to the membrane surface the membrane flux is consistently 9 – 12 L/m²/h (LMH) greater than the test without antifouling potential applied. The permeate flux followed the same initial trend as the test without antifouling potential with the flux decreasing with testing time for ~10 minutes before maintaining a steady flux of 9 LMH. The initial decrease in permeate fluxes both with and without applied antifouling potential was a result of the increased shear force due to the applied potential. The flux decreased further due to the increased fouling that occurred.

4.2.4 Membrane Testing

Figure 14: Antifouling CV of SS membrane in 1-10th solution for -1.45 to -0.2 V at 1 mV/s following potentiostatic tests at -0.5 (dark blue dash), -0.8 (light blue) and -1.0 V (orange).
potential for ~10 minutes is the result of some pore fouling, as the flux decreases linearly with time before achieving steady state. The difference in the initial value of the permeate flux (time 0.1 hr) with and without antifouling potential is the positive result of the antifouling potential, which was applied prior to time zero, before the organic wastewater was introduced, proving antifouling works (Figure 15, dark blue). The initial decrease in permeate flux for MilliQ water and electrolyte, with and without applied potential, is the result of a small amount of pore fouling due to hydrated ions, before achieving steady state. The difference between the permeate flux of the clean MilliQ and electrolyte waters versus the wastewater was the organic content; hence organics caused significant fouling for the wastewater, not salts (Figure 15, orange line). It must be noted that at no stage did the membrane have the same flux with wastewater as either the MilliQ water or the electrolyte (whose flux remained relatively constant regardless of whether potential was applied or not). This indicates that the applied potential was not successful at preventing all fouling, but rather it was able to successfully maintain the permeate flux at ~30% of the pure water value.

Figure 15: Membrane antifouling at -1.3 V SHE, showing successful antifouling of 50% standard solution (50% synthetic stick water diluted with 50% electrolyte). Electrolyte was antifouled initially and wastewater was introduced to the already negatively charged membrane electrode, at low current density, resulting in repulsive electromotive force and fouling avoidance, for effective antifouling. Error is ±7%.

The potentiostatic trace for this membrane (Figure 16) shows the current density increases with time and presumably increased fouling based on the flux results in Figure 15. The current density (between -0.7 and -0.85 mA/cm²) is broadly consistent with that seen when the membrane was
operated solely as an electrode (Figure 12, green line). Interestingly, the increase in current density is relatively constant over time and does not reflect the change in flux performance around 0.15 hours where the flux shifts from decreasing to steady state. After 0.15 hours the constant membrane flux and relatively constant current density is consistent and indicates that the reaction to remove or prevent fouling is in equilibrium with the deposition of new fouling onto the membrane surface.

Figure 16: Potentiostatic test for membrane run in antifouling mode at an applied potential of -1.3V

A second test was conducted to see what happens if the antifouling potential is removed and then reapplied (Figure 17). A new membrane was used but the startup procedure was identical to the previous run. In this case the membrane flux for the 50% synthetic stick water solution with applied potential did not follow the same trend as the test without antifouling potential applied. Rather for the first 15 minutes the flux more closely resembled the electrolyte control tests and suggested the antifouling potential was able to maintain ~100% of the permeate flux. This was due to inherent differences in pore sizes of the membranes used, i.e. pore size enlargement of used membranes, due to acid cleaning between membrane tests. This is evidenced by the higher steady state flux (30 LMH) of the 50% synthetic stick water control (i.e. without antifouling potential applied) and of MilliQ water (36 LMH).

At 15 minutes the antifouling potential was removed for 2 minutes and then reapplied. A clear drop in membrane flux (~30%) is observable in the next time step and indicates rapid fouling, followed by the maintenance of steady state at this reduced flux by the reapplied potential. Indeed, the flux decline is of similar magnitude to the initial fouling observed for the test without antifouling potential (i.e. slope of orange line between 5-10mins). Once the antifouling potential was reapplied the flux did not recover but remained steady (at ~10 LMH higher than the 50% synthetic stick water control) for the remainder of the test. In this case the flux was maintained at 75% of the electrolyte control tests. These results suggest that antifouling potentials are not sufficient to recover membrane
flux once fouled and that the antifouling potential needs to be constantly applied for optimal membrane operation. These results do suggest that antifouling potentials are successful at maintaining high flux (75% to 100% of electrolyte control) given appropriate membrane pore sizes are used, antifouling potential is applied prior to wastewater introduction, and antifouling is maintained continuously during operation.

![Figure 17: Membrane antifouling test at -1.3 V SHE, showing successful antifouling of 50% standard solution (synthetic stick water). Applied potential being turned off briefly and restarted shows repulsion maintains antifouling. Error is ±7%.](image)

At lower potentials antifouling was unsuccessful. Figure 18 shows that the membrane flux cannot be maintained above 0.2 LMH with an antifouling potential of -0.8 V SHE, with the flux following the same trend observed by the synthetic stick water control in Figure 15. The permeate flux was on average lower in this test than in previous tests due to incomplete cleaning by the acid wash, which required a longer residence time in acid for the smaller pores of the new membrane and varied between membranes.
Figure 18: Membrane antifouling test at -0.8 V SHE, showing unsuccessful antifouling of 50% standard solution (synthetic stick water). Error is ±7%.

Permeate from the membrane antifouling test at -0.8 V SHE was tested using UV-Vis to quickly show whether the membrane had successfully filtered the synthetic stick water solution (Figure 19). There is a clear reduction in absorbance between 200 – 300 cm⁻¹ illustrating that the membrane was largely successful at removing oleic acid and gelatine from the feed.

Figure 19: UV-Vis spectra for permeate samples taken from membrane test at an antifouling potential of -0.8 V SHE.
4.3 Discussion

The concept of membrane antifouling, where fouling from organics such as oils and proteins, can be prevented or minimised by using a conductive membrane as a negatively charged cathode is complex and includes several mechanisms across a range of applied potentials. These are illustrated in Figure 20. At low (i.e. close to zero) negative applied potential there is a polarization of the membrane surface which repulses negatively charged fats and proteins. Repulsion is a function of the electromotive force (EMF) in solution between the electrodes and aims to inhibit adsorption of organics at the surface by maintaining a negative electrode polarization to repel negatively charged organics. As the EMF is a function of potential and capacitive polarization occurs regardless of sorption or electrochemical reactions at the membrane surface. Therefore, increased repulsion requires increased negative electrode polarization, that is, a more negative potential, however this can lead to reduction reactions at the electrode surface, such as hydrogen evolution, hydrogenation or base-catalysed polymerization. Reductive desorption of organics commonly results in hydrogenation given sufficient hydrogen ions are present at the electrode surface, such as in water at pH 0-8.

![Repulsion, Adsorption, Desorption Diagram](image)

**Figure 20:** Schematic illustrating the antifouling concepts of repulsion and desorption depending on applied potential. Adsorption mechanisms are shown to illustrate which functional groups of the fats and proteins adsorb. Reductive desorption commonly results in hydrogenation.

In cyclic voltammograms, capacitance is seen as a separation between the forward and reverse current curves.

Figure 4 shows negative capacitive polarization starts at ~ -0.4V SHE and continues as the dominant electrochemical mechanism until ~ -1.2V. The EMF is still present at more negative potentials but the capacitance is overwhelmed by cathodic current to reductive reactions. In solution the capacitive polarization manifests as a double layer containing solvated / charged molecules or neutral molecules with a dipole moment. The double layer acts as an antifouling barrier and prevents physisorption of molecules unless the transmembrane pressure (i.e. static pressure applied on the feed side) exceeds the EMF. This means that increased transmembrane pressures, to promote
higher membrane flux, will require increased negative potentials to maintain repulsion. The trade-off here is that increased negative potentials will result in electrochemical reactions at the electrode surface beyond ~ -1.2 V SHE. Likewise, if the solution is so concentrated with charged molecules that surface charge is small in comparison to the bulk charge, then the capacitive polarization is insufficient to prevent adsorption.

Repulsion during a potentiostatic test appears as start-up capacitive current due to the charging of the electrode surface and rearrangement of organics and other charged molecules in solution. As this process reaches steady state the current levels off to a constant value. For low negative potentials this value is near zero and indicates only that capacitive polarization is preventing adsorption of organics, as evidenced by the SEM images in Figure 8 and Figure 9. As the applied potential becomes more negative, the current values are increased which indicates electrochemical reactions start to proceed. This is observed at ~ - 1.2 V SHE for this system (Figure 12). In practise however, this force was not sufficient to prevent a decline in membrane flux as membrane tests showed that antifouling was only successful at potentials of -1.3V SHE. At lower potentials (-0.6V SHE) the rate of fouling induced by flow through the membrane was greater than the EMF and so the organics could not be prevented from attaching. This finding is significant as it illustrates that for waters with a high organic loading, repulsion only is unlikely to ever be successful because the potential required to generate a large enough EMF will be negative enough to initiate electrochemical reduction of hydrogen or adsorbed organics.

The second mechanism of antifouling is desorption of physisorbed or chemisorbed organics (Figure 20). Desorption of physisorbed materials occurs when the Van der Waals forces and hydrogen bonds are overcome. Desorption of chemisorbed materials requires reductive potential and occurs when an electron that is shared in a chemical bond by the HOMO of the metal cathode with the LUMO of the adsorbed functional group is passed to the functional group, de-hybridizing the electron orbitals and breaking the chemical bond.

Desorption is caused by changes in potential, pH, and ionic strength. Oleic acid and gelatine have different desorption potentials reflecting the different electrical energy required to break the different physisorbed (weak physical) and chemisorbed (strong chemical) bonds [126]. Metals are usually slightly positive without an applied cathodic potential, so anion adsorption dominates. Noble metals have a more neutral change, so zwitterion adsorption dominates. In multilayer adsorption, the first several layers are ordered by ions in response to the surface potential, followed by zwitterion adsorption [134]. Chemisorption can be induced by increased heat and pressure, such as in the conditions of membrane separation of abattoir wastewater. This means that changes in operating conditions can change the potential required to desorb materials which happens at a potential less extreme than the potential of reaction [126].
The pH of solution will determine the ionized form of the gelatine and oleic acid, which determines their emulsification and adsorption conformation onto the membrane surface. Emulsification is important in the abattoir waste water context for two reasons:

1. BSA (which is being represented by gelatine in the synthetic stick water) has optimal emulsifying properties with oil at the isoelectric point (pH 4.7 to 5 [49, 135]), which is close to the pH of the stick water, and
2. Emulsification makes antifouling and in particular desorption more complex because proteins unfold (BSA partially) as they bind to the oil [135], exposing more reactive sites to the membrane surface.

Hence the pH of the solution determines the likelihood of adsorption of oleic acid and gelatine onto the membrane surface and consequently the ease at which they can be desorbed. At alkaline pH’s far from the isoelectric point, the zeta potential and repulsion of oils and proteins is increased, emulsion is minimal and adsorption is unlikely. Under acidic conditions the proteins are positively charged and the opposite is true. This means zwitterion adsorption can dominate a large potential range (Figure 21).

![Figure 21: Ionization forms of protein and oleic acid versus pH. Glycine pKa’s are used as the common amino acid in protein.](image)

By contrast oleic acid adsorption occurs by primarily through physisorption - Van der Waals forces and hydrogen bonding (Figure 21). The double bond of oleic acid forms pi bonds with neutral or negative metals where the double bond is the acceptor and the electrode is the electron donor [126]. Desorption is mainly through repulsion of the pi bonds by the electrode and is typically weaker and occurs as less negative potentials (-0.8 V vs -1.8 V) than gelatine adsorption as seen in the SEM images (Figure 8 and Figure 9).
Ultimately these results show that antifouling is successful but probably requires potentiostatic operation at potentials negative enough to initiate the hydrogen evolution reaction or reductive desorption. The commercial implications of this are likely to be power requirements, on the order of 10W/m$^2$ (using the -1.3V with a current density of ~0.8 mA/cm$^2$) to maintain membrane flux of 10 LMH. Or to put it another way, this translates to an energy requirement of 1 kWh/kL of permeate flux through the membrane, which for treating a stick water stream in typical abattoir [119] may mean a total electricity requirement of 300-400 kWh/d or 12-17 kW. It must be stressed that this power requirement is likely to be highly variable based on the membrane setup and feed conditions.
5 Defouling

5.1 Introduction
This chapter demonstrates the concept of membrane defouling, where fouling from organics such as oils and proteins, is physically or chemically removed using a conductive membrane and electrochemistry. Defouling can use direct or indirect methods at either reductive or oxidative potentials. Indirect methods physically remove organic fouling using bubbles which could be hydrogen bubbles at reductive potentials or oxygen bubbles at oxidative potentials. Direct methods use redox reactions to either oxidize organics when the membrane is operated as an anode or reduce organics when the membrane is operated as a cathode. The operating window is likely to be >0 V SHE for oxidative defouling, bearing in mind that corrosion of the conductive metal membrane will occur at oxidative potentials; and more negative than ~ 1.5V SHE for reductive defouling. Reductive desorption reactions are a direct defouling method that can happen simultaneously to polarization and repulsion. They happen at the transition potential between antifouling discussed in Chapter 4 and defouling as discussed here. The approach taken in this chapter is to characterise metallic membranes for defouling using applied potentials < -1.5V and > 0V SHE. Membranes were first examined as electrodes using cyclic voltammetry, potentiostatic testing and imaging via scanning electron microscopy. Full membrane tests, where the membrane electrode was operated as a membrane, examined the flux and rejection performance at applied defouling potentials of -0.8 V and -2 V.

5.2 Results

5.2.1 Defouling using reductive potentials
Stainless steel hollow fibre membranes were deliberately fouled by applying a thick (~1mm) gel layer of fats (oleic acid) and proteins (gelatine) to the membrane surface. Figure 23 shows scanning electron microscopy images of the heavy fouling on the control (i.e. no potential applied) membrane. The fouling can be characterised as a uniform layer of organics ~1 mm thick, compared to the clean, non-fouled surface (Figure 6).

Figure 23: Heavy fouled control membrane using congealed oil-gelatine emulsion at 50x (a), 150x (b), 500x (c) and 1000x (d) magnification.
Defouling tests (Figure 25) showed the heavy fouling was removed from the membrane surface after 2 hours of applied potential at -2.0 V, -2.5 V and -3.0 V SHE with average current densities at -1.75, -6.20 and -7.35 mA/cm² respectively (Figure 26). Defouling tests were run in succession of each other on the same heavily fouled stainless steel membrane. A portion of the membrane was removed after each test and the remaining section of membrane was tested. Hydrogen bubbles were observed in all tests as froth on the liquid surface above the membrane and as bubbles on the membrane surface at the completion of defouling. SEM images of defouled membrane sections had no visible corrosion and a clear reduction in gel or organic film at the membrane surface. Of note defouling increases with increasing negative applied potential: at -2.0 V SHE fouling is approximately 40% removed (Figure 25(a)), whilst for -2.5 V SHE fouling is approximately 75% removed (Figure 25(b)) and at -3.0 V (Figure 25(c)) fouling is approximately 90% removed. At -3.0 V, a geometric gel pattern (ovals and diamonds as seen in Figure 25(c)) developed across the otherwise clean membrane. Close up images (Figure 25(d)) showed the dark geometric pattern consisted of a polymeric gel. The gel layer was fairly uniform in height with occasional ridges at turning points and intersections. It is hypothesized that the geometric gel pattern was produced by electrochemical polymerization, along the paths of least resistance of the membrane surface, likely during the hydrogen evolution period, given they remain after defouling.
Figure 25: Fouled membranes after defouling at potentiostatic tests at -2.0 V (a), -2.5 V (b) and -3.0 V SHE (c) on SS membrane in 1-10th organic solution for 2 hours (at 50x). Testing at -3.0 V shows hexagonal gel pattern (at 50x magnification). Close up (d) of gel line from defouling test at -3.0 V for 2 hours at 1000x magnification shows raised gel ridge at turning point.

At -2.0 V (Figure 26, blue line) defouling was characterised by a steady reaction at constant current for 1.25 hours and this manifest visually as continuous frothing. At 1.25 hours the current density increased from 1.6 mA/cm² to 2.8mA/cm² indicating a shift in what was happening at the membrane surface. The rate of frothing also increased. It is hypothesized that at this time enough fouling has been removed to allow HER to occur on unfouled surface sections, which in turn increased the rate of hydrogen production. In practise this represents a point at which electrochemical defouling is no longer suitable as it is preferentially producing hydrogen on a clean surface instead of producing hydrogen bubbles to remove the fouling.

High rates of hydrogen production in solution were evident from direct observation and in the potentiostatic curves for -2.5 V and -3.0 V SHE (Figure 26). The noisy nature of the trace indicates here larger bubbles are produced, coalesce and leave the membrane surface, which alters the electrode resistance (and in turn current) at the membrane surface. The high rate of hydrogen evolution is a result of high current density and increased current density was observed at increasingly negative applied potential. At -2.5 V (Figure 26, red line) uniform defouling occurred in the first 25 minutes, observed as tiny bubbles initially coating the membrane and fat, the fat coating the membrane turned from pale yellow to white, followed by frothing with small hydrogen bubbles for 25 minutes. After 25 minutes, an increased rate of hydrogen production led to increased frothing, seen as the noisy current density at 0.5 hrs. However, overall the current density decreased to less than the initial value. Again, this is due to HER occurring on primarily unfouled membrane. At -3.0 V (Figure 26, black line), high rate hydrogen production and frothing was observed for the duration of the test. Defouling current density at -3.0 V shows a similar pattern to -2.5 V, indicating uniform defouling for the first 18 minutes, followed by steady HER for the remainder of the test.
Figure 26: Potentiostatic graphs for defouling tests at -2.0 V (blue), -2.5 V (red) and -3.0 V (black) on stainless steel hollow fibre membrane with heavy fouling (congealed oil-gelatine) in 1-10\textsuperscript{th} organic solution for 2 hours.

The effect of prolonged hydrogen evolution during defouling was tested, by evolving hydrogen bubbles for 2 hours at -2.0 V on a membrane submerged in a synthetic stick water solution (Figure 27). A thin, speckled organic layer was observed and there was some evidence of disruption of the layer by hydrogen bubbles. The formation of the organic film is interesting as it occurred during defouling and hydrogen evolution which is the opposite of the desired result. This suggests that initially applying a negative potential sufficient to generate hydrogen bubbles was effective at defouling the membrane surface but prolonged hydrogen evolution caused a polymerisation reaction to proceed and deposit a thin organic layer on the membrane surface that could not be removed. There are two possibilities: either the hydrogen evolution is directly reducing the organics into a gel layer or the change in local pH caused by prolonged HER is initiating a base catalysed polymerisation.
Figure 27: Prolonged hydrogen evolution at -2.0 V in synthetic stick water solution at 1000x (a) and 2000x (b) magnification. Close inspection shows an organic layer disturbed by circular cavities from hydrogen bubbles.

The CVs and potentiostatic test do not show evidence of direct reduction and so the base catalysed polymerisation theory was tested. The pH of the solution was adjusted from 7 to 14 by adding NaOH to simulate a change in the local pH. Gelling and polymerisation was evident at pH’s more alkaline than 13.5 (not shown). The ratio of organics in the synthetic stick water was adjusted to determine which was more susceptible to base catalysed polymerisation and the results are shown in Figure 28. The centre line represents an equimolar ratio of gelatine to oleic acid and indicates that as the total organic content increases so does the degree of polymerization. Secondly, pure oleic acid polymerized, but pure gelatine did not. This suggests that defouling in situations where significant quantities of hydrogen are produced is likely to have an adverse effect on the system by inducing local pH changes strong enough to polymerize the fat portion of the stick water.
Figure 28: Concentration ratio of oleic acid versus gelatin to determine contribution to polymerization at pH 13.5. The centre line demonstrates that polymerization increased with increasing organic content.

5.2.2 Defouling in the oxidative range

Porous stainless steel hollow fibres were characterised using cyclic voltammetry in both an electrolyte control solution and the synthetic stick water described in Chapter 3. In house made porous stainless steel hollow fibres [122] were a proxy for the commercial AccuSep membranes from Pall due to ease of testing. The cyclic voltammagrams (Figure 29) show a series of organic reactions overlayed on corrosion. Expanding the oxidation potential range of the cyclic voltammagram (Figure 29, red to blue) demonstrates the recurring organic (i.e. defouling) and inorganic (i.e. corrosion) oxidation reactions. Corrosion is evidenced by the overall positive slope of the cyclic voltammagrams, without a flat passivation range. Corrosion begins at ~0.7 V, seen by the increase in current in electrolyte (Figure 29, green). Organic oxidation suppresses oxygen evolution, from ~1.4 V until ~2.3 V, seen by the decrease in current density slope and relative levelling off until 2.3 V. Kolbe decarboxylation [126], oxygen evolution and corrosion happen simultaneously from ~2.3 V until ~3.0 V, where the Kolbe reaction ends and the OER rate increases. The Kolbe decarboxylation reaction on more noble electrodes happens at potentials between 2.1 to 2.8 V, regardless of exact substrate structure [126], giving an overpotential on the corroding membranes of ~0.2 V.
Cyclic voltammetry demonstrated the preferred operational window for defouling stainless steel hollow fibre membranes; however, it did not provide any information about the impact of the oxidative potential on the level of fouling, or the longer-term performance of the electrode, particularly the level of corrosion. The stainless steel hollow fibre membranes were deliberately fouled in a synthetic stick water solution, operated at constant potential (2, 2.2 and 2.4 V) for two to three hours and then the fouling was characterised via scanning electron microscopy (SEM) as outlined in Chapter 3. In some cases, membranes were fouled and defouled repeatedly to observe the impact of corrosion on the propensity to defoul. Control tests (without applied potential) for the electrolyte solution and synthetic stick water solution are shown in Figure 3 and 4 of Chapter 4 and are not reprinted here for conciseness.

SEM images taken after potentiostatic testing for 3 hours at 2.2 V showed >90% of organics were removed from the membrane surface (Figure 30 (a) through (c)). However, significant and uniform corrosion was evident on the membrane surface (Figure 30(b) and (c)). SEM images of repeated tests (Figure 30 (d) through (i)) showed primarily clean membrane with mild corrosion at the top of the membrane, farthest from the reference electrode (and the set applied potential), a thin organics layer with mild corrosion at the centre of the membrane, and a thick organics layer with heavy corrosion at the bottom of the membrane (closest to reference electrode and applied potential).
There is some evidence of circular cavities closest to the reference electrode (Figure 30 (f) and (g)), possibly indicating oxygen bubble breakthrough points in the fouling.

![Figure 30: Potentiostatic test at 2.2 V for 3 hours (1st run) shows clean surface with extensive corrosion at 30x (a), 1000x (b) and 2000x (c) magnification. For the second run at the same conditions we see at 50x magnification a primarily clean membrane at top (farthest from reference electrode) (d), mild corrosion and organics in the middle of the membrane (e), and heavy organics and corrosion at the bottom (closest to reference electrode) (f). The same can be seen at 1500x for the top (g), middle (h) and bottom (i) of the membrane.](image)

SEM images at 2.4 V showed 40-50% of organics were removed from the membrane surface (not shown) with simultaneous corrosion and oxygen evolution. Across multiple tests the removal of organics dropped to 10-20% (Figure 31). Circular cavities in less fouled areas showed what appear to be bubbles presumably removing organics from the surface (Figure 31(a). There is also significant evidence of pitting and other forms of corrosion.
Figure 31: Potentiostatic operation at 2.4 V (third run); showing circular cavity which looks like a bubble which has exploded defouling the membrane surface at 1500x magnification (a). At 30x magnification (b) the membrane is visible in a few places with smooth, heavy gel-like fouling and corrosion covering the rest.

In order to understand the process of repeated fouling and defouling / corrosion cyclic voltammagrams were run after successive defouling runs (Figure 32). Corrosion was measured after the first test (Figure 32, black), seen as the reductive tail of exposed metal from 0.65 to -0.3 V. Passivation, defined here as the increase in surface resistance, was observed after repeated tests in two places. The first is as expected in the passivation of the metal surface with oxides from 0.65 to -0.3 V and the second as the increased oxidation current at ≥1.4 V which from SEM images looks like an increased in adsorbed organics on the membrane surface reducing the effective electrode surface area. Counterintuitively this means the organic adsorption was suppressing corrosion and prevented the metal from being re-oxidized.
Figure 32: Cyclic voltammograms after defouling potentiostatic operation at 2.2 V for 2 hours, shows corrosion on first run (black), then passivation and corrosion on following runs (blue dash). Oxygen evolution & organic oxidation begins ~1.3 to 1.4 V.

Defouling occurred by oxygen bubbles removing organics (oxygen evolution started at ~1.4 V) and possibly corrosion removing attached organics. Passivation occurred by subsequent organic adsorption to the defouled surface. SEM images at 2.0 V showed 20-30% of organics were removed with simultaneous oxygen evolution and heavy corrosion (not shown) in the first test and 10% in the third test. Circular cavities in the soft organics presumably showed bubbles removing organics from the surface. Corrosion underneath organics indicated corrosion after defouling, followed by continued organic deposition and (possibly) continued defouling.

The potentiostatic and cyclic voltammetry information closely fits with the SEM images in that there was a transition from oxygen evolution and defouling to corrosive defouling to surface passivation with adsorbed polymerized organics in the first run. This was followed by continued passivation in repeated tests. This demonstrates that increased oxidative potential increases the rate at which organics adhere to the surface and passivate the corrosive defouling. Ultimately these results show that there is no operational window for successful oxidative defouling with a stainless steel membrane because corrosion starts before effective defouling through oxygen evolution and / or oxidation of the organics can begin. The corrosion then both inhibits oxidative removal organics and in fact actively helps organics adhere to and passivate the membrane surface. This process occurs faster at increased potentials.
5.2.3 Defouling on a platinum electrode

Corrosion was a significant issue for oxidative defouling on a stainless steel membrane. It must be remembered that stainless steel membranes were chosen as a low cost example of a conductive membrane suitable for electrochemical cleaning. Hence the corrosion in the oxidative range was not unexpected. However, to provide a full picture for oxidative defouling a platinum electrode was used as a comparison. This allowed both better characterisation of the reactions happening at the membrane surface and an opportunity to see what happens when corrosion is removed from the system. The cyclic voltammagrams of pure electrolyte, gelatine (in electrolyte), oleic acid (in electrolyte) and their emulsion (synthetic stick water solution) is shown in Figure 33. Here we see increased capacitance with the addition of oleic acid and gelatine in the oxidative and reductive range. Gelatine was not fully dissolved for the gelatine only test, giving reason to why it initially had minimal capacitance. After it was emulsified, i.e. fully dissolved as the synthetic stick water solution, oleic acid dominated the capacitance profile. Emulsification leads to similar capacitance as oleic acid, a HER reduction peak similar to that of oleic acid and an OER oxidation peak between the two. Gelatine OER follows electrolyte OER, while oleic acid and the emulsion OER occurred prior to electrolyte OER, indicating oxidation reactions. Gelatine HER slightly preceded electrolyte HER, while oleic acid and emulsion HER occurred prior to electrolyte HER, indicating hydrogenation reactions occurring in each. The visible OER range (oxygen bubbles) on platinum occurred $\geq -2.1$ V. The onset of oxidation reaction current started at 1.3 V. A passivation range occurred from $\sim1.3$ V to 0.2 V, where the Platinum oxide reduced. The reduction reaction range occurred from 0.2 V to $\sim -1.05$ V, where visible HER (Hydrogen bubbles) occurred at $\sim -1.05$ V. Defouling was tested over the range of visible oxygen evolution ($\geq 2.0$ V) as oxygen bubbles were expected to be the defouling mechanism.
Figure 33: Cyclic voltammagram of electrolyte, then added gelatine, then added oleic acid, then emulsified gelatine and oleic acid, on platinum at pH 7. Shows organics increase capacitance and the onset of oxidation current in organic solution is \( \approx 1.3 \) V SHE. Shows oleic acid is more electroactive than gelatine in the reductive range of \( \leq -0.7 \) V SHE.

Looking more closely at the oxidative range, the CV (Figure 34) shows a distinctive peak for the reductive desorption of organics, demonstrating that oxidation during cyclic voltammagrams increases the chemisorption of organics. The position and decrease of the reductive peak with each cycle of the emulsion with oxidation (Figure 34, green) indicates reductive desorption of organics, just prior to hydrogen adsorption and HER.
5.2.4 Power Requirements of Defouling

Finally, it is important to consider the power requirements of using electrochemical methods to defoul a membrane in situ. For reductive defouling, which appears to be the only successful method for defouling, the SEM images combined with the potentiostatic information suggest that short pulses of more negative applied potential will be more effective at defouling than longer pulses at less negative potentials. First we consider that after two hours -2.0 V the effective defouling was ~ 40% of the membrane, at -2.5 V the effective defouling was ~ 75% and at -3.0 V the effective defouling was ~ 90%. Then we define two new units to describe the membrane defouling: energy intensity (Wh/m²) to reach the HER threshold as describe in section 5.2.1 and power supplied to the membrane (W) as displayed in Table 2. From the standpoint of energy used to defoul unit area of membrane, there is very little difference across the range of applied potentials. However, this analysis doesn’t include what happens to the membrane flux and a separate unit, energy requirement per litre of permeate would be more useful. Therefore, the precise operational strategy must include the flux recovery when the system is operated as a membrane rather than simply removing fouling.
Table 2: Energy data for defouling membranes

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>Membrane Area defouled (total) (cm²)</th>
<th>Current Density (mA/cm²)</th>
<th>Power supplied to membrane (W)</th>
<th>Energy Intensity (Wh/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2</td>
<td>0.452 (1.13)</td>
<td>1.6</td>
<td>3.6</td>
<td>87</td>
</tr>
<tr>
<td>-2.5</td>
<td>0.525 (0.75)</td>
<td>7.6</td>
<td>14.3</td>
<td>87</td>
</tr>
<tr>
<td>-3</td>
<td>0.33 (0.37)</td>
<td>6.8</td>
<td>7.5</td>
<td>90</td>
</tr>
</tbody>
</table>

5.2.5 Membrane Testing

Membrane tests were conducted for defouling as described in Chapter 3. Briefly the membrane module was first flushed with electrolyte solution so that it was permeating and then the feed was switched to the synthetic waste water solution (at 50%). It was important to ensure the membrane was already fouled before the defouling potential was applied. In the first instance the membrane was fouled for at least 0.25 hours before the defouling potential of -0.8V SHE was applied (Figure 35). The membrane clearly began to defoul with almost a doubling in flux from 4.4 to ~8 LMH over the next 10 minutes. This was in direct contrast to the synthetic stick water without applied potential which fouls the membrane to such an extent that there is almost zero flux after 20 minutes and no recordable flux after 25 minutes. The defouling potential was not turned off in this test and it is clear that there is a negative impact on flux after 10 minutes, wherein the flux gradually declines to 2.5 LMH after 45 minutes of testing (30 minutes of defouling potential). This corresponds well with the electrode testing in Section 5.2.1 where prolonged defouling resulted in a polymerized gel layer on the membrane surface.
Defouling at -0.8 V SHE

In the second instance a defouling potential of -1.5V SHE was applied after 0.04 hours (it was not possible to maintain sufficient current densities at higher potentials as per the electrode tests in Section 5.2.1) and then after in a cyclic manner (Figure 37). The membrane used had been tested for
both antifouling and defouling and had significant acid wear which contributed to its low initial flux by enlarging the pore size and leading to significant pore fouling (and rusting) before testing. Pure water flux prior to testing (not shown) was exceptionally high. The increased pore size meant the initial flux of organic wastewater was high, leading to a greater initial rate of irreversible fouling through pore blockage.

Figure 37: Membrane defouling at -1.5V SHE. The potential was applied in cycles with the arrows indicating when the potential was applied and turned off. Error bars are ±7% but the absolute error of the setup is ± 0.2 LMH.

The cyclic defouling results at -1.5V SHE were ultimately unsuccessful. The positive effect of the defouling potential can been seen with limited resolution. Very small amounts (one or two drops) of permeate were collected periodically and correspond to the small increases around 0.21, 0.29 and 0.42 hours. However, given the length of the permeate line between the membranes and the trap it is unclear whether the collection of these drops has any relation to the applied potential or just coincidence. Regardless it is clear that once the membrane fouled, recovering flux to an acceptable level was not possible at -1.5 V SHE over 5 minute intervals. This also suggests that the membrane fouling is rapid and the defouling potential needed to be applied very close to the zero-time point.

Defouling of heavy fouling was successful for potentiostatic tests at -2.0 V SHE and more negative (Section 5.2.1, Figure 25), where defouling potential was applied for ~2 hours. Defouling did not show considerable recovery from heavy fouling at -0.8 V and -1.5 V at short time intervals (Figures 35 & 37) and these potentials may be appropriate for antifouling only. The differences between the tests were both the more negative potential and the longer time interval of the successful defouling tests. Defouling of the (pall) membranes at ≥-2.0 V SHE was not performed due to equipment limitations. Defouling with less negative potentials (≤-1.5 V SHE) may be successful at longer
applied times (≥18 minutes to 2 hours), not 5 minute intervals. Defouling with more negative potentials (≥ -2.0 V SHE) will most probably be successful at moderate applied times (≥18 minutes) to achieve significant flux recovery. Defouling at short time intervals (5 minutes) may be most successful at highly negative potentials, e.g. -3.0 V SHE.
5.3 Discussion

Desorption of chemisorbed species in the reductive range requires electrochemical reduction reactions, instead of dosing with acid, base or defouling surfactants. Reduction reactions include both reductive desorption, usually hydrogenation, and the hydrogen evolution reaction (HER). Ideal desorption is hydrogenation, as it is a simple organic electrochemical reaction and is fast in aqueous solutions, depending on the material, resulting in immediate defouling. Defouling using hydrogen bubbles can occur simultaneously with reduction reactions at a given potential, however most reactions happen slower than HER.

Defouling tests using the membrane as an electrode demonstrated desorption of heavy fouling from the membrane surface with hydrogen bubbles from -2 to -3 V SHE. Operation at -2.0 V (Figure 26, blue line) produced a smooth, increasingly negative current density due to lower current density for HER. The change in electrochemical reduction rate at ~1.25 hours indicated the increased current density due to the lowered resistance to HER on the defouled sections of membrane, which then slowed the overall defouling rate but increased the HER rate. The continued negative slope of the current density when the test stopped at 2 hours indicates it had not reached steady state and was likely still achieving some defouling at a lower rate.

Operation at -2.5 V (Figure 26, red line) produced an initial steep negative slope in current density, characteristic of reductive desorption, followed by a change to a positive slope demonstrating a sudden transition from reductive desorption to the HER. This was accompanied by the fat coating turning white in the first thirty minutes and then the rate of hydrogen bubbles increasing after the transition in current density. Reductive desorption could occur with the adsorbed organics at the surface as the heavy fouling omits water from performing HER. As these organics are reduced at the large negative potential with the minimal water available, they desorb and water is able to permeate the fouled cake. This operation potential is usually beyond that experienced by organics in operation in aqueous solution tests because it is beyond HER, which dominates with water available. After ~30 minutes, the sudden delamination of the cake leads to newly exposed surface area being available for HER, which now dominates the reaction rates. The transition occurred because the surface of the defouled section of the membrane had lower resistance than the fouled section, which likely resulted in a slower defouling rate in favour of hydrogen production, based on comparison of the SEM images (Figure 25). Transition to the HER did not signal complete defouling, as the SEM showed a small portion of fouling remained on the surface. The positive slope shows the HER required less current density than reductive desorption. This is supported by galvanostatic tests (Appendix C) that showed steady state HER occurred at a minimum potential of -2.1 V after less than an hour in operation and so with increased potential less current is required for
HER. This means that operation at -2.5 V had not achieved steady state after 2 hours as the surface was still (charged) partially fouled and was discharging (fouling) as hydrogen bubbles were produced.

Operation at -3.0 V (Figure 26, black line) produced an initial steep negative slope in current density for the first ~18 minutes, similar to that at -2.5 V, due to reductive desorption of the heavily fouled organics, follow by steady state current density displaying the jagged peaks of HER. The transition demonstrates a sudden desorption, similar to -2.5 V, however the steady state current density thereafter demonstrates more reactions are happening, in addition to HER. Specifically, we believe this is a reductive polymerization with the organics in solution at this exceptionally negative potential as outlined below. The SEM images (Figure 25(c)) showed a geometric pattern of gel on otherwise completely clean surfaces, indicating non-random production of reductive polymer on the defouled membrane surface, giving evidence of a reduction reaction in addition to HER. The gelling that occurred at -3.0 V resulted from the reductive polymerization of organics in solution on the relatively clean membrane surface. Therefore, at -3.0 V, gel is also being formed in a side reaction to HER on the electrode during general removal of organics by a mechanism of radical anions and/or dianions.

The applied potential for organic reduction reactions and reductive desorption of chemisorbed materials overlap with the applied potential range for desorption of physisorbed materials by polarization (Chapter 4) and is shown schematically in Figure 38. The point at which the HER becomes visible is where we consider the limit of the antifouling range and point where the mechanism for defouling begins.

![Figure 38: Range of defouling potentials and associated defouling and/or electrochemical phenomena](image)

Hydrogenation dominates organic reduction reactions and occurs at potentials where hydrogen is adsorbed to the electrode surface, prior to HER without organics (-1 V). Metals with low hydrogen evolution overpotential easily adsorb atomic hydrogen and hydrogenate organics at lower potentials than metals with high hydrogen overpotential. Organic adsorption is preferential to hydrogen adsorption below the adsorption isotherm potential and shifts the (visible) HER to a more negative potential. Increased hydrogen partial pressure makes catalytic hydrogenation thermodynamically favourable, meaning the increased pressure at the membrane surface will favour organic hydrogenation. Oleic acid undergoes saturation and ionization, with possible polymerization with
insufficient protons availability. Gelatine is reductively desorbed and simultaneously hydrogenated and ionized.

5.3.1 Reduction reactions of oleic acid

The electrocatalytic hydrogenation of unsaturated carbonyls of olefins is well established and the C-C double bond is reduced before the carbonyl. Hydrocarbon anion radicals, the intermediates of olefin reduction, are powerful nucleophiles that readily hydrogenate to saturated monomers when hydrogen production has a low overpotential, such as on nickels, platinum/palladium, and cadmium [126]. The unsaturated version of an olefin usually has a less negative half wave potential than the saturated version. For poly-unsaturated carbonyls of olefins of the form \( \text{CH}_3(\text{CH}==\text{CH})_x\text{CHO} \) at pH 7, the \( E_{1/2} \) = -0.7 to -1.05 with increasing \( x \) from 2 to 5 [126]. Therefore it is reasonable to estimate the electrocatalytic hydrogenation \( E_{1/2} \) of oleic acid to be \(-0.7 > x > -1.4\) SCE (or \(-1.25\) on iron complexes for similar material [114]). The differences in half wave potentials of hydrocarbons from one solvent to another is very small [114] implying the saturation potentials in literature can be used as a guideline.

The mechanism of electrocatalytic hydrogenation (protonation) happens by homogeneous electron transfer [114] on electrodes with lower hydrogen overpotentials, for example the hydrogenation of the double bond of oleic acid is shown in the reaction schema below.

1. Homogeneous electron transfer

\[
A + e^- \leftrightarrow A^-^* 
\]

2. Mono protonation of the radical anion; anion radicals occur because the bonding or non-bonding single occupied molecular orbital is always lower energy than antibonding LUMO (rate determining step). Two possible polymerisation side reactions with the double bond are possible, detailed after.

\[
A^-^* + H^+ \leftrightarrow AH^* 
\]

3. Disproportionation (a) is preferred depending on electrode, leading to possible complexes including another polymerization, detailed after.

Either (a) \( AH^* + A^-^* \leftrightarrow AH^- + A \) or (b) \( AH^* + e^- \leftrightarrow AH^- \)
4. Irreversible mono protonation

\[ \text{AH}^+ + \text{H}^+ \rightarrow \text{AH}_2 \]

The reductive polymerization reactions for step 2 include:

Polymerization side reaction, negative radical with double bond [126]

Dimerization of two anion radicals (desorption), followed by neutral molecule addition [126]

Disproportionation of 2 radical anions to dianion (1) and neutral (1) molecule [114]

The reductive polymerization reactions for step 3 include:

Dialkylation (polymerizing alkylation), neutral radical R* with double bond, possibly terminated by another neutral radical [126]
Monomeric polymerization occurs if hydrogenation of the anion radicals is avoided (step 2), such as on metals with low adsorption of hydrogen ions, like mercury, lead, graphite, and tin [126]. The reduction potential of the hydrocarbon predicts whether the second reduction will be by the electrode or another anion radical (step 3). Transfer from another anion radical, homogeneous electron exchange, is fastest when the potential is $-1 < E^0 < -2.3$ V vs. SCE, and slower beyond $-2.3$ V [126]. Monomers without stearic hindrance can lead to extensive polymerization because the radical anions grow by either radical addition (dimerization) or neutral molecule addition. Alternatively, radical anions may self-protonate [114] or disproportionate to starting material and dianions [126]. Higher potentials produce dianions during hydrocarbon reduction, which readily undergo hydrogenation. When hydrogenation is avoided, dianions can desorb and polymerize with neutral molecules or disproportionation [126]. Salts and counter-anions have an electrostatic stabilizing effect on dianion formation, increasing the disproportionation reaction constant and shifting the delta $E_0$ by up to 600 mV more positive, increasing the probability of polymerization on electrodes with high hydrogen overpotentials, and increasing the probability of hydrogenation on electrodes with low hydrogen overpotentials [114].

The electrochemical reduction of carbonyl acids is difficult and sometimes impossible, including carboxylic acids, however aldehydes can be obtained (at potentials $\sim -1.2$ V on rhodium [114]. Saturated aldehydes are easily reduced to alcohols, or reduced and dimerized (hydrodimerized) to glycols. Generally, the highest glycol yields are in alkaline media and from longer chain saturated aldehydes. Carbonyl intermediates are hydrogenated using metals with low hydrogen overpotentials. [126]. Alkali metal cations enhance activation of the carbonyl, by enhancing its electrophilicity.
5.3.2 Reduction reactions of gelatine

The electroreduction of gelatine involves the ionization of the amino acids and structural hydrogen bonds, the reductive desorption and simultaneous hydrogenation of the chemisorbed functional groups, and the repulsion of the negatively charged gelatine globule. Because the oleic and gelatine will be negatively charged, positive ions allow for some coagulation. The electroreduction of amino acids from ketones to alcohols in protic conditions is one route of ionization, the other being indirect ionization by pH changes to solution resulting from hydrogen production [114]. Ionization of the gelatine can occur by various routes, the simplest of which is by hydroxide ions produced during HER. Organic reductions that require a large conformation change in the transition state are rare, because there is the time for transition and the energy of solvent rearrangement, which makes the activation energy very high for these reductions [114]. Therefore, ionization and reductive desorption will be kinetically favourable to complete electroreduction of a gelatine globule. Reduction of the intermolecular disulphide bonds present in proteins [42] leads to their chemical detachment, reducing electrostatic interactions and decreasing fouling.

The mechanism of reductive desorption is the reduction of the metal bond to the organic functional group, which happens at the potential of the bond reduction, M-N for example, or at the potential of hydrogen evolution, whichever comes first based on the pH of the solution [123]. Reductive desorption in alkaline conditions gives reduced functional groups and (temporarily) oxidized metal surfaces. Reductive desorption with hydrogenation occurs prior to HER above the organic (preferred) adsorption potential, and therefore hydrogen bubbles occur after desorption.

5.3.3 Prolonged defouling

Ultimately, defouling improved with more negative potential. The mechanism is a combination of hydrogen bubbles by HER when there is access to water and reductive desorption without access to water. The defouling rate increased and the transition to defouled surfaces where HER could occur happened faster at more negative potential. To improve (i.e. reduce) the power used for defouling, pulsing the potential until the current transitions from smooth (reductive desorption) to bumpy (HER) would be an effective method and indicator for defouling.

Prolonged hydrogen gas production leads to alkali changes of the pH close to the electrode, by stripping H⁺ ions from water to produce H₂, leaving OH⁻. We used pH tests to simulate the alkali pH profile developed at the membrane surface (pH ≥13.5) showed oleic acid is subject to base catalysed polymerization, however gelatine is not. Specifically, this was base catalysed polymerization of the double bond in oleic acid (Figure 39), which caused precipitation of the polymer and re-fouling.
Figure 39: Base catalysed polymerization of oleic acid

Base catalyzed polymerization is a step-growth polymerization process where many small chains are made initially and the polymer chain length increases exponentially as they join. The base catalyzed polymer was negatively charged, according to pH readings, which allows repulsion by the electrode and makes removal by back-flushing more successful. The operation at -2.0 to -3.0 with heavy fouling did not experience base catalyzed polymerization because the organics attached to the surface were still being reduced continuously, at varying rates. This means there was no additional hydroxide ion production as the HER was not proceeding.
6 Conclusions and Recommendations

This work demonstrates the concept of membrane antifouling and defouling, where fouling from organics, such as oils and proteins, can be removed and prevented or at least minimised by using a conductive membrane as a negatively charged cathode. Maintaining a negative charge on the membrane surface repulsed negatively charged organics in solution, which in turn, both inhibited adsorption and/or induced them to migrate away from the negatively charged membrane surface, preventing concentration polarization and membrane fouling and improving permeate flux. There is an ideal operating window for negative potential to perform antifouling, enough to induce repulsion but not negative enough to initiate redox reactions at the membrane surface. To avoid redox reaction scenarios, including hydrogen evolution and the associated alkali pH increase, the operating window is recommended between -0.4 V to -1.2 V. Continuous operation is recommended at -1.2 V to ensure repulsive rather than reactive scenarios. Whilst operation at -1.5 V showed the better results, continuous operation will lead to alkali pH profiles causing base catalysed polymerization.

There is also an ideal operating window for negative potential to perform defouling, enough to produce high rate HER defouling but not negative enough to initiate reductive polymerization reactions at the membrane surface. To effectively defoul the membrane with short operating times and minimal power, the operation potential is recommended at -3.0 V for short pulse applications, without continued hydrogen production following defouling to avoid reductive polymerization.

To improve organic cake removal, high negative potentials should be combined with increased crossflow until the current density readings show the dominant reduction reaction has transitioned from reductive delamination to HER. Combined application of the two methods is ideal for continuous membrane performance. It serves to repulse organics at high pressure with negative potentials that avoid reduction reactions whilst defouling as needed with short high negative potentials at ≥ -3.0 V with increased cross flow for the duration of reductive defouling. If the conductivity of the solution limits power efficiency, it is recommended to use sodium bicarbonate to increase conductivity, as this will increase bubble production and avoids electrochemical side reactions that would decrease product value.

To improve power efficiency, catalytic materials are recommended for membrane production. Nickel and its alloys are recommended as the best low cost material for electrocatalytic reductive desorption and hydrogenation of organics.
7 References


8 Appendix

8.1 Appendix A

Figure A1: Control SEM images for adsorption of oleic acid at 50x (a) and 1000x (b) magnification and gelatine at 50x (c) and 1000x (d) magnification in electrolyte. Oleic acid appears as smooth, iridescent pool of oil and gelatine as semi-transparent gelatinous coverage.
8.2 Appendix B

Several tests were performed with a smooth stainless steel bar so as to limit corrosion and further explore oxidative defouling. The cyclic voltammograms of electrolyte and organics on 316L stainless steel show increased current density and capacitance with increased organic concentration (Figure B2). Organic oxidation occurs after the onset of oxygen evolution (OER) at 1.3 V.

Figure B2: Cyclic voltammagram of electrolyte (orange) and increased organic concentration, 1/10th (light blue) and standard (dark blue) on 316 stainless steel at pH 7. Shows increase of current density and capacitance with increased organic concentration and organics oxidation (increased current density) occurs after the potential of oxygen evolution, 1.3 V. The increased current density at the foot of the oxidation peak is combined capacitance and chlorine gas evolution. Fe||Fe2+ -0.41 V, Fe||Fe3+ -0.04, Fe2+||Fe3+ 0.77 V

Cyclic voltammagrams on 316L stainless steel bar in standard organic solution before and after defouling tests (Figure B3) demonstrated corrosion on new stainless steel at ~0.9 V and corrosion of stainless steel after corrosive potentiostatic tests starting at ~0.65 V, indicating the protective oxide layer had been removed by potentiostatic operation at ≥ 0.65 V. Cyclic voltammagrams of stainless steel 316 in electrolyte before and after potentiostatic tests demonstrated corrosion on new stainless steel at 0.7 V and after corrosive potentiostatic tests at 0.65 V with significantly increased current density (not shown). The extension of the passivation range and positive shift in corrosion potential on new stainless steels (0.7 to 0.9) is due to the organic coating. Defouling potentiostatic tests in electrolyte showed pitting corrosion at 1.14 V (Figure B4 and B5). Corrosion results in increased
current density in cyclic voltammagrams, therefore cyclic voltammagrams with increased current density could be due to both organic oxidation and corrosion, requiring comparison of organics versus electrolyte.

Figure B40: Defouling cyclic voltammagram for stainless steel bar in standard organic solution at 500 mVs before (black) and after (red dash) potentiostatic tests at 2.2 V; before testing (black), shows passivation region up to ~0.65 V, increased capacitance from 1 V to 1.8 V and oxygen evolution and organic oxidation begins ~1.35 V (black); after testing (red), shows passivation up to ~0.5 V, then steady corrosion from 0.65 V to 1.35 V, and corrosion combined with organic solution oxidation at 1.35 V. Fe || Fe2+ -0.41 V, Fe || Fe3+ -0.04, Fe2+ || Fe3+ 0.77 V

Figure B4: Clean stainless steel 316 bar at 50x & 1000x, shows smooth oxide layer with shallow grain boundary oxidation. Long lines in 50x image are extrusion marks from manufacturing.
Defouling tests on smooth stainless steel 316 showed increased defouling and minimal corrosion at 2.0, 2.2 & 2.4 V (2 hours). The defouling tests showed increased anodic current density with increasingly positive potential. Defouling tests showed defouling and corrosion initially (Figure B6, black) and ongoing passivation in repeated runs (Figure B6, blue). Passivation resulted from the combination of organic oxidation leaving a thin protective layer of organics on the surface and corrosion reaching steady state. The smooth stainless steel showed clearer defouling results than the membranes, likely due to the smooth surface being better able to desorb oxidized organics and had less rough surface susceptible to corrosion. A thicker chromium oxide layer may also be responsible.

Defouling Potentiostatic Tests on Stainless Steel 316

Figure B6: Defouling potentiostatic tests at 2.2 V SHE for 2 hours (3x) in standard organic solution, showing corrosion in run 1 (black), passivation in run 2 (not shown) with greater current than run 3, and continued passivation in run 3 (blue dash).

SEM images show the effectiveness of increasingly positive potential to remove organics (Figure B7). At 2.0 V, ~25% of organics were removed with minimal corrosion, however pitting corrosion was observed (Fig. 28, top left). Organics appeared in the grain boundaries of some of the surface, reducing the visible corrosion there. At 2.2 V, ~55% of organics were removed with minimal corrosion, no observable pitting and organics in the grain boundaries of most of the surface. At 2.4 V, ~95% of organics were removed with minimal corrosion, no observable pitting and an extremely
thin layer of organics in the grain boundaries. The presence of an organics layer in the grain boundaries was correlated to significantly fewer corrosion products on the surface in all tests. This implies the thin organic layer in the grain boundaries is protecting the surface from more extensive corrosion, which often initiates at grain boundaries.

Figure B7: Defouling on stainless steel 316 bar in standard organic solution at 2.0 V (left), 2.2 V (middle) and 2.4 V (right), showing decreasing organic coverage with more positive potential at 50x (top) & 1500x (bottom). A pit can be seen in the 50x image of the defouling test at 2.0 V (top, left).
8.3 Appendix C

The galvanostatic defouling tests showed increased anode current density resulted in increased potential, which settled during operation to 2.1 V (Figure C1), the potential of visible oxygen evolution. The cyclic voltammograms for each galvanostatic test showed exactly the same behaviour as the potentiostatic tests (Fig. 30), at higher current density. This demonstrates the same reactions happened at greater current density, specifically oxygen evolution, corrosion and possibly organic oxidation. Current density increased on the cyclic voltammograms as current density increased in galvanostatic tests. SEM images showed successful largescale defouling, however revealed a thin layer of organics and mild corrosion in each test. Increasing current density resulted in larger oxygen bubbles at 2.1 V. Increasing current density resulted in increased defouling at 2.1 V, however the slightly thicker organic layers at 2.72 and 4.08 mA/cm² were due to larger bubbles not defouling as effectively as small bubbles.

![Figure C1: Defouling galvanostatic tests at increasing current density for 2 hours in standard organic solution, showing potential levels off to the potential of corrosion and then organic polymerization and corrosion.](image)

Defouling at low current density (1.36 mA/cm²) resulted in low potential (≤1.92 V) (Figure C1, black). The lower current density and corresponding potential agrees with the cyclic voltammogram for the best potentiostatic defouling test (at 2.2 V) and operated below the potential for visible oxygen evolution. SEM images showed surfaces that appeared to be 100% defouled with uniform corrosion, however a thin uniform organic layer remained, blocking the membrane pores (Figure...
C2, left). This implies small bubbles, as indicated by a small current density, are better at defouling than large bubbles created at high current density.

Defouling at increased current density (2.72 mA/cm²) resulted in increased potential, which settled to 2.1 V. SEM images showed surfaces that appeared 90% defouled, however a thin organic layer remained of variable thickness thicker than the layer at 1.36 mA/cm², across the membrane (Figure C2, middle). Corrosion products were visible below the thinner organic layers. Active defouling was only evident (circular cavities from bubbles) for the large scale remaining organics. SEM images showed no signs of active defouling at the small scale for large portions of this thin organic layer, which were uncharacteristically smooth. (Figure C2, middle). Oxygen evolution is visible at 2.1 V and the current density was sufficient to produce oxygen bubbles; however, the lack of small scale defouling can be explained by bubble channelling. Areas of lower resistance, such as the top of the membrane, produced more and/or larger bubbles at high current density than high resistance areas, resulting in uneven and incomplete defouling at the small scale. It is also possible that the membranes were initially defouled and then continued operation at high positive potential caused organics to adsorb.

Defouling at further increased current density (4.08 mA/cm²) resulted in increased potential, which settled to 2.1 V, and vigorous oxygen bubble evolution. SEM images showed surfaces that appeared defouled, however a thin organic layer remained of similar thickness to the test at 2.72 mA/cm². This thin layer however showed the classic signs of active defouling and membrane pores appeared

Figure C2: Defouling galvanostatic tests at 1mA (left), 2 mA (middle) and 3 mA (right) showing large-scale successful defouling at 50x (top), however close up inspection at 1500x (bottom) reveals uniform corrosion at 1 mA (left), uniform organic deposition/polymerization at 2 mA (middle), and heavy corrosion and thick organic deposition at 3 mA (right).
regularly. Some pores appeared to be the epicentre of circular cavities from bubbles, implying the bubble was produced inside the pore and escaped from it, defouling the membrane in the process. Cracks in the organic layer made it appear cake-like and may have been in the delamination process. Corrosion products were visible. Active defouling of the remaining large scale fouling even showed clean membrane underneath the circular cavities left by bubbles (Figure C3). This demonstrates that increased current density does lead to increased defouling. It also supports the idea that channelling was occurring and limited the effectiveness of defouling at the small scale.

Figure C3: Active defouling at 4.08 mA/cm² showed clean membrane underneath the circular cavities left by oxygen bubbles (at 150x). Demonstrates possible channelling at the top of the membrane where resistance was lower.

The potential repeatedly settling to 2.1 V at increased current density demonstrated the oxygen evolution reaction was at 2.1 V and excess current resulted in excess oxygen bubbles. The cyclic voltammagrams show no change in slope at 2.1 V, meaning the oxygen evolution that started at ~1.4 V simply became visible at 2.1 V and no organic oxidation (Kolbe) reaction is occurring. Therefore, 2.1 V is the limiting potential at which oxygen evolves from the surface. Galvanostatic defouling was technically most effective at low current density, as this had the smallest organic layer and used the least power, however only at 4.08 mA/cm² do membrane pores become regularly visible again due to vigorous defouling. In conclusion, galvanostatic defouling works well for largescale defouling, however was unable to completely defoul the membrane sufficient for reuse.
8.4 Appendix D

8.4.1 Fundamental electrochemical reactions of defouling

Electrochemical reactions can occur by (1) direct reaction with the electrode or (2) indirectly with an intermediate, which reacts directly with and is regenerated by the electrode. Direct reactions require adsorption of the reacting species. Reactions can occur between adsorbed species or between adsorbed and solution species depending on the rate of electron transfer in a given reaction. Desorption regenerates the reactive site on the electrode and depends on the reaction, the electrode material and the potential. If species do not desorb, then the electrode loses reactive surface sites and continued surface reactions cannot be completed, i.e. poisoning. Adsorption, desorption and poisoning depend on the adsorption kinetics of the electrode material for any given reaction.

A series of electrochemical and chemical reactions occur in organic electrochemistry to complete a redox reaction and achieve desorption, usually electrochemical, followed by chemical, follow by electrochemical (ECE). The order depends upon the electrode material and reaction. Chemical reactions are usually rate limiting and include molecular reconfigurations while attached to the surface.

Electrochemical reactions require a transfer of charge, electrons, between species. The energy of reactions is plotted by their theoretical Standard Electrochemical Potential \([E^\circ(V)]\), however real systems always have a loss in energy, called an overvoltage, which adds to the potential \([E^\circ(V)]\) of reactions. Cathodic reaction potentials become more negative and anodic potentials become more positive. Different materials perform reactions by different processes resulting in different rates (kinetics) and overvoltages. Tables of standard electrochemical reaction potentials are in the appendix.

Electrons are shared in a bond between the adsorbed species and electrode by either physisorption (hydrogen bonds & Van der Waals forces) or chemisorption (ionic & covalent chemical bonds). Chemisorption has hybridized electron orbitals and the small amount of charge shared is measured by electrochemical instruments, however physisorption is not. The amount of charge passed in electrochemical redox reactions is greater than that of adsorption, due to the complete transfer of the electron. Desorption is not automatically favourable simply because the shared electrons may be in a lower energy state while adsorbed. Changing the energy state of the electrode, the Electrochemical Potential \([E^\circ(V)]\), changes the energy state of the shared bond and can induce desorption of physisorbed species or activation and further electrochemical reaction of chemisorbed species.
Electrochemical reactions occur on the surface and in the pores of the membrane. According to Ohm’s law, the potential difference changes down the pore as material resistance increases, making reactions at higher potential possible inside the pores [56, 136], such as OER or HER. In porous electrodes, this can result in bubble formation and reduce flux [137].

8.4.2 Defouling electro-reduction

The reduction of organics with hydrogen, hydrogenation, is a simple organic reaction and common industrial practice used for the production of hydrogenated oils, such as petrochemical cracking and margarine. Hydrogenation requires hydrogen gas and a catalyst surface, to reduce the activation energy of electron transfer. Catalytic hydrogenation is performed at high temperature and pressure to solubilize high concentrations of hydrogen gas and achieve high production rates. In margarine production, by-products can include isomers, trans-fats. Electro-catalytic hydrogenation (ECH) of organics is possible at low temperatures and pressure on catalytic cathode surfaces. Industrial ECH is carried out on high surface area cathodes in flow through conditions. ECH margarine production results in smaller isomerization ratios. Organics will not auto-hydrogenate with H₂ gas, therefore hydrogen bubbles released from the cathode will only defoul a membrane by physical cake displacement.

The electro-reduction of organics with hydrogen, specifically electro-catalytic hydrogenation (ECH), occurs at and above the potential of hydrogen evolution, HER, as the electrocatalyst facilitates the transfer of an electron and hydrogen ion to the organic. Hydrogenation of the double and triple bonds in hydrocarbons and proteins occurs at lower potentials before the reduction of other functional groups, such as the carboxyl and amine groups. The saturation of bonds results in release from the catalyst surface [138]. Reduction without desorption can happen if the adjacent adsorption sites are not hydrogenated, such as in organic (aprotic) solvents, or heavily fouled membrane surfaces where cake compression has excluded water. Organic reduction reactions that occur at HER potentials or greater are typically carried out in inert organic solvents to avoid hydrogenation. Reductive anionic polymerization is possible only if hydrogenation is avoided [126] (p.266 & p.969). The protonation potential is minimized by the stability of the intermediate anion radicals, such as by the pi orbitals of unsaturated hydrocarbons, resulting in highly reducible large hydrocarbon compounds with double and triple bonds to more saturated compounds. Hydrogenation of organics can be achieved on platinum, palladium and nickel surfaces, which have a low hydrogen overpotential. Reductive desorption of bonds other than carbon, such as nitrogen, phosphorous and sulphur found in proteins, also occurs by a hydrogenation mechanism, however at elevated potentials to the carbon bond [106, 114, 123, 126].
The general reaction mechanism for electrochemical hydrogenation (protonation) mechanism of organics with simultaneous hydrogen evolution is (1) the formation of a stable anion radical, followed by (2) the addition of a protons until a neutral molecule is produced. The chemisorbed bond desorbs with the last proton transfer that achieves neutrality. Hydrocarbon double bonds are hydrogenated in more basic conditions, at highly cathodic potential, by an EEC mechanism with two electron transfers to produce a dianion, followed by double protonation. In more acidic conditions, at less cathodic potential, hydrogenation follows an ECEC mechanism with one electron transfer (producing a radical anion), followed by protonation (producing a neutral radical), and then the process repeats a second time. Hydrocarbon radicals of carboxyl groups are either immediately reduced to carbanions and protonated to aldehydes, or form an alkyl radicals and protonate to an alkane [113]. Electrocatalytic hydrogenation of aldehydes and ketones convert the carbonyls to alcohols. Isomerization is a result of partial hydrogenation, re-adsorption and desorption of chiral molecules [138]. Isomerization does not consume electrons, so it cannot be detected by electrochemical measurements. For the majority of hydrocarbons, anion radical formation and hydrogenation occurs at the position of the greatest highest occupied molecular orbital (HOMO) charge density. Exceptions include when the electric field affects the charge distribution of the molecule and in aprotic solvents. Protonation in protic solvents, such as water or methanol, have fast kinetic rates and small activation energies [126]. The protonation rate at the electrode is diffusion controlled in aqueous solution, including for most hydrocarbon hydrogenations. Olive oil and many other fatty acids and oils can be electro-catalytically hydrogenated at high rate and low temperature and pressure on catalysts such as nickel and its alloys [125]. Electro-fenton indirect reduction mechanisms are not covered here, however they are noteworthy since stainless steel membranes were used and industrial processes exist.

8.4.3 Defouling electro-oxidation

Theoretically, the oxidation of organics to CO$_2$ is possible at potentials less than the potential of oxygen evolution (1.23 V SHE) and never exceeds 0.2 V SHE. However, the kinetics are extremely slow [106] and in practice the organic oxidation potentials of short chain hydrocarbons vary between 0 and 0.70 V RHE [139], depending on the species and electrode. Oxidation of organics on noble metal electrodes commonly produce CO (i.e. poison), requiring the need raise the potential to the oxygen production potential and oxidize the CO to CO$_2$, cleaning the electrode [139]. Oxidation on catalysts, which increase the electrochemical rates by lowering the overpotential, commonly produce polymers (poisoning) at potentials below the OER point, and include Pt, Pd, and certain metal oxide anodes including IrO$_2$, Ru-TiO$_2$, Ir-TiO$_2$ and PbO$_2$ [106]. The general mechanism of
organics oxidation on catalytic metal oxide anodes (MOx) uses both adsorbed oxygen and adsorbed hydroxyl radicals and produces radical derived products, which form with other radicals or solvent. Products include dimers (R-R), disproportionation by-products, and hydrogenation products (RH + RH-H2). The general electro-oxidation reaction mechanisms of oleic acid include the ubiquitous Kolbe decarboxylation mechanism is [126], which commonly results in an irreversible dimer polymerization, and the Hofer-Moest disproportionation mechanism, resulting in alcohols and esters (ROH & ROOCR).

The general reaction mechanism for electrochemical oxidation/combustion of organics with simultaneous oxygen evolution is (1) the oxidation of water to an OH radical on the metal oxide surface, removing one hydrogen ion and electron, (2) the option of either (a) oxidizing the OH radical further to temporarily adsorb it into the lattice of the oxide anode and removing the second hydrogen ion and electron, or (b) reacting the hydroxyl radical with organics in solution to remove the second hydrogen ion and electron along with the oxygen [106] [140]. If the lattice adsorbs the hydroxyl radical (2a) then the metal oxide anode can selectively oxide organics and/or produce oxygen (O2). Organic oxidation and oxygen evolution are competitive reactions [59] and OER is not a guarantee of complete organic oxidation at a potential, as catalysis depends on the material. Further, intermediates may not easily oxidize and poison the electrode. Carbon monoxide is a common poisonous intermediate for organic oxidation/combustion [139]. Intermediate reactions may favour oxidation into polymer chains instead of mineralization (CO2). Polymerization is another form of poisoning. Materials that adsorb the hydroxyl radical (2a) have a low oxygen (OER) overpotential and result in incomplete organics oxidation, including carbon, graphite, IrO2, RuO2, Pd and Pt [106, 140]. If the lattice reacts the hydroxyl radical (2b) then the metal oxide will non-selectively oxidize adsorbed organics and/or produce oxygen (O2). Non-selective oxidation results in complete organics oxidation, i.e. organic mineralization (CO2), given enough hydroxyl radicals (reactants) are produced for reaction completion, near the surface of the electrode. Materials that react the hydroxyl radical have a high oxygen (OER) overpotential, including SnO2, PbO2 and BDD [106, 140] [58].

Producing oxygen bubbles at high rate will require low OER overpotential materials. Adsorbed organics will selectively oxidize and desorb, simultaneous to OER, resulting in polymerization and poisoning during operation given the heterogeneity of the abattoir wastewater. Therefore, the ideal electrode material for defouling the reactive membrane surface would be OH radical catalysts. Raising the anodic potential of materials with a low OER overpotential past OER into the potential of hydroxyl radicals will only produce more oxygen and expand the potential range to include
additional organic reaction mechanisms, like Kolbe, and will not produce large quantities of hydroxyl radicals. Oleic acid electro-oxidation is limited at high potential by the Kolbe reaction on metal oxides, however on catalytic mixed metal oxides, MMO, and other AEOP electrodes, high potential oxidation and oxygen evolution are not limited and their use can result in improved flux performance.

The potential of oleic acid oxidation, specifically decarboxylation, occurs at a similar potential to the solvent oxidation [127]. Organics suppress electrolyte decomposition, allowing organic electrosynthesis to happen at potentials far more positive or negative than electrolyte decomposition. Oleic acid decarboxylation has been shown at ~1.45 V SHE in aqueous solution, resulting in greater current density than electrolyte [127].

Oleic acid oxidation on RuO$_2$ Dimensionally Stable Anodes (DSA) [76] similarly showed oleate had the same oxidation onset potential as the electrolyte, however with lower current density for oleate at 0.64 V SHE, attributed to surface adsorption inhibiting OER. Based on that, the reaction was determined to be indirect likely indirect oxidation. Further, it was found anodic degradation of oleate by electrolysis poised the potential close to the oxygen generation potential (1.445 V SHE on RuO$_2$) did help improve anaerobic degradability [75].

Olive mill (olive oil) wastewater from 48 to 10 gCOD/L showed electrolyte oxidation suppression over the range of potentials measured by cyclic voltammagram ($-0.56 < E < 1.84$ V SHE) and shifted the OER more positive than electrolyte (~1.42 to 1.6 SHE) and HER more negative than electrolyte (~-0.35 to -0.55 SHE) [77]. The lower current density of the waste demonstrated indirect oxidation.

The electro-oxidation of olive mill wastewater was investigated to decrease the organic load before anaerobic digestion. Various anode materials were tested at high voltages [78] and high current densities (200 to 300 A/m$^2$ [141] [73]) and it was concluded that conductive diamond electrodes were superior, due to the fact that they are efficient enough to be mass transferred controlled, not kinetically controlled [74].

Given the size and complexity of proteins and their oxidation intermediates, incomplete oxidation is common during electro-oxidation. Protein desorption may be readily achieved using hydroxyl radicals. The repulsive force on the protein molecule in an electric field [54] can be increased by increasing the overall zeta potential of the molecule. The hydroxyl groups on carbon chains,
including proteins and oils, can be oxidized to carboxyl groups with hydrogen peroxide, \( \text{H}_2\text{O}_2 \), which increases the zeta potential of the molecule. Hydrogen peroxide can be produced by either AEOP at an anode or by water reduction at a cathode with oxygenated water [71, 142]. In an undivided cell, such as used in this work, anodes made of AEOP materials could produce hydroxyl radicals sufficient to improve the zeta potential and ionization charge of proteins, assisting in migration away from the cathode. If produced at the cathode, \( \text{H}_2\text{O}_2 \) will defoul the cathode surface, however this is assuming wastewater treatment where COD can be reduced and spoilage by chemical auto-oxidation is a non-issue. For product recovery of organics, alternate membrane materials are preferred to electrochemically hydrogenate and desorb organics or physically defoul by hydrogen bubbles, resulting in intact and even quality improved organic filtrate cakes.