Overcoming fouling in desalting industrial organic solutions by electrodialysis

Ananya Yuvaraj

Delft University of Technology

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By

Ananya Yuvaraj

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Thesis committee:	Prof. dr. Jules van Lier,	TU Delft
	Dr. Ir. Ralph Lindeboom,	TU Delft
	Dr. Ir. David Vermaas	TU Delft
Supervisors:	Ir. Giacomo Bandinu	Lenntech
	Ir. Pooja Halvawala	Lenntech

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All I am I owe to my mother.
-George Washington

Abstract

Lignocellulose is an abundant source of feedstock and consists of hemicellulose, cellulose, and lignin. Pre-treatment of lignocellulose is done to fragment lignin and hydrolyse the hemicellulose and cellulose fractions into simple sugars which is then converted into high-end products like bioplastics in a bio-refinery. The pre-treatment generates a mix of sugar solutions, lignin breakdown products and inorganic ions from the chemicals used in the pre-treatment. However, the high concentration of inorganic ions acts an inhibitor for fermentation and needs to be removed. Ion-exchange is traditionally used to remove the inorganic contaminants, but the high concentration of ions in the process solution makes it unfeasible. Hence, electrodialysis is investigated as an alternative process to desalt the sugar solutions for downstream processes. However, while the sugars are neutral compounds, the other organics are negatively charged and can cause fouling on the positively charged anion-exchange membrane.

The main objective of this research is to analyse whether electrodialysis is a feasible solution to desalt two organic lignocellulosic process waters when accounting for organic fouling. The process waters are C_5C_6 and C_5 sugar solutions and the main ions present are sodium and sulphate. A desalting rate of 60% is set as a target for these two ions and the experiments are done using a lab-scale electrodialysis set-up. Tests are run to check the desalting rate, effect of treatments such as filtration, powdered activated carbon (PAC) and acidification, persistence of fouling and the effect of cleaning-in-place. The increase in average resistance and run time is used as an indicator of membrane fouling.

The raw C_5C_6 sugar solution could not reach the desalting target due to the formation of a sludge-like precipitate and has an extremely high resistance of 215 ohms. However, once the solution is filtered, a desalting of 75.5% (Na^+) and 66.5% (SO_4^{2-}) is achieved. The average resistance also drops to the range of 40-50 ohms. The fouling after a set of four repeat runs is removed by a CIP. This restores the resistance and hence the fouling is deemed to be 'reversible' in nature. On the other hand, the C_5 sugar solution did not show an improvement in performance after filtration. Although a desalting of 65% (Na^+) and 81% (SO_4^{2-}) could be achieved after filtration, the average resistance rose to 130 ohms. A CIP did not have any effect as the average resistance continued to rise with each experimental trial. This increasing resistance also increased the run-time and led to a drop in efficiency of desalting. The main reason for fouling in both cases is attributed to the presence of lignin degradation compounds. Due to its recalcitrant nature, lignin is not easily broken-down during pre-treatment and is more concentrated in the C_5 sugar as compared to the C_5C_6 sugar solution due to its production process. In C_5 sugar, the irreversible fouling pattern is hypothesized to be due to adsorption whereas in case of C_5C_6 sugar the reversible fouling pattern is cake fouling. PAC was dosed to remove the organic foulants in C_5 sugar and improved the average resistance to 48 ohms and significantly reduced the run time. Desalting of 61.4% (Na^+) and 87.2% (SO_4^{2-}) was reached. Acidification protonated the feed and reduced the charged interactions, thereby both reducing run time and the average resistance. Desalting of 65.79% (Na^+) and 68.02% (SO_4^{2-}) was reached after acidification.

To conclude, the studied ED system could desalt the organic C_5C_6 and C_5 sugar solutions after a treatment step. Lignin degradation products were found to heavily foul the AEM membranes as its increased presence in C_5 sugar solution led to a more severe fouling which could not be restored even with a chemical CIP. However, mitigation of the degradation products in the pre-treatment step could ensure that the solution was desalted by the ED unit. Thus, quantifying the composition of organic solutions is imperative to predict the propensity of fouling in an ED unit.

Acknowledgement

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Contents

List of Abbreviations

AEM	Anion Exchange Membrane
CEM	Cation Exchange Membrane
CEEM	Cation Exchange End Membrane
ED	Electrodialysis
EC	Electric Conductivity
ERS	Electrode Rinse Solution
I	Current
IEX	Ion Exchange
mol	mole
min	minutes
EPS	Extracellular Polymeric Substances
LCD	Limiting Current Density
NOM	Natural Organic Matter
HMF	Hydroxymethylfurfural
R	Resistance
V	Voltage
CIP	Cleaning-in-place
ATR-FTIR	Attenuated Total Reflectance- (Fourier-transform Infrared)
AC	Activated Carbon
RO	Reverse Osmosis
EDR	Electrodialysis Reversal
π-π	Pi-Pi (hydrophobic-hydrophobic interaction)
DC	Direct Current
COD	Chemical Oxygen Demand
PAC	Powdered Activated Carbon
R_i	Run number (R1 is Run 1)
T	Trial (consists of 4 runs)
2,4- DHBA	2,4-Dihydroxybenzoic acid

1
Introduction

1.1 Background: Separation of lignocellulosic process solutions

A biorefinery is a renewable equivalent of a petroleum refinery, and is used to manufacture useful products such as bioplastics, biochemicals, biofuels etc. from a variety of feedstock [1]. The feedstock consists of the non-edible portions of the food production chain and lignocellulose (dry plant matter) is the most abundant biomass with a production of $1x10^{10}$ MT annually worldwide [2]. Lignocellulose consists of lignin, hemicellulose and cellulose, the latter two being polysaccharides, a source of sugar monomers and undergoes fermentation to be converted into high-value products [3]. The lignocellulose is pre-treated with dilute acid to fragment the lignin and hydrolyse the hemicellulose and cellulose to sugars. This process generates a solution which is rich in inorganic ions from the acidic pre-treatment, organic sugars from the hydrolysis and lignin fragments in the form of lignin degradation compounds. For downstream fermentation processes, the inorganic ions act as inhibitors and hence have to be removed [4]. The desalting of inorganic ions is traditionally done by ion exchange. Ion exchange is a process in which unwanted soluble ions are removed by exchanging with other ions of the same charge using an ion-exchange resin. Separate anion and cation exchange resins are used to remove anions and cations respectively, whereas uncharged organics remain in the solution. The resin can be tailored to target specific ions and hence is a popular process used in industries. These resins have a high capacity to remove specific unwanted ions, provided the concentrations are low [5]. However, resin materials have a finite exchange capacity and when the resin is unable to exchange ions any longer, it must be regenerated [6]. Regeneration of the resin is done using concentrated acid or base. If the concentration of contaminants are high (in the order of several grams/L), the ion exchange cycle becomes very short and the regenerant quantity required reaches unsustainable levels [7]. Hence, for desalting solutions with a higher concentration of inorganic ions, electrodialysis can be a more feasible and economical solution.

1.2 Electrodialysis and fouling

Electrodialysis (ED) is a membrane separation process which transfers salts through an ion-exchange membrane under the driving force of electric potential. The ion exchange membrane stack consists of alternating negatively charged cation exchange membrane which allows cations through and a positively charged anion exchange membrane which allows anions through. The ions are transferred from the feed solution by passing through this stack, to produce a concentrated saline stream (the concentrate) and a demineralized stream (the diluate), under the influence of electric field. Electrodialysis is a fairly mature technology but has found many new applications recently such as a separation process in the food industry to desalinate cheese whey, molasses, fruit juices etc [8]. ED can handle higher ionic concentrations as it is used commonly for treating brackish water. ED is also preferred when desalting larger volumes of water making it suitable for larger scale applications. Moreover, unlike ion exchange it does not require regeneration, thus reducing use of concentrated chemicals. Greiter et al. have compared electrodialysis and ion exchange process to desalinate salt from organics (sodium gluconate salt from whey protein) [19]. It was found that the electrodialysis process had a lower

energy demand, lesser wastewater production of lower COD and a lesser environmental impact.

However, some organic by-products can be charged compounds and organic compounds generally carry a negative charge [9]. The positively charged anion exchange membranes are more prone to interaction with these negatively charged organics and can cause a phenomenon termed 'fouling'. Fouling is a term used to describe the unwanted attachment of species on the surface or the inner part of the membrane [10]. Fouling is an unwanted phenomenon and can cause negative effects such as alterations in membrane structure, decreased transfer of inorganic ions through the membrane and reduced process performance [10]. As lignocellulosic waters contain high concentrations of organic compounds, fouling is a cause for concern.

1.3   Previous research and research gap:
In a review paper on the membrane processes in biorefinery applications, desalination by ED only covered the desalination of glutamic broth, amino acid solutions and spent black liquor from Kraft pulping process [20]. The few literature references which treated lignocellulose solutions used the wastewater effluent from producing bio-ethanol as the feed solution [21].
The lignocellulosic wastewater effluent after production will have a different composition and properties as compared to the process water solution used in the production process. Scientific literature on the topic of desalting lignocellulosic process water with electrodialysis was not available to the best of the author's knowledge. Hence, it is interesting to investigate whether the lignocellulosic process water could be used in the ED unit for desalting.

1.4   Research Objective and sub-research questions
The main objective of this research was to analyse whether a lignocellulosic organic-rich process solution could be desalted using electrodialysis considering possible organic fouling in the membrane.
   - The first objective was to characterise the two lignocellulosic feed solution and identify the potential foulants.
   - The second objective was to check if target desalting could be achieved and observe the interaction between the solution and the membrane.
   - The third objective was to observe the fouling pattern of the two solutions and investigate potential pre-treatment strategies.

To answer the main objective, the main research question was derived as noted below:
"Is electrodialysis a feasible option to desalinate lignocellulosic process solutions when accounting for organic fouling?"
Based on the literature search, the research gaps and the main research question described above, four sub-research questions were formulated to structure the research framework.

   1   Can 60% desalting be achieved using ED without any anti-fouling strategies when desalting the lignocellulosic process solution?
   2   What impact does the composition of the organic solution have on the membrane fouling?
   3   What is the interaction between the organic solution and the membrane which leads to membrane fouling?
   4   Can membrane fouling be reduced by implementation of a pre-treatment?

1.5   Research approach

Through a literature study, the treatment scheme of a lignocellulosic process solution in a biorefinery and its characteristics are described in Chapter 2. The various types of fouling, fouling mechanisms and its effect on an ED unit is also covered in Chapter 2. This helped to formulate a hypothesis on the expected behaviour of an ED unit to desalt a lignocellulosic process solution. The experiments were designed keeping the hypothesis in mind as described in Chapter 3. The results of the experiments are explained in Chapter 4 and discussed with reference to scientific literature. The conclusions drawn from this study are detailed in Chapter 5, in the form of answers to the sub-research questions. Finally, recommendations are provided in Chapter 6 for future research and potential improvements.

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2

Background literature

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2.1 Lignocellulosic process solutions

Lignocellulosic biorefineries utilize non-fossil fuel feedstock to produce biofuels, bioplastics, biochemicals, energy etc. This lignocellulosic feedstock is termed 'second-generation' feedstock and is sourced from agricultural waste (corn stover, wheat grass, sugarcane bagasse etc.), forestry waste (wood chips, poplar wood, sawmill residues) and grasses [22]. It is approximated that 1.5×10^{11} tons of agricultural waste alone is generated globally every year, and the prospect of its reuse as feedstock in manufacturing useful products, has both economical value and environmental benefits [22]. Figure 1 shows the main steps in the conversion of lignocellulosic biomass to bio-based products in a lignocellulosic biorefinery.
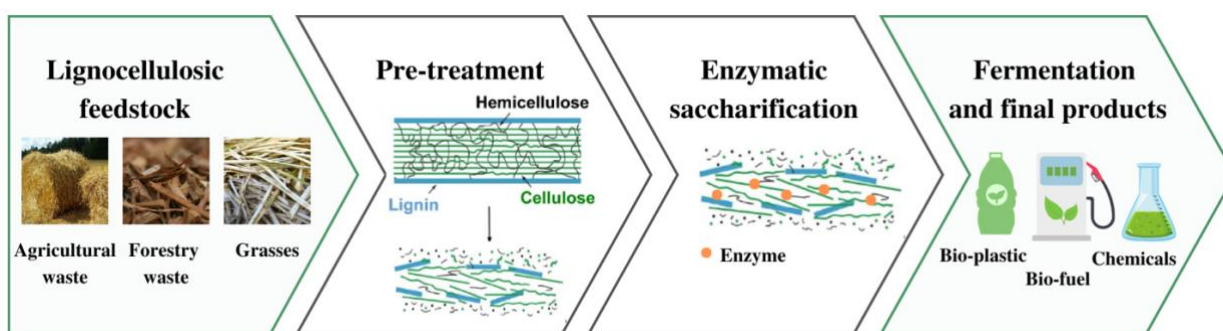

Figure 1:The main steps in the conversion of lignocellulosic biomass to bio-based products. Image retrieved and partially modified from [23].

The internal structure of lignocellulosic biomass consists of cellulose, hemicellulose, and lignin, bound together in a matrix. Several pre-treatment processes have been developed to disintegrate lignocellulosic biomass into cellulose, hemicellulose, and lignin fractions as seen in Figure 1 (Pre-treatment). The main aim of the pre-treatment is to make the cellulose and hemicellulose accessible for enzymatic saccharification by disrupting the lignin. Both hemicellulose and cellulose fractions are polymers of sugars and hence is a valuable source of fermentable sugars [2]. Lignin plays an inhibitory role in the enzymatic hydrolysis process by forming a physical barrier and limits the access of enzyme to cellulose and hemicellulose [24]. Lignin is resistant to microbial attacks and in undesirable during downstream fermentation processes [25]. A few commonly used chemical pre-treatment processes of lignocellulose are described briefly below:

- *Alkaline pre-treatment:* This is a widely used method and alkaline reagents such as sodium hydroxide, calcium hydroxide and ammonia is used. The lignin and hemicellulose fragments solubilize in the alkali medium, thereby making the cellulose available for enzyme interaction for further conversion to sugar solutions. By using NaOH, the process conditions are generally mild and result in high lignin solubility and limited formation of degradation products such as HMF and furfural [2].
- *Acidic pre-treatment:* Acidic pretreatment of lignocellulose is based on the ability of the acid catalyst (such as sulfuric acid) to generate hydronium ions, which break down the cellulose and hemicellulose into soluble sugar via hydrolysis [26]. The hydrolysis

<div style="text-align: center">4</div>

of hemicellulose can produce sugars (glucose, xylose, mannose, and galactose) and organic acids (formic and acetic acid), whereas cellulose can be hydrolyzed to glucose The acidic pre-treatment can be done using either a concentrated acid or a dilute acid catalysis.

- *Organosolv pre-treatment:* Organosolv pre-treatment methods utilize a mixture of organic solvents (such as ethanol, methanol, acetone etc.) to remove lignin before enzymatic hydrolysis of the cellulose fraction [2].

The cellulose and hemicellulose fractions are then converted to sugars upon hydrolysis and further microbial fermentation to bio-ethanol or other bio-chemicals [27]. Other pre-treatment strategies such as mechanical pre-treatment, combined chemical and mechanical pre-treatment and biological pre-treatment also exists. The process water solutions used in this thesis are lignocellulosic sugar solutions, extracted after a dilute acid pre-treatment.

2.1.1   Sugar extraction process solutions

Two lignocellulosic sugar solutions (C_5C_6 and C_5 sugars) were supplied by OÜ Fibenol and its extraction procedure after a dilute acid pre-treatment is shown in Figure 2.
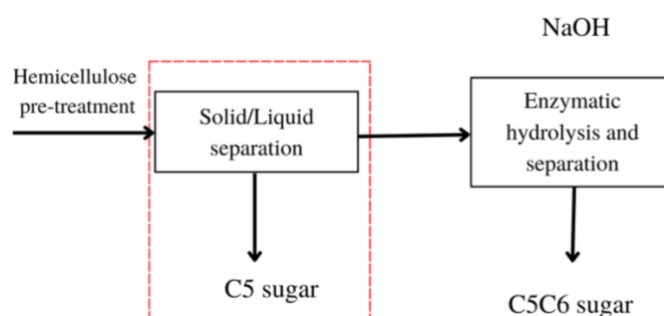

Figure 2: C_5 and C_5C_6 sugar extraction process after dilute acid pre-treatment.

As mentioned in Section 2.1, the acidic pre-treatment disrupts the lignin wall and exposes the hemicellulose and cellulose. The dilute acid can also readily hydrolyse hemicellulose to C_5 sugar solution together with some fragments of soluble lignin [28]. This liquid fraction and biomass solids [29] is separated in a single-step by a solid-liquid separation by centrifugation. The liquid fraction contains the C_5 sugar, organic acids, some soluble lignin in the form of lignin degradation products such as phenols, aldehydes, furans, and other aromatic compounds [30]. It also contains a significant inorganic ion concentration due to the chemicals added for pre-treatment, pH adjustment and the process equipment.

The C_5C_6 sugar extraction process had two steps- after the dilute acid pre-treatment, the pH is first raised by the addition of NaOH to 5 for enzymatic hydrolysis to occur. The enzymatic hydrolysis hydrolyses the cellulosic material to sugar [31]. Then separation is done by means of a filter press. The neutralizing step (addition of base) also effectively removes lignin, phenolic acids, furfural, and aldehydes [32]. This is because these organic molecules are readily soluble in bases, and alkaline reagents are more efficient for lignin removal (delignification) as it reacts primarily with lignin [25]. This method is found to have very low level of lignin bound to sugar (1-3%)[33].Thus, the C_5 sugar is taken to have a higher concentration of lignin and degradation products as compared to the C_5C_6 sugar.

2.1.2 Characteristics of lignocellulosic process water solutions

Process solutions in lignocellulosic biorefineries are characterised by high-strength organic and salt loading with a wide particle size range [34]. The organic content consists of the sugars and other by-products such as lignin, its degradation compounds, humics etc. The presence of significant inorganic ion concentration is attributed to the chemicals added during pre-treatment, pH adjustment and hydrolysis and possibly from the process equipment as well [35]. The presence of these salts can cause an inhibitory effect during fermentation (downstream process) and hence requires a desalting step. After sugar hydrolysis/saccharification, a complex mixture of hexose (and/or pentose depending on the treatment), lignin degradation products and inorganic ions is obtained, which needs further downstream separation [36].

The main components of the lignocellulosic C_5C_6 and C_5 sugar solutions are outlined in Table 1. Sodium and sulphate are the two most abundant inorganic ions in the process water. Glucose is the main sugar component in the C_5C_6 sugar solution and xylose is the main sugar component in the C_5 sugar solution.

Table 1:Main components of the two lignocellulosic process water solutions

Parameter	Unit	C_5C_6 Sugar	C_5 Sugar
pH	-	4.9	3.7
EC	mS/cm	9.4	8.1
COD	g O_2/L	107	143
Sodium	mg/L	3807	3186
Sulphate	mg/L	3764	4576
Glucose	g/L	23.36	22.12
Xylose	g/L	10.77	58.25

Dilute acid pre-treatment can also produce additional lignin by-products such as furans, weak organic acids, lignin degradation products, humins, and phenols [37]. Lignin is a complex organic polyphenolic polymer which is aromatic in nature and hence cannot be analysed as a single compound. Lignin degradation products on the other hand can be analysed and are usually either aromatic, polyaromatic, phenolic or aldehydic in nature [2].

2.2 Desalting of organic process solutions

As mentioned above, desalting is necessary to prevent the high concentrations of sodium and sulphate from acting as inhibitors in the downstream fermentation process. Currently, this process is carried out by ion exchange. Ion exchange is a separation process which separates ionic and polar compounds based on the affinity of the compound (due to charge) to be adsorbed on the ion exchange resin. In the ion exchange process, the ionic contaminants to be removed are replaced from cation exchange resin and anion exchange resin respectively. Ion exchange technology is the most efficient desalting process for removing contaminants in low concentrations [7] but, the sulphate and sodium concentrations in the given feed solutions are significantly high. This leads to drawbacks such as frequent regeneration of resin. Once the resin is saturated it must be regenerated with strong acid or base [18]. It was shown that for one equivalent of ionic salt removed, 1.2-3 equivalents of strong acid or 1.3-2 equivalents of a base is needed [18]. Hence, operation costs for desalting are high, the waste streams produced are highly saline and large quantities of acid and base are needed which makes the ion exchange process environmentally unsuitable. The volume of water treated in ion exchange is inversely proportional to the ionic concentration and the regenerant consumption per unit volume of treated water increases with increase in salinity [40]. Hence, for desalting significant volume

of solutions with high inorganic ion concentrations, electrodialysis can be a more feasible alternative.

2.3 Electrodialysis

Electrodialysis (ED) is a membrane separation technology which uses ion-exchange membranes to separate ions from an aqueous stream using electric potential. The ions are transferred from the feed solution to the concentrate, by passing through alternating cation and anion exchange membranes (CEM and AEM), to produce a concentrated saline stream (the concentrate) and a demineralized stream (the diluate), under the influence of electric force as seen in Figure 3. The electrodes provide the driving force (electric potential) when connected to an external power source and the ions in the presence of the electric field migrate to oppositely charged electrodes through the membranes leading to formation of the concentrate and diluate. Spacers are placed between membranes to separate it and prevent contact. The complete system of ion exchange membranes, spacers and electrode is called an ED stack (Figure 4). The two outer compartments recirculate an electrode rinse solution (ERS), which is a highly conductive salt solution separated from the diluate and concentrate streams [41]. The ERS allows the transfer of current from the electrodes to the stack.
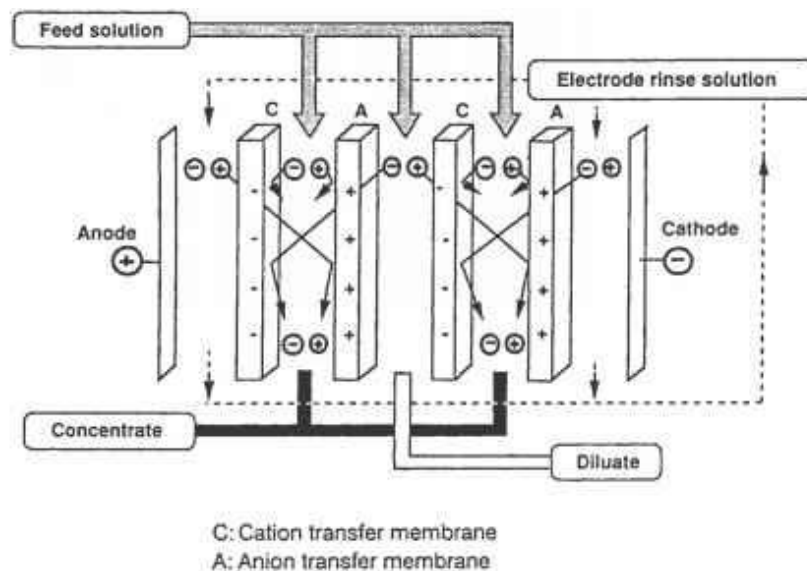
Figure 3: Schematic diagram of working of an ED cell. Image retrieved from publication by Heiner Strathmann [42]
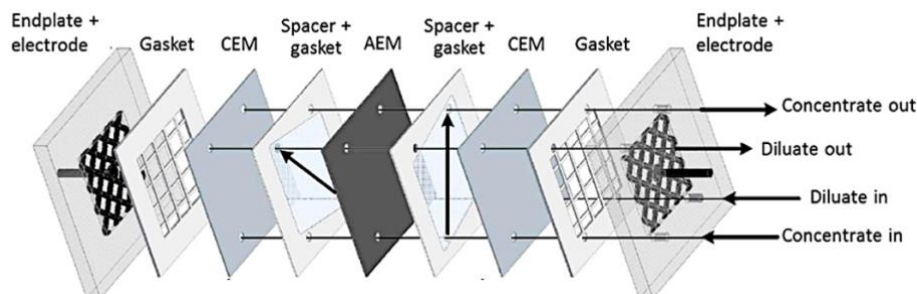
Figure 4:Different components of an electrodialysis stack. Image retrieved and adapted from Sosa-Fernandez et al.[43]

ED has found multiple applications in industries from desalination of brackish water/seawater, recovery of organic acids to effluent treatment of large-scale bio-refineries [44]. Compared to pressure driven membrane processes (such as nanofiltration and reverse osmosis), ED has several advantages. It is able to separate charged species, is less prone to fouling, can reach a

higher brine concentration due to lack of osmotic pressure limitation, higher water recovery ratio, longer membrane lifetime and doesn't require any additional chemical dosage [45].

2.3.1 Ion exchange membranes

The ion-exchange (IEX) membranes control the separation of charged ions in electrodialysis. The ion-exchange membranes are primarily semi-permeable membranes with ionic head groups attached to polymer matrices [46]. CEMs possess fixed, negatively charged ions (such as sulfonic acid or carboxylic acid groups), whereas AEMs have fixed positively charged ions (such as ammonium groups). The backbone for most membranes is formed by a cross-linked aromatic polymer structure (generally polystyrene) [47]. Upon contact with the electrolyte solution, co-ions (ions that have the same charge as that of the fixed ions) are repelled by the membrane, while counter-ions (ions that have the opposite charge as that of the fixed ions) pass through as seen in Figure 5 [41]. Depending on the surface charge, the ED membranes are preferentially selective for only a certain type of ions and reject other ions, in contrast with membranes used for ion-exchange columns where ions on the membrane surface are exchanged with ions in the solution. This property of preferentially selection in ED membranes is called 'permselectivity' [48]. High permselectivity is a desirable trait of membranes because it is a measure of the ability of the membrane to transport more counter ions [49]. Apart from high permselectivity, other desirable properties include low electrical resistance, good mechanical, and chemical stability [50]. Mechanical stability is necessary to have a minimal reaction to the transition from dilute to concentrated solutions in the form of shrinking or swelling and chemical stability is necessary to ensure the membrane can withstand varying pH ranges and oxidizing agents [50]. All membranes have different basic properties such as size, composition, thickness and resistance [47].
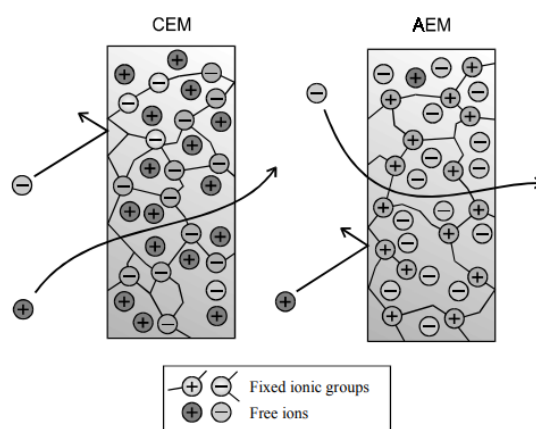

Figure 5: Cation Exchange Membrane (CEM) (Left) and Anion Exchange Membrane (AEM) (Right).

2.4 Electrodialysis for desalting organic solutions

While ED was predominantly used as a desalination technique, its applications in industries today involve investigating its role as a separation technique as well. Separation by ED works on the concept that the ionic salt species are transported through the anion and cation exchange membrane, whereas the neutral organic species are rejected by the membranes [51] As seen in Figure 6, when the feed solution (consisting of inorganic ions and neutral organics) is fed to a ED unit, the application of electric field causes a transfer of charged ions from the feed to the concentrate. The neutral organics remain in the feed solution as the electric field has no effect on it due to its charge neutrality. In case of the C_5C_6 and C_5 sugar solutions, the glucose and xylose are neutral sugars whereas the sodium and sulphate are charged inorganic ions. ED is thus one of the technologies which can separate charged and neutral components in the feed solution [52]. Previous literature studies have shown the feasibility of separating natural

organic matter (NOM) from brine, demineralization of molasses, juices and desalinating solutions containing amino acid [51][52]. This study will focus on the feasibility of desalting the lignocellulosic C_5C_6 and C_5 sugar solutions.
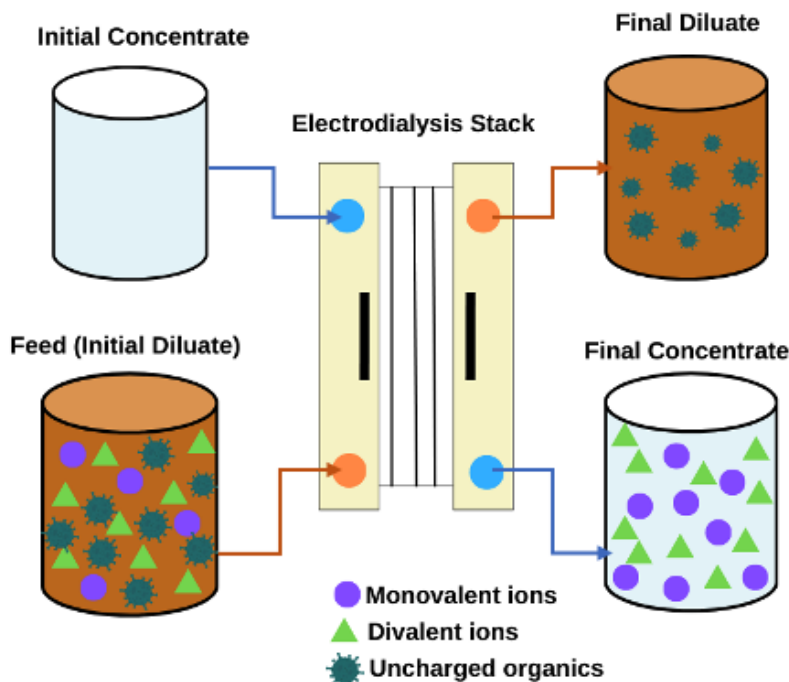

Figure 6:Pictorial representation of ideal separation of charged ions and uncharged organics in electrodialysis. Final diluate and concentrate are shown separately from the initial feed and concentrate for pictorial purposes only. In practical applications some cross migration of ions and organics is expected. Adapted from Kum et al.[53].

2.5 Fouling in ED membranes

As separation of organic compounds and inorganic ions in ED are based on charge and the influence of an electric field, difficulties can arise when some of the organic compounds are also charged. Charged organic compounds generally carry a negative charge at neutral pH [9]. These negatively charged organics are deposited on the positively charged AEM and cause an increase in electric resistance of AEM. This phenomena is termed as fouling and is defined as the "undesirable phenomenon of deposition of substances on the surface or in the pores of the membrane, leading to a change in the membrane performance"[54]. The negative consequences of membrane fouling is the deterioration of membrane performance and increase in electric resistance [55].

Lignocellulosic sugar solutions contain high amounts of organic sugars and organic by-products. While the organic sugars are neutral as mentioned in Section 2.4, the organic by-products such as the lignin degradation products (phenolic compounds) are predominantly negatively charged [56]. These compounds are low molecular weight organics and can cause significant fouling. The initial properties of organic foulants can vary depending on the feedstock, the pre-treatment, and the presence/absence of additives etc. and can further change characteristics depending on the pH, temperature, and ionic content during the experimental process. This type of fouling due to organic compounds is referred to as organic fouling. Organic fouling can occur both on the ion exchange membrane and inside the membrane [57]. Two main factors affecting the fouling of AEMs was (1) the electrostatic interaction between negatively charged organics and the positively charged membrane and (2) the affinity interaction (pi-pi interactions) between the aromatic compounds in the backbone of IEX membrane and the aromatic organics [58].

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2.5.1 Fouling mechanisms

Fouling can occur both on the surface of the membrane and internally, within the membrane. The most common fouling mechanisms are described below and in Figure 7. All fouling processes can reduce membrane permeability and decrease the performance of the membrane.

2.5.1.1 Pore blocking

Pore blocking occurs when the foulant particles physically block the pores of the membrane. Complete blocking occurs when the foulant particle or multiple particles attached together has a size equivalent to that of the membrane pores [59]. Standard blocking occurs when the foulant particle size is smaller than the pores, which leads to its accumulation inside the membrane and in turn reducing its permeability. Pore blockage can close the membrane pores either fully or partially.

2.5.1.2 Adsorption:

In case of adsorption, the organic foulants interact and adhere to the membrane surface due to electrostatic interactions, hydrogen bonding and van der Wal's force. Adsorption can occur on the membrane surface or in the pores.

2.5.1.3 Cake/gel layer formation:

Cake formation is the accumulation of both small and large sized particles on the membrane surface to form the 'cake layer' of increasing thickness [60]. The cake layer can also act as a base for more foulants to be attached to it.
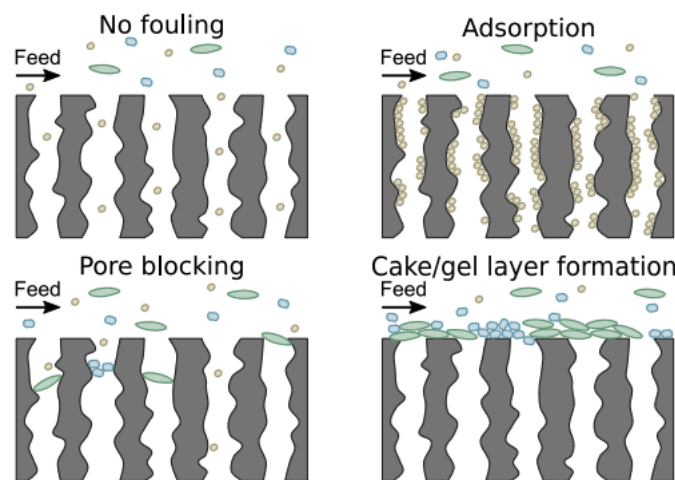
Figure 7: Schematic illustration of different types of membrane fouling. Image taken from Rudolph, G.(2021)[34].

2.5.2 Persistence of fouling

Membrane fouling can be of two types namely reversible and irreversible fouling. A membrane which loses its ion exchange capacity and must be replaced is referred to as a spent membrane.

2.5.2.1 Reversible fouling

Fouling, which is removed when the membranes are rinsed, allowing the membranes to be reused is called reversible fouling. Reversible fouling is usually formed only on the membrane surface.

2.5.2.2 Irreversible fouling

Irreversible fouling is a type of irremovable fouling which cannot be removed by a single chemical cleanse [61]. Irreversible fouling can be formed both on the surface and internally in the membrane.

2.5.3 Factors affecting fouling in Electrodialysis

Membrane fouling negatively impacts the efficiency of the process, increases the energy consumption and hydraulic resistance and leads to frequent membrane cleaning/replacement which further increases operation cost [57]. The energy consumption increases because a higher electrical potential will be required to maintain the ion flux if resistance keeps increasing due to membrane fouling. Several factors affect membrane fouling such as membrane properties, foulant, feed water characteristics, operating conditions (pH, temperature) etc. [62]. In case of membrane properties, roughness and hydrophobicity can influence the probability of membrane fouling [63]. Increasing roughness led to the formation of 'valleys' of aromatic polyamides which in turn attracted preferential deposition of colloidal particles and organic foulants [64][65]. Organic foulants generally have hydrophobic aromatic chains (aromatic amino acids, polyphenols etc.) and it can accumulate on hydrophobic membranes causing the formation of a fouling layer [66]. In lignocellulosic process water the main foulants are cellulose fibers, lignin and its degradation products, and polysaccharides such as hemicellulose, wood extractives, proteins and inorganic compounds [34].

Foulant properties which play a vital role in fouling are foulant zeta potential, its concentration and particle size [63]. Zeta potential monitors the electrostatic interaction between the organic compound and the membrane [45].

Feed water characteristics which influence fouling are the ionic strength (and presence of divalent salts), pH and temperature. Salt concentration has a major impact on the fouling of organics in electrodialysis.

It was seen that controlling hydrodynamic conditions, such as an increase in flow rate and introduction of spacers promoting turbulence could prove to be advantageous in mitigating fouling [57]. High velocity flow rates can induce higher mixing, high shear rates and decrease concentration polarization near the membrane surface [67].

2.5.4 Resistance in Electrodialysis and fouling:

Most fouling tests are destructive in nature which can limit its applications especially in industries. A non-destructive method of quantifying fouling is by analysing the electric resistance over the course of the experiment. Fouling will increase the electric resistance, resulting in higher power consumptions and lower efficiency of treatment [68]. However, resistance in an ED cell can be due to both fouling and concentration polarisation. Concentration polarisation could also lead to an increase in resistance. One difference between concentration polarisation and fouling is that the former is mostly reversible whereas the latter is more complicated can be both reversible and irreversible depending on the interaction between the membrane and solution [69].

During an ED operation, an electric potential (V) is established between the two electrodes of the unit which acts as the driving force for transfer of ions. The current through the unit is proportional to the voltage as per Ohms law. The equation for Ohms law is given by

$$U\,[V] = \,I.R$$

where U is the potential driving force, I is the electric current and R is the electrical resistance. While a higher voltage can seem like a higher driving force for faster transfer of ions, steric hindrance due to hydration shells of ions and concentration polarization can reduce the migration rate of cations [70]. The increase in fouling can be seen by monitoring the changes in electric current (under fixed-voltage conditions) or electric voltage (under fixed-current conditions) and ionic conductivity.

High electric resistance also corresponds to high residence time of ions in the feed solution [71]. The ions in the feed solution take longer to be desalted as the increase in resistance

decreases the electric field across the IEX membranes and in turn a decrease in desalting efficiency. In this thesis, average electric resistance is a key performance indicator of fouling.

2.5.5 Mitigation strategies
Various mitigation strategies to prevent and control membrane fouling has been proposed in literature and a few are listed below:

2.5.5.1 Membrane modification:
One method of controlling IEM fouling was by membrane modification. Membrane modification targeted membrane properties such as surface charge, hydrophilic-hydrophobic balance and roughness to reduce the occurrence of fouling [57]. Organic fouling was more likely to occur in membranes with a hydrophobic and rough surface [62]. Thus, by introducing a hydrophilic barrier layer onto the AEM, it could act as a shield to physically block the foulants and let ions in the solution pass through.

2.5.5.2 Pre-treatment
Using a pre-treatment unit in front of ED, such as activated carbon, coagulation, filtration, NF, RO, pellet reactors etc., can reduce the concentration of substances (organic matter, high molecular weight compounds, inorganic salts etc.) which can potentially clog the ED membrane [57]. Rapid Sand Filters (RSF), micro/nano filtration are effective pre-treatment strategies in case of feed water with large organic macromolecules or larger organic anions [72]. Another pre-treatment method commonly employed in industries is the conditioning of feed water. Controlling the pH and the addition of anti-scalants (EDTA, bi-carbonates) could also reduce fouling in certain cases [45]. For instance, EDTA will form complexes with the salts of calcium and magnesium in the feed water and reduce scaling on the membrane [72].

2.5.5.3 Cleaning-in-place
Cleaning mechanisms can use chemicals (acidic/alkaline solutions, chelating agents, and surfactants) depending on nature of the foulant. Acidic agents are effective against scaling, whereas basic and surfactants are effective against organic and colloidal fouling, and biocides are utilized to counter biofouling [72]. However, chemical cleaning can have a detrimental impact on the membrane performance by degrading the polymer matrix (ageing) or the ion exchange groups [57]. Cleaning can also be done physically, by water flushing. However, water flushing can only remove recoverable fouling whereas chemical cleaning is required for irrecoverable fouling.

2.5.5.4 Electrodialysis Reversal (EDR)
EDR works on the principle that reversing the direction of electric field (polarity) will remove foulants stuck to the membrane surface, thereby creating a 'self-cleaning' mechanism. Figure 8 illustrates a typical EDR cell and shows the migration of negatively charges foulants away from the AEM and into the bulk solution upon reversal of polarity and restoration of membrane. One requirement is that of special equipment to switch the diluate and concentrate streams upon reversal of polarity. Another drawback is also that after the polarity reversal, both concentrate and diluate are automatically diverted back to the feed tank unless intervened [57].
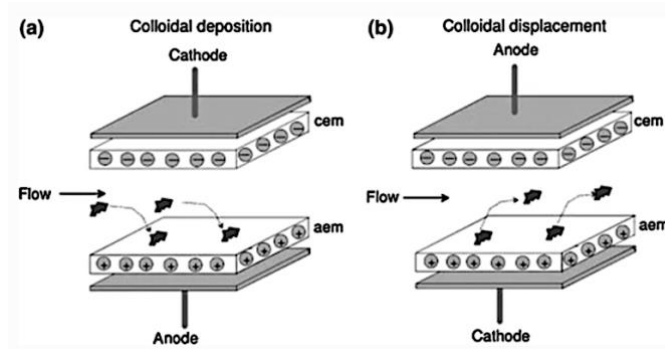
Figure 8: Fouling mitigation in an Electrodialysis Reversal (EDR) cell [47].

The literature thus illustrates the components of the lignocellulosic process water, and the expected foulants in case of its use as diluate in an ED unit. The working of an ED cell, its components, and possible interactions between the ion exchange membranes in the cell and the organic solutions are covered in this section. A few commonly used mitigation strategies to overcome organic fouling in ED membranes is also elaborated.

Materials and Methods

3.1 Materials

All the experiments were conducted using a standard electrodialysis unit. This section details the complete characteristics of the two feed solutions, specifications of the ED unit, its components, the experiments conducted, and the subsequent analytical equipment used to analyse the results.

3.1.1 Characteristics of the lignocellulosic feed solutions

The two lignocellulosic C_5C_6 and C_5 sugar solutions are 40% w/w and 50% w/w respectively. The solutions were diluted to 10% w/w for use as the feed (diluate) in all the experiments. The complete characteristics of the C_5C_6 and C_5 feed sugar solutions are shown in this Section. Table 2 shows the inorganic ion constituents of both solutions and Figure 9 and Figure 10 shows the distribution of organic sugars and acids. The characteristics of the undiluted solutions are given in Appendix A1.

Table 2: Characteristics of C_5C_6 and C_5 feed solutions.

| Parameter	Unit	C_5C_6 Sugar	C_5 Sugar
pH	-	4.9	3.7
EC	mS/cm	9.4	8.1
COD	g O_2/L	107	143
Bicarbonate (HCO_3)	mg/L	<0.1	<6.1
Ammonium (NH_4)	mg/L	<0.1	<1.8
Nitrate (NO_3)	mg/L	34.1	110
Chloride (Cl)	mg/L	63.5	77.3
Potassium (K)	mg/L	97.4	156
Sodium (Na)	mg/L	3807	3186
Calcium (Ca)	mg/L	137	56.1
Magnesium (Mg)	mg/L	39.4	139
Phosphate (PO_4)	mg/L	56.0	79.8
Silica (Si)	mg/L	12.0	10.7
Sulphate (SO_4)	mg/L	3764	4576
Iron (Fe)	µg/L	27.4	1949
Manganese (Mn)	µg/L	4117	7036
Zinc (Zn)	µg/L	2164	6359
Boron (B)	µg/L	732	798
Copper (Cu)	µg/L	7.0	116
Molybdenum (Mo)	µg/L	205	< 9.5
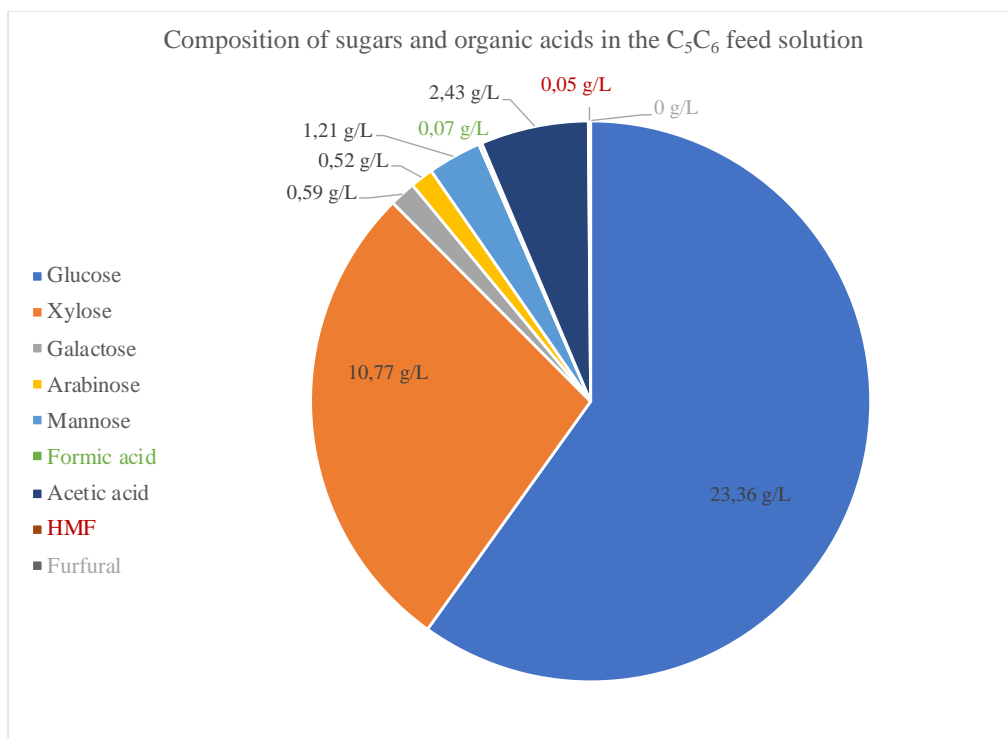
Figure 9: Composition of sugars and organic acids in the C₅C₆ feed and the main sugar is glucose.
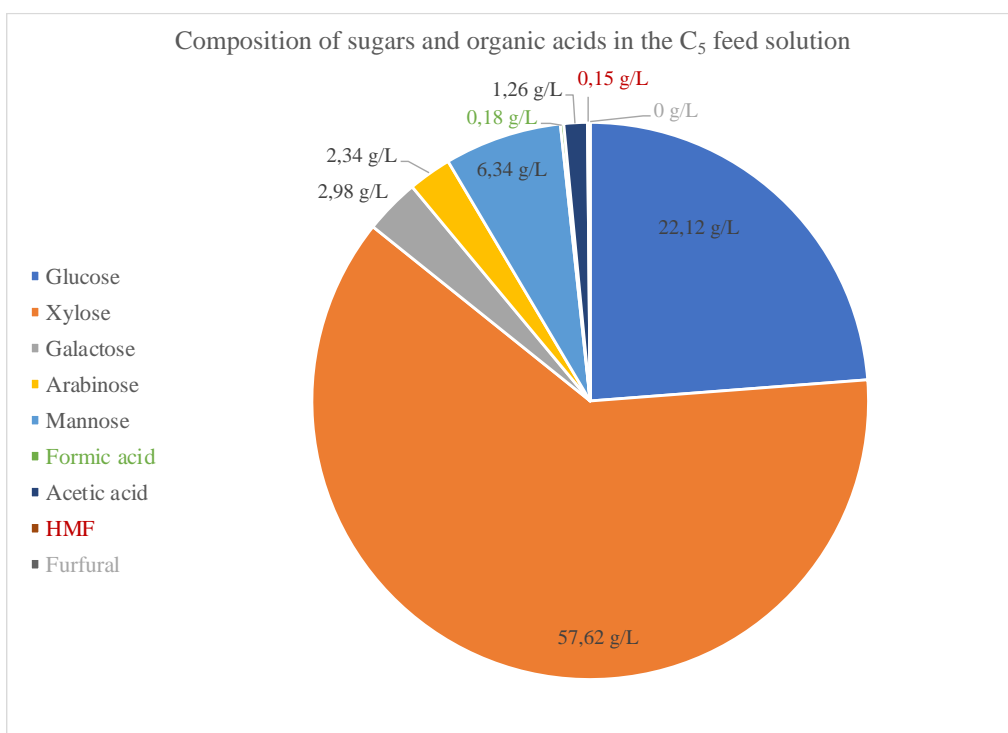

Figure 10: Composition of sugars and organic acids in the C₅ feed and the main sugar is xylose.

3.1.2 Electrodialysis Module

The ED module used was a standard PC Cell supplied by PCCell GmbH (model: ED 64002). The anode was a Pt/Ir-coated Titanium and the cathode was V4A Steel. The membrane stack used were supplied by PCA GmbH. The 'Standard Series' PCA ion exchange membranes were used in this research and consisted of the following:

- Nine standard cation exchange membranes (PC-SK)
- Ten standard anion exchange membranes (PC-SA)
- Two standard end membranes (cation exchange- CEEM)

PC-SK membranes are strongly acidic (sulfonic acid) and PC-SA are strongly alkaline (ammonium). Each membrane had a size of 110 x 110 mm and an active membrane area of 64 cm^2. The ED membrane stack was organized as ten 'cell pairs' where a pair consisted of one CEM and one AEM. The two cation exchange end membranes were places at the extreme ends of the stack and separated the rest of the stack from the electrodes to prevent leakage and migration of ions from the electrode rinse solution into the feed [73].

3.1.3 Analytical equipments

The equipment used for measuring the required parameters for analysis and logging experimental data are reported below:

- *Electrical conductivity (EC), pH:* A multimeter (WTW Multi meter 3630) was used to simultaneously measure the EC, pH, and temperature of the diluate and concentrate when conducting the experiment. The EC sensor (WTW TetraCon 925) and the pH sensor (WTW pH electrode SenTix 940) were both calibrated with respective standards before use. The measured data was exported to a Microsoft Excel document via a USB. The data was recorded at a fixed interval of 5 seconds per measurement.
- *Electrical power supply:* A DC power source (TENMA 72-2535; 30V 3A) was used to supply an external potential to the ED system. The power source was connected to a laptop, to automatically log the values of current and voltage during the experiment using the supplied operational software for TENMA. This data was recorded at fixed interval of 1 second per measurement.
- *Sample Analysis (Ion Chromatography):* The feed water and the samples after the ED experiment were analysed for the inorganic ion concentration using the ion chromatography (IC) method.
- *Sample Analysis (Chemical Oxygen Demand):* The feed water and the samples after the ED experiment were analysed for COD using the NANOCOLOR COD 15000 tube tests. The tubes were analysed in a Macherey-Nagel Spectrophotometer.

3.2 Experimental Methods

This section details all the experiments conducted in this research. A visual image of the ED set-up used is shown in Figure 11. The three solutions (diluate, concentrate and the ERS) were recirculated through the system continuously using a peristaltic pump (Watson & Marlow 530S). Three associated pump heads (one for each solution- 323 external pump head 4 roller) were used to pump the solution into tubes (Rehau tubes with an internal diameter of 1.6mm) into the ED cell. These solutions were stirred continuously using a magnetic stirrer to ensure the solution was thoroughly mixed. The external voltage was set at a constant of 20V and supplied using a DC power source as detailed in Section 3.1.3, via copper cables. The power source was connected to a laptop to automatically the run time, voltage and current.

The experiments were conducted in batch-mode and the initial volumes of diluate, concentrate and ERS were fixed at 0.5L. The ERS used in all the experiments was 0.3 molar $NaNO_3$ solution. Choosing the ERS is important to avoid production of any undesirable chemicals or

gases which can cause corrosion of the electrodes. For instance, NaCl solution as ERS can form chlorine gas at the anode which is corrosive, toxic and can shorten the lifespan of the electrodes [41]. The configuration of the stack can also be tweaked by placing two CEMs on the outer most ends of the stacks to prevent the migration of chlorine ions to the electrode compartment. EC and pH probes were used to measure the conductivity, pH, and temperature of the diluate and concentrate during the experiment. The weight and volume of the solutions was checked in the beginning and end of the experiment. The cross-flow velocity of the solutions through the stack was kept constant at around 2 cm/s (90 RPM) [74].
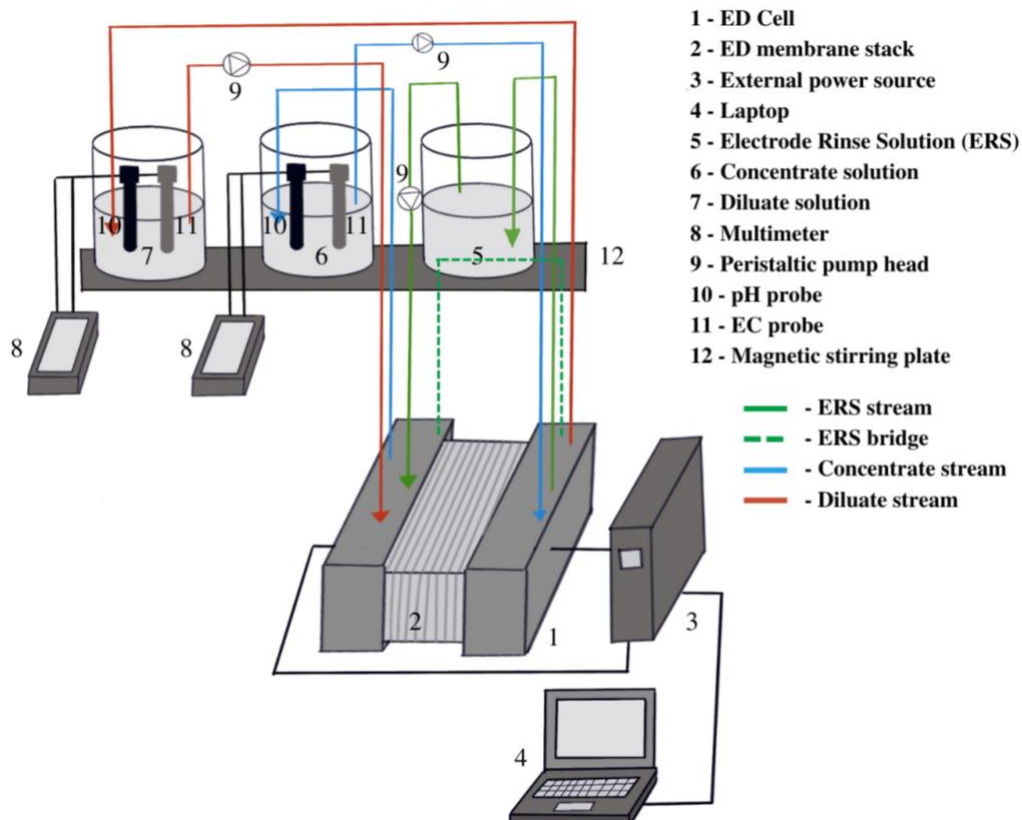
Figure 11: Visual Representation of the experimental set-up. Retrieved and partially modified from [75].

A flowchart of the experimental scheme is presented in Figure 12. The base case experiment consisted of testing the feed solution (without any pre-treatment) for target desalting. The C_5C_6 sugar solution was tested first. Then a filtration pre-treatment was introduced, and the sugar solution was fed to the ED unit to test for its desalting percentage and fouling potential. An intermediate water rinse was considered and analysed for the same. Then, this was repeated in case of the C_5 sugar solution. The intermediate water rinse was not tested due to its unsatisfactory results with the C_5C_6 sugar solution. Additionally, an activated carbon and acidic treatment was also tested for the C_5 sugar solution.

Explanations of the desalting and fouling experiments, the intermediate water rinse, application of activated carbon and acidic treatment is elaborated in the sections below.

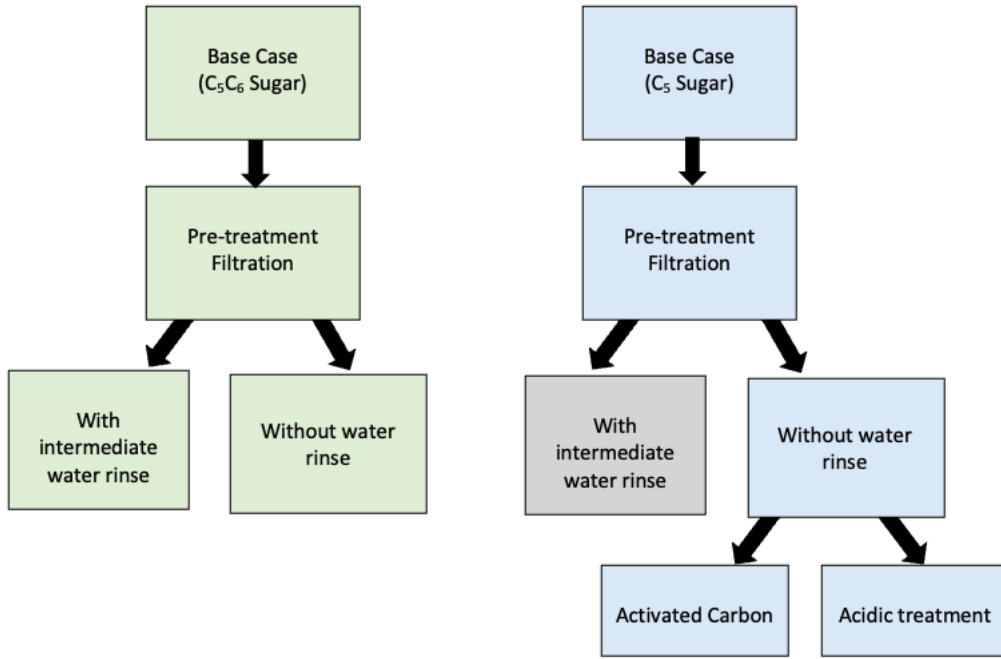*Figure 12: Flowchart of conducted experiments.*

3.2.1 Desalting tests:

Desalting tests constituted the bulk of the experiments in this research. By applying current to the ED system in batch mode, the conductivity of the diluate begins to decrease as the ions are transported through the IEX membrane to the concentrate, thereby increasing the conductivity of the concentrate solution. The EC and pH probes in the diluate and concentrate track and record the changes in conductivity and pH respectively. The external voltage was applied till a target of 60% desalting was achieved. The EC is directly related to the inorganic ion concentration and hence 60% EC removal is taken as representative of salt removal when running the experiment and the desalting is later confirmed by Ion Chromatography. The percentage of salt removal was calculated from the initial and final values of inorganic ion concentration as shown in the equation below:

$$Desalting~(\%) = \frac{(C_o - C_t)}{C_o}$$

where C_o and C_t are the initial and final values of the inorganic ion concentrations.

3.2.2 Fouling tests

The effect of fouling of the two industrial sugar solutions in the ED unit was compared. The experiments were conducted in the same way as described in Section 3.2.1, each experiment is termed as a 'run' and is repeated four times. The four runs together are termed as one 'trial'. A pictorial depiction of a 'trial' is shown in Figure 13. The resistance for a run was calculated from the recorded current and voltage data according to Ohms's law and plotted in a graph.
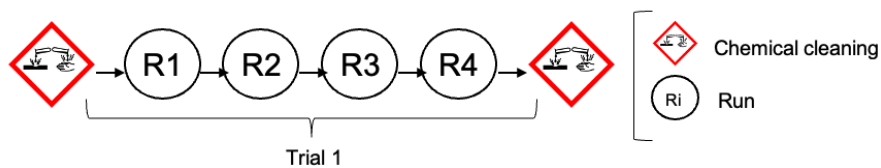

Figure 13: Pictorial representation of a Trial consisting of four runs.

The average resistance over the four runs of a trial $\left(\frac{R1+R2+R3+R4}{4}\right)$ is also calculated. After the fourth run- R4 (end of a trial), the membranes were first flushed with water, and then chemically cleaned to recover its performance ability from fouling. The 'trial' was repeated 3-4 times and the average resistance (R_{avg}) was plotted for each trial to check whether chemical cleaning could restore the membrane after fouling.

A 2% HNO_3 and a 2% NaOH solution was used for the acidic and basic rinse, to remove any potential inorganic and organic foulants respectively. Acidic cleaning aims to remove multivalent cationic salts such as hardness salts and metal hydroxides, whereas basic cleaning can breakdown polysaccharides, proteins, and other organics into smaller compounds and be removed [76]. 500mL of acidic solution was taken in a beaker and recirculated in the ED stack for 30 minutes. Then, the stack was flushed with water and the basic solution was recirculated for 30 minutes. The stack was then flushed with water twice.

3.2.2.1 Effect of intermediate water rinse

A water rinse was added after every 'run' to test if potential foulants could be removed with the water flush. At the end of a run, 500mL of water was used to flush the membrane, and then the next run was repeated. A pictorial depiction of a 'trial' with an intermediate water rinse is shown in Figure 14.
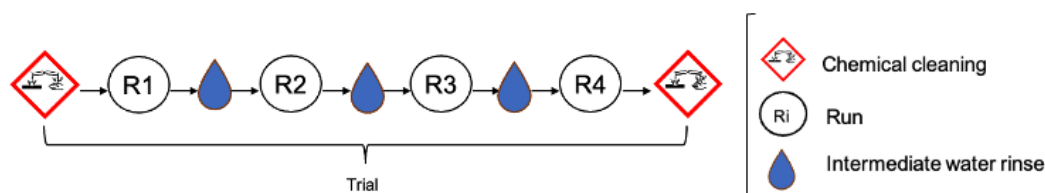

Figure 14: Pictorial depiction of a trial with an intermediate water rinse

3.2.3 Effect of pre-treatment and mitigation:

3.2.3.1 Filtration:

The diluate was filtered through a 1-micron bag filter (Snapring), and the performance of the filtrate in the ED unit was compared to that of the raw solution in terms of fouling potential.

3.2.3.2 Activated Carbon

Powdered Activated Carbon (PAC) (Unicarb L-D48D M325) was used to precipitate potential organic foulants in the diluate before treating the stream in an ED unit. A batch test was done with varying concentrations of activated carbon to determine the optimum dosage as described in the Appendix A4. 500 mL of organic solution was dosed with 30 g/L of PAC and kept in a shaker (VWR Mini Shaker) overnight at 240 RPM. The dosage was determined by batch testing various concentrations of PAC as explained in the Appendix. After 24 hours, the solution was filtered with a syringe filter of 0.45µm and used as the new diluate without dilution in the ED unit. The experiment was then conducted as described earlier in Section 3.2.1.

3.2.3.3 Acidic treatment

The pH of the diluate feed was acidified to protonate the organic by-products in the solution and reduce the charge interaction between the organics and the AEM. The pH of the feed C_5 sugar solution was maintained at 2.5 constantly using 2% sulfuric acid. The experiment was carried out as described above and the pH was monitored to ensure that it remained constant at 2.5. Acidification of the feed ensures that the organic compounds remain in the feed whereas

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inorganic compounds can migrate to the concentrate compartment [77]. An alternative method to precipitate the lignin degradation compounds by lowering the pH was also tried and is elaborated in Appendix A3.

4

Results and Discussion

4.1 Results of an experimental run

This section explains in detail the results of an experimental 'run'. As described in the previous section, one run is a single experiment with ED to check if the target of 60% desalting is reached. After each experimental run, the EC values of both the diluate and concentrate recorded by the multimeter is plotted against time. Similarly, the current recorded throughout the experiment is also plotted against time. A representative example of these two graphs is shown in Figure 15 (a) and (b). (a) depicts the decrease in conductivity of the diluate as ions are transported through the IEX membrane under the influence of the external voltage, subsequently increasing the concentrate conductivity. (b) shows the change in current with the run time of the experiment. Initially, the current increases as the ions are all present in the diluate and conductivity is high. Also, initially the concentrate conductivity is very low. As the ions migrate to the concentrate, the conductivity decreases and hence there are fewer ions to be transported in the solution and hence the current decreases.
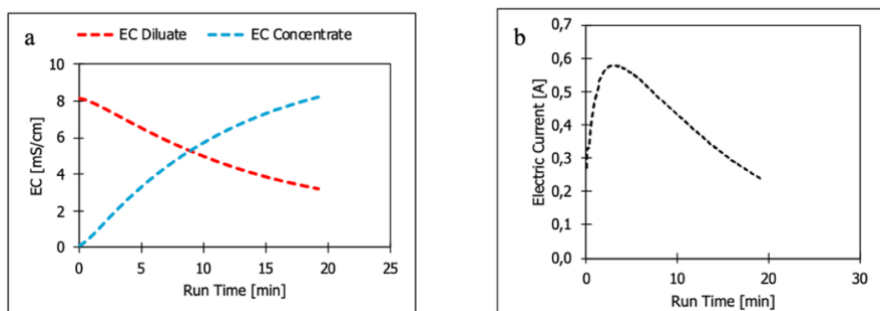

Figure 15: (a) EC and (b) electrical current values of one run of ED experiment. (a) shows the decrease in conductivity of the diluate and increase in conductivity of the concentrate over time due to transfer of ions through the IEX membrane. (b) shows the initial increase in current due to high initial ionic conductivity. The ions migrate to the concentrate and hence the conductivity decreases leading to a drop in current. These graphs were plotted for all the experiments conducted in this research.

As mentioned in Section 3.2.2, the experiments were carried out as four runs (R1, R2, R3 and R4) which constitute one trial (T_i). The evolution of current and time over the four runs is seen in Figure 16. The membrane is chemically clean at the beginning of R1 which allows for a high current to pass through (low resistance) and hence the desalting time taken is lower. However, by the fourth run (R4), the membrane undergoes fouling and faces an increase in electric resistance, which decreases the electric current. This increases the time taken to reach the desalting percentage. Although experimental conditions remained exactly the same in all 4 runs, the decrease in current and increase in run time shows the presence of resistance. Organic matter (polyphenols, proteins, NOM etc.) can either form a layer on the membrane or penetrate it, leading to an increase in electrical resistance which in turn results in higher energy consumption, lower membrane permselectivity and current efficiency [66]. Although it is equally common for an increase in resistance to occur due to polarization and change in ionic concentrations, the high organic content in the feed solution increases the likelihood that fouling could be the main reason behind the increase in resistance. This is elaborated in upcoming sections.

The values of current and time taken vary with change in sugar solution, different pre-treatments etc. and C_5C_6 sugar solution is used as a representative example in Figure 16.
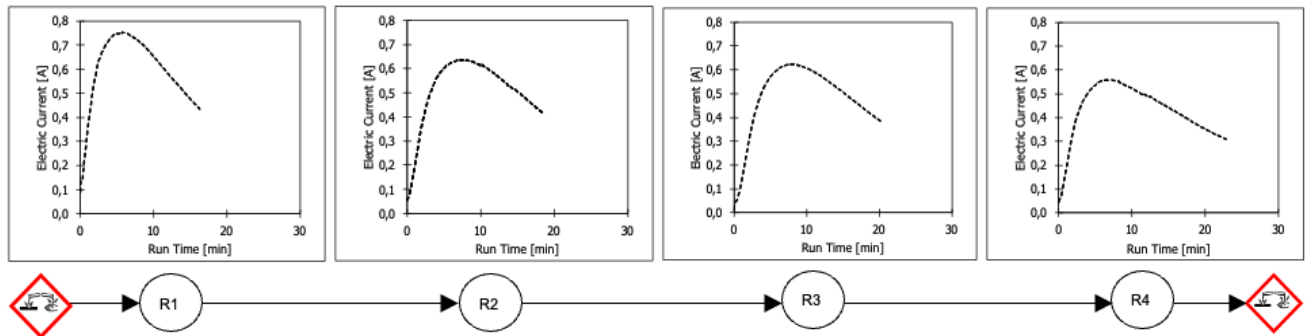

Figure 16: Pictorial representation of evolution of current and time over one trial (four experimental runs). All experiments were at a constant voltage of 20V.

The electric resistance is calculated for each run using Ohms law (from recorded current and voltage data) and is plotted as seen in Figure 17 (C_5C_6 sugar solution is used as a representative example in Figure 17). As mentioned above, the initial resistance (R1) is low due the membrane being chemically clean. The increasing resistance is interpreted as an increase in fouling. The average resistance of the four runs $\left(\frac{R1+R2+R3+R4}{4}\right)$ is calculated and plotted in the later sections.
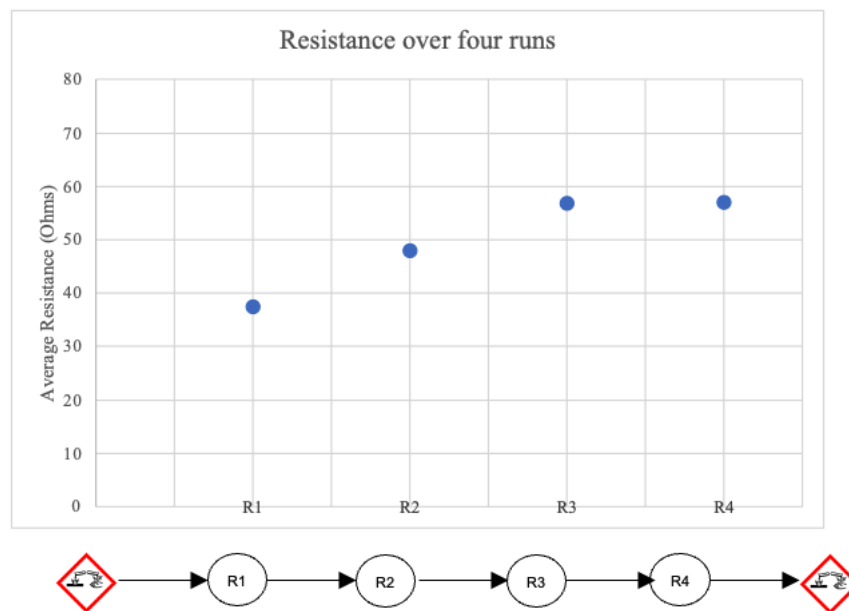
Figure 17: Pictorial representation of resistance over one trial (four runs).

4.2 Fouling and desalting tests

This section covers the results of the base case experiments of the two sugar solutions, the effect of pre-treatment and the intermediate water rinse. The results are condensed from the graphs of EC vs time and calculated average resistance plotted for each experiment as described above. The final solution concentrations used to calculate the desalting percentage is presented in Appendix A2.

4.2.1 Base cases and effect of filtration

Unfiltered 10w/w C_5C_6 sugar was first used as a diluate in the base case experiment. It was observed after the desalting experiment that the second run could not achieve the desalting target of 60%. Sodium was desalted by 53.7% and sulphate by 59.3%. The resistance was

significantly high (over 200 ohms), and the run time was over 2.5 hours for the above-mentioned desalting percentage. Hence, the experiment was stopped and upon opening the membrane stack, a bead-like sludge substance was found on the AEM. Filtration through the 1-micron filter also yielded sludge on the filter. Both images can be seen in Figure 19. The filtrate was used as the new diluate, and the resistance dropped drastically from 215 ohms to 50 ohms as seen in Figure 18(a). The run time also decreased drastically to around 20 minutes. The filtered sample achieved a desalting of 75.5% in case of sodium and 66.5% in case of sulphate, thereby meeting the target of 60% desalting.

In case of the C_5 sugar, the base case (unfiltered 10w/w) did not show a significantly high value of average resistance. Moreover, there was also no sludge-like substance observed on the AEM or the filter. As seen from Figure 18(b), filtration did not have such a significant impact on the resistance (only a 3% difference). The samples achieved the target for desalting with 65% in case of sodium and 81% in case of sulphate. To maintain uniformity, all further experiments with both C_5C_6 and C_5 sugar were conducted with filtered samples.
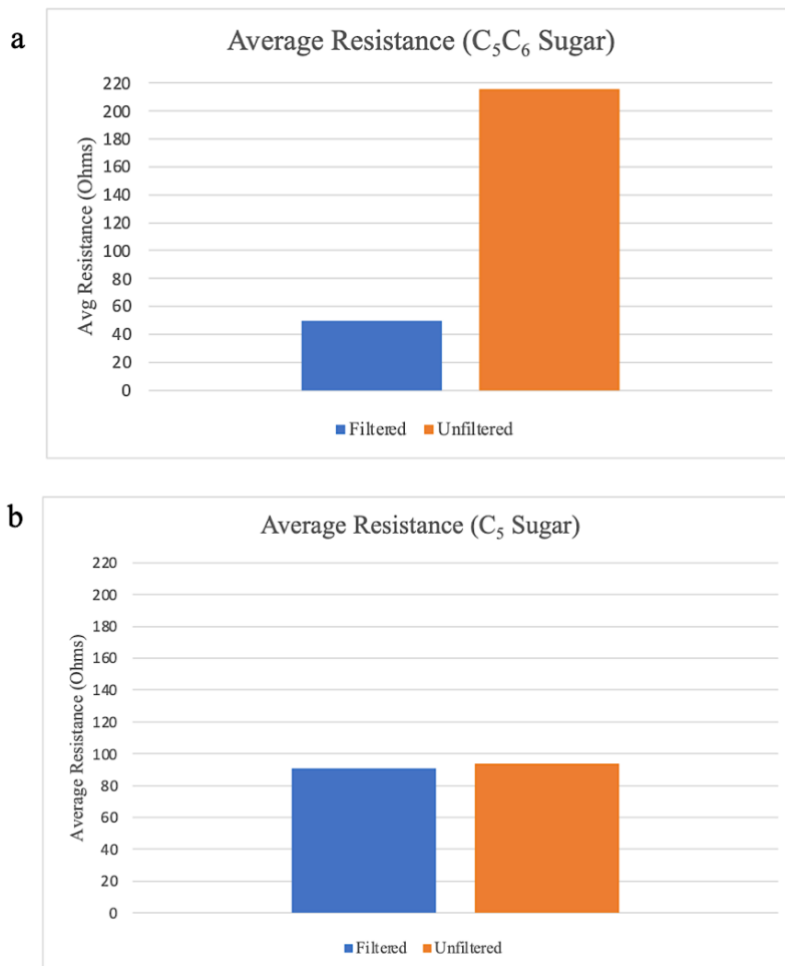

Figure 18: (a)Average resistance in C_5C_6 filtered and unfiltered samples. The unfiltered solution could only reach 41% desalting (b) Average resistance in C_5 filtered and unfiltered samples.
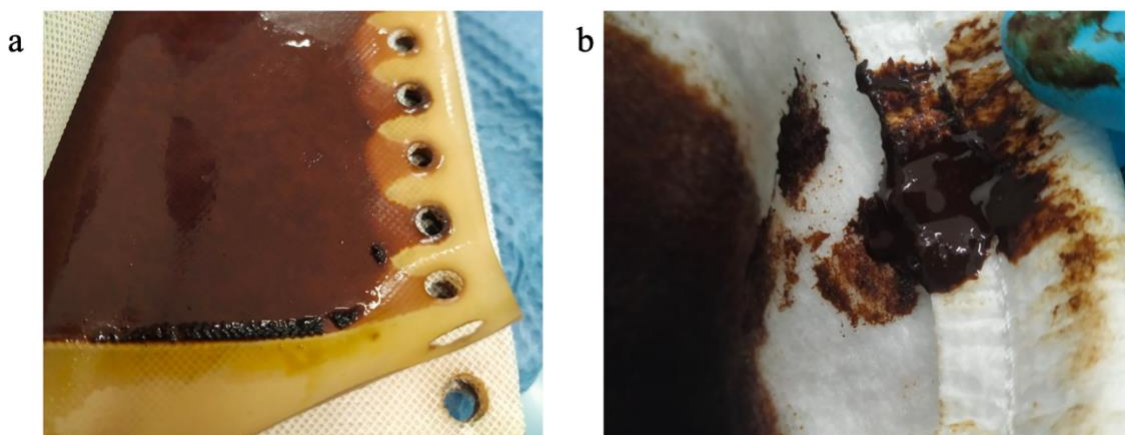
23

Figure 19: (a) Bead-like sludge on anion exchange membrane (AEM) after partial desalting of C_5C_6 sugar. (b) Sludge like substance on the one-micron filter after filtering the C_5C_6 sugar solution.

This lack of sludge formation in C_5 sugars may be attributed to the difference in sugar production (one step versus two steps) between C_5C_6 and C_5 sugars. In the two-step process of extracting C_5C_6 sugar, the alkaline NaOH will aid in delignification and hence could change the properties of the lignin and other organics. The sugar solutions were diluted to a 10 w/w to be used in the ED unit, and as water is a poor solvent for lignin, it could cause aggregation and precipitate on the filter surface.

4.2.2 Effect of intermediate water rinse

When filtered C_5C_6 sugar was used as the diluate, trials were performed with an intermediate water rinse as described in Section 3.2.2.1. It was hypothesized that an intermediate water rinse could flush out the organics attached to the membrane surface, partially recover the membrane resistance after each run and reduce the frequency of cleaning the membranes chemically with the strong acids/bases (CIP- Cleaning-in-place). Cleaning membranes frequently with a strong acid/base can reduce its lifespan as extreme pH values can affect membrane stability, structure and properties and must be avoided unless necessary [78].
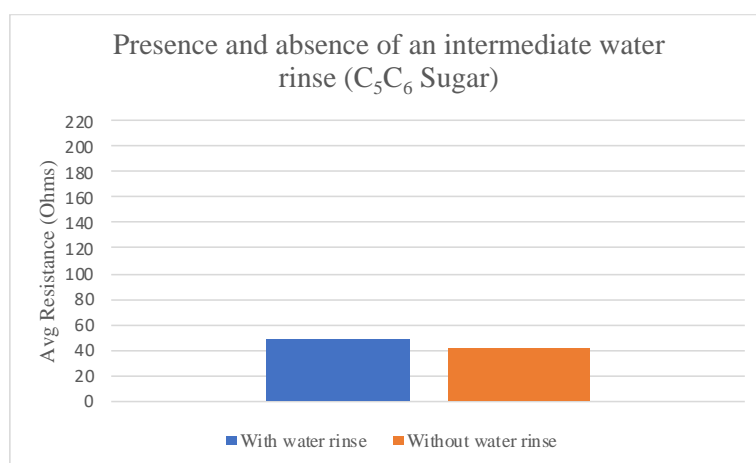
Figure 20: Effect of an intermediate water rinse on the membrane resistance with the C_5C_6 sugar. The experiments without an intermediate water rinse showed a 16% lesser resistance value.

From Figure 20, it is seen that the average resistance of a trial without water rinse is 16% lower a trial with a water rinse. While a 16% reduction doesn't seem significant, it reduces the time taken to desalt multiple batches and doesn't require additional water. This can be explained by literature studies which state that the internal structure of IEX membranes could be more

porous after continued immersion in a solution, resulting in lower resistance [79]. Desalting multiple batches without a water rinse keeps the membranes in contact with the solution for longer. This change in internal structure is thought to offset (albeit partially) the effect of fouling [79]. The target desalting could also be reached in the experiments without a water rinse (75.5% of sodium and 66.5% of sulphate). All experiments henceforth were conducted without the intermediate water rinse.

The water rinse is expected to remove any hydrophilic substances attached to the membrane. As the intermediate water rinse did not have a significant impact on reducing the average resistance, it can be hypothesized that the contaminants responsible for fouling were more hydrophobic in nature. The major organics in the two sugar solutions- the acids (benzoic, cinnamic, vanillic etc.), HMF and furfural consists of both hydrophilic and hydrophobic parts, and hence it is assumed that the hydrophobic interactions are stronger.

To summarize, the initial fouling tests done on both the C_5C_6 and C_5 sugar solutions yielded different results:
- The use of C_5C_6 as a feed in the ED yielded a sludge-like substance on the AEM unlike the C_5 solution. Filtration through a 1-micron filter also showed a sludge-like substance in the C_5C_6 solution.
- The base case (unfiltered) C_5C_6 solution could not meet the required desalting percentage.
- The filtered C_5C_6 solution and C_5 solution could both meet the target desalting.
- Filtration had a strong impact on reducing the electric resistance by 76.88% in case of the C_5C_6 solution. However, it did not such a significant impact on the C_5 solution (reduction of 15%).
- Trials of experiments were conducted with and without an intermediate water rinse and the experiments without the water rinse showed a 16% reduction in electric resistance, better desalting and hence can save water and time.
- All experiments henceforth were carried out with a filtered solution through a one-micron filter and without an intermediate water rinse.

4.2.3   Reversible and Irreversible fouling

C_5C_6 and C_5 sugar solution fouling experiment trials were carried out as described in Section 3.2.2 and the average resistance over each trial was plotted. A CIP was performed after each trial and this repetition was to check whether the CIP could restore the membrane functionality even after exposure to heavily organic solutions.

Figure 21(a) shows the average resistance over multiple trials for C_5C_6 sugar and Figure 21(b) shows the average resistance over multiple trials for C_5 sugar.
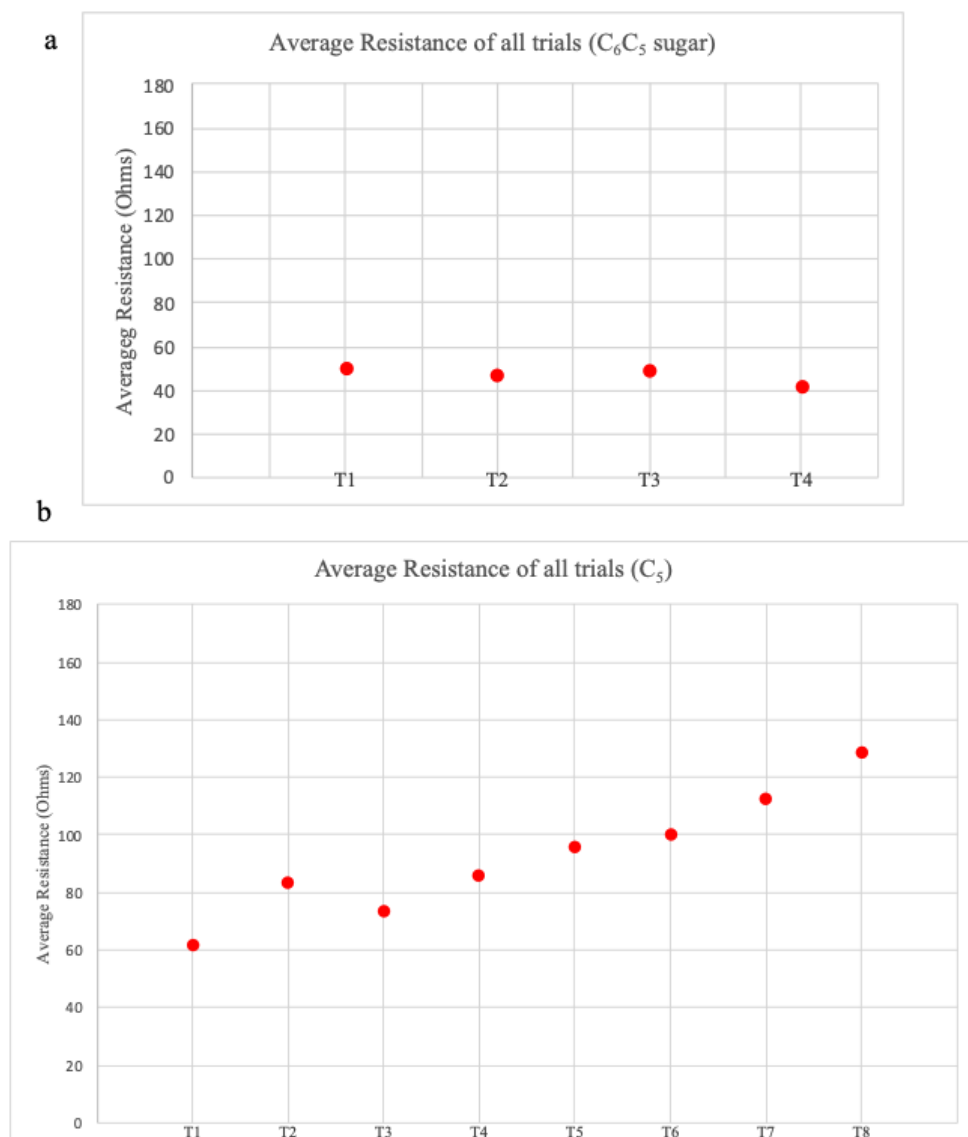
Figure 21: (a) Average resistance over four trials for C_5C_6 sugar; (b) Average resistance over eight trials for C_5 sugar. T1, T2, T3 etc. refer to the trial number. Each trial consists of four runs and the average of the four runs is plotted on this graph. A chemical cleaning was performed after every single trial (i.e., between T1 and T2 and so on) for both sugars.
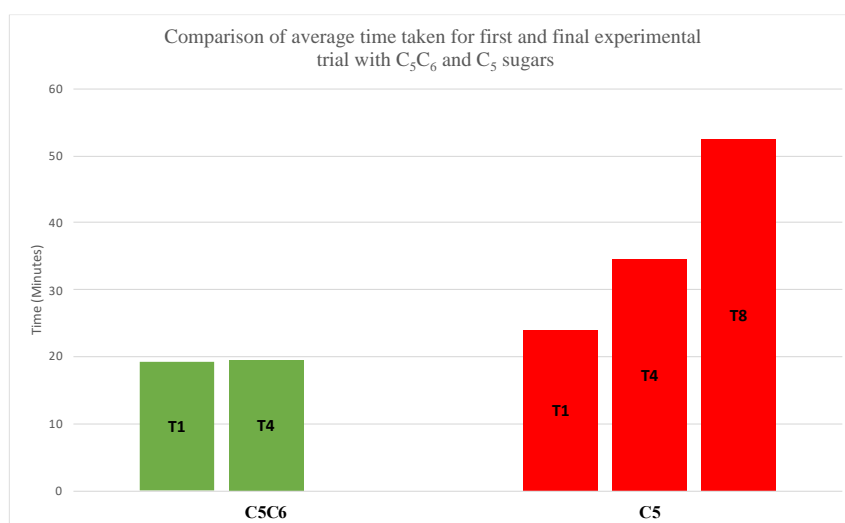
Figure 22: Comparison of average time taken for the first and last trial of both C_5C_6 and C_5 sugar solutions.

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It is seen that the trend is very different for both sugars and the explanation is as follows: In Figure 21(a), it is seen that after every trial, the CIP could restore the electrical resistance back to nearly the same value (around 40-50 ohms), indicating that the resistance developed during the experiment was reversible. However, in case of Figure 21(b), the resistance increased steadily despite having a CIP after every trial, reaching a value of 130 ohms from the initial value of 60 ohms. This indicates that the fouling was irreversible and that an additional pre-treatment would be necessary. As indicated in Section 4.2.1, desalting of 60% and above could be achieved even with the irreversibly fouled membranes. However, the sharp increase in resistance would make it unsustainable to be used for desalting, as the efficiency of the system would decrease due to a drop in the current under the experimental conditions of constant voltage. It is also possible that after a certain point when the membrane is highly fouled, the target desalting cannot be achieved due to a decrease in permselectivity [50].

Figure 22 shows the average run time of the first and last trial of C_5C_6 and C_5 feed solutions. The run time is the time taken for the experiment to achieve 60% desalting. In case of the C_5C_6 solution, the run time of the first and fourth trial is almost the same and corresponds to the earlier observation that the average resistance across four trials also remained constant (i.e., the resistance was recoverable). However, in case of the C_5 feed, the time taken for both the fourth and last trial was higher than the initial trial. The run time increased steadily with each trial. This once again corresponds to the steady increase in average resistance and depicts reduced efficiency.

Lignin consists of three basic building blocks namely *p*-hydroxyphenyl, guaiacyl and syringyl [38]. The most common lignin degradation compounds listed in literature are as follows: Guaiacol, creosol, catechol, vanillin, syringol, vanillic acid, syringaldehyde, phenol, cinnamic acid, p-coumaric acid, ferulic acid, 4-hydroxybenzoic acid etc. to name a few [38][39]. The common lignin degradation compounds and phenolic acids in C_5C_6 and C_5 feed sugar solutions are shown in Figure 23. It is interesting to note that all the compounds listed are aromatic. All the compounds have a molecular weight in the range of 125-200 g/mol except for phenol and furfural which are around 95 g/mol. Phenol and guaiacol are hydrophobic whereas the other compounds have both hydrophilic and hydrophobic properties. In line with the explanation from Section 2.1.1, it is seen than the C_5 sugar had a significantly higher content of lignin degradation products as compared to the C_5C_6 sugar, due to the difference in extraction. Due to this, it is expected that the fouling (and in turn the electrical resistance) would be higher as compared to the C_5C_6 solution. However, irreversible fouling in case of C_5 sugar indicates that the fouling layer formation could be formed differently in both cases. As the C_5C_6 sugar showed reversible fouling, it is implied that the fouling is generally formed on the membrane surface and can be removed by cleaning. In case of the C_5 sugar, the irreversible fouling shows that the foulants were either permanently adsorbed to the membrane or that the CIP was not sufficient to remove the accumulation of organics on the membrane surface.
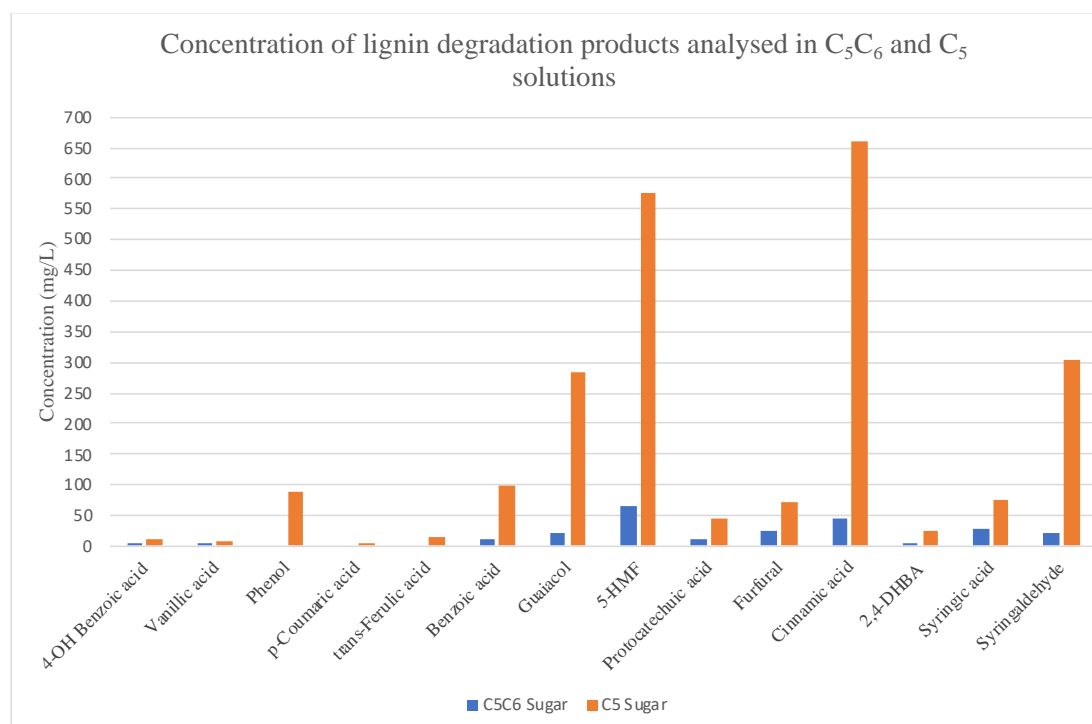
Figure 23: Comparison of lignin degradation products in C₅C₆ and C₅ feed solutions. 5-HMF is 5 Hydroxymethylfurfural; 2,4-DHBA is 2,4-Dihydroxybenzoic acid.

4.2.3.1 Possible interaction of foulants with the membrane

A few reasons for organic fouling on AEM membranes as mentioned in the literature review in Section 2.5 are (1) the presence of electrostatic interactions, (2) π-π interactions between the aromatic compounds and polymer IEX membrane matrix [80]. The lignin degradation compounds quantified in the feed of ED are all aromatic organic compounds. Due to the negative charge possessed by most organic by-products, the accumulation of organics on or in the membrane surface of AEM is expected. The C_5 feed has a significantly higher concentration of organic and the effect of accumulation on the membrane will be higher.

Firstly, as noted in Section 2.1.2, the organic by-products (lignin degradation compounds) are all aromatic and are classified as low molecular weight organics. The molecular weights of the compounds ranged from 95-198 Daltons (Da) and the molecular weight cut-off of the membrane used was 200 Da. It is possible for the bigger sized molecules (phenolic acids) to form an initial cake layer upon which smaller sized molecules (phenols, furfural, acetic and formic acid) can be deposited. These organics can all be adsorbed on the membrane as well. According to literature, phenolic acids such as p-coumaric acid, ferulic acid, benzoic acid, protocatechic acid and vanillic acid were adsorbed on fouled IEX ED membranes [80]. Phenolic foulants (the lignin degradation products) were also found to polymerize and form aggregates and colloids in the membrane [80]. It was also noted that phenolic acids rarely exists in its free state, but rather combined with other organic compounds [80]. Moreover, as mentioned in (2) the π-π (hydrophobic and hydrophobic) interactions between the aromatic compounds and polymer IEX membrane matrix can cause severe organic fouling as all the lignin degradation compounds are aromatic, and the backbone of IEX membrane contains an aromatic ring. In case of the C_5C_6 sugar solution, HMF, cinnamic acid, syringic acid and syringaldehyde are the most prominent degradation products with the latter two having a molecular weight (198 Da) almost the size of the MWCO of the membrane. Hence, it is possible that the organics accumulate on the surface like a 'cake layer' which was also seen as a sludge-like substance on the AEM. Literature also reports cake layer fouling to be reversible as the

layers form on the surface due to rejection of the molecules by the membrane and can be cleaned hydraulically [81]. This is observed during the experimental studies and hence formation of cake layer is assumed to be the fouling mechanism of the C_5C_6 sugar solution.

In case of the C_5 sugar solution, the concentrations of all the lignin degradation products were significantly higher. As the organic load increases, it is implied that the severity of fouling would increase. Phenol is only present in the C_5 sugar solution and by virtue of being hydrophobic and having a low molecular weight, is reported in literature to cause severe fouling due to adsorption on the membrane [80]. Adsorption and pore blocking is hypothesised to be the mechanism of fouling in the C_5 sugar solution due to the irreversible fouling seen in this case. This is further supported by literature studies which also reported fouling due to adsorption to be largely irreversible [81]. Furthermore, the basic rinse of the CIP of the C_5 feed was analysed for lignin degradation compounds to better understand which compounds caused irreversible fouling. It was assumed that the presence of lignin degradation products in the CIP could prove that the fouling was only an accumulation on the surface and not adsorbed on the membrane and that the CIP was sufficient. However, from Figure 24 only very few lignin degradation compounds were present in the basic flush and most compounds were either absent or insignificant in concentration. The only compounds of significance were 27% of phenol and 20% of 2,3-dihydroxybenzoic acid in the basic CIP which indicates that these compounds could have interacted with the membrane on its surface. Less than 4% each of vanillic acid, guaiacol, cinnamic acid and syringaldehyde were also present. This can also indirectly confirm the adsorption or pore blocking of these aromatic compounds on the membrane.
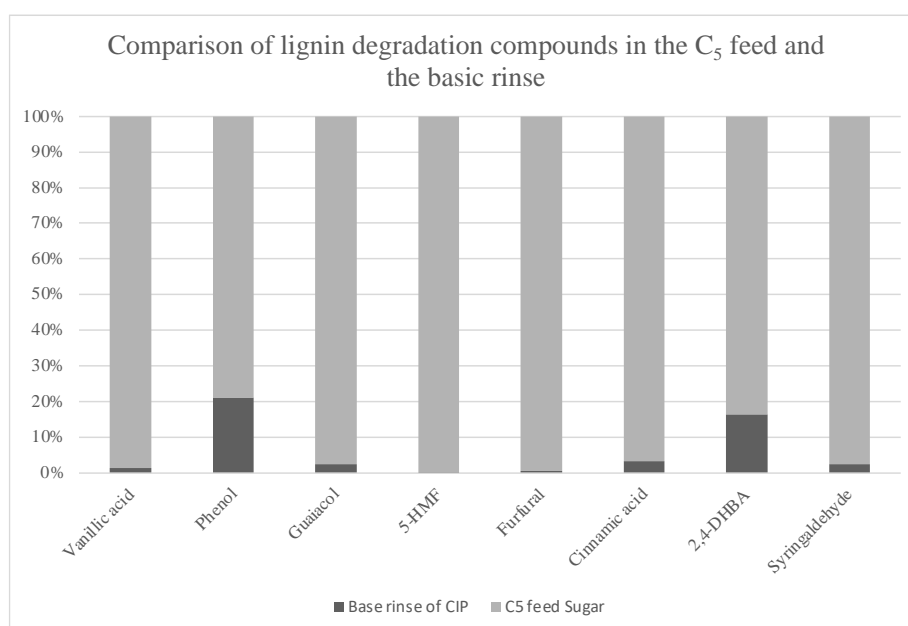
Figure 24:Comparison of lignin degradation compounds in the C_5 sugar solution feed and in the basic rinse after a cleaning-in-place procedure. The compounds not shown in the graph (4-OH benzoic acid, p-coumaric acid, ferulic acid, benzoic acid, and syringic acid) were not present in the basic rinse.

Thus, while the C_5C_6 sugar solution could be desalted without a significant loss of performance due to organic fouling, the C_5 sugar solution faced irreversible membrane fouling, even though desalting was possible. Irreversible fouling of the membrane can lead to a loss of system efficiency and after a certain time needs membrane replacement. This process is unsustainable both technically and economically.

To summarize:
- The C_5C_6 sugar solution demonstrated reversible fouling. The fouling could be removed after each trial by a CIP (acid-base). The average resistance stayed between 41-50 ohms.
- The C_5 sugar solution on the other hand showed irreversible fouling. The fouling could not be removed even with a CIP and the average resistance increased steadily from 60 ohms to 130 ohms. This was deemed unsuitable for desalting by ED.
- This difference in fouling phenomena was attributed to the significantly higher concentration of organic lignin degradation compounds (which in turn stem from the different steps in the pre-treatment scheme) in the C_5 sugar solution.
- All the lignin degradation compounds were aromatic. Literature studies have shown the possibility of adsorption of some phenolic acids on AEM membranes and the negative effect due to the π-π interactions between the aromatic compounds and polymer IEX membrane matrix.
- The fouling mechanism in case of the C_5C_6 feed was hypothesized to be cake formation and that of the C_5 feed was adsorption and pore blocking. Lignin degradation compounds in the basic CIP of the C_5 feed was very low which further supports the fact that most compounds were adsorbed on the membrane. However a change in the concentration or duration of CIP may desorb the foulants.
- The desalting target was successfully reached in both cases. However, the irreversible fouling in case of C_5 sugar solution can reduce the efficiency of the ED unit due to increasing resistance. This is seen by comparing the run time of experiments.

4.2.4 Effect of Activated Carbon

Activated carbon was used as a pre-treatment strategy to remove the excess organic foulants from the C_5 sugar solution before introducing the filtrate into the ED system. It is critical that any pre-treatment used should not remove the sugar content (and remove only the organics) due to the fermentation process downstream which requires the presence of sugars. Figure 25 also shows that the AC pre-treatment did not adsorb the sugar content and hence is satisfactory for fermentation. Specifically, xylose was barely adsorbed (1%) by the activated carbon.
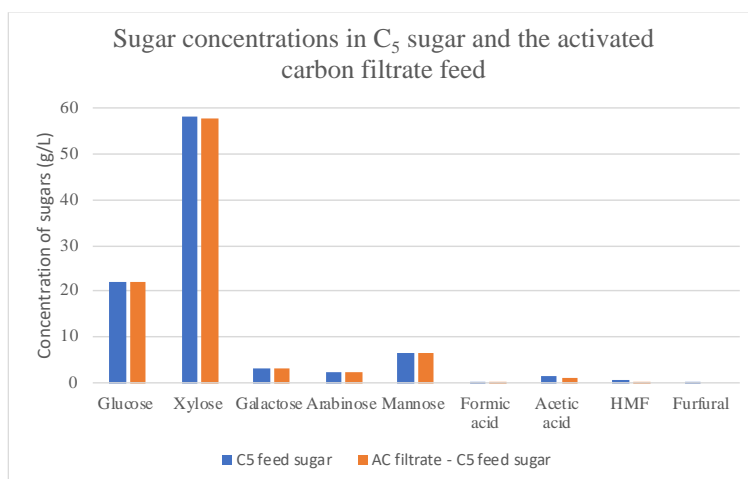
Figure 25: Sugar concentrations in C5 feed solution and the filtrate of C5 feed solution after dosing AC.

Figure 26 shows the average resistance over three runs of AC filtrate. It is seen that after pre-treatment with AC, the C_5 sugar solution can now be easily desalted by the ED unit by keeping the electrical resistance reasonably low. The desalting target was successfully achieved with sodium reaching a value of 61.4% and sulphate a value of 87.2%. From the last average

resistance of 130 ohms in Figure 21(b), the resistance dropped to 48 ohms with the same membrane (and without changing any other operating conditions). The experimental run time also averaged 22 minutes, which is significantly lesser than the time taken with just filtration.

The low fouling potential exhibited by the AC filtrate can be attributed to the removal of organic foulants by the AC. To confirm this hypothesis, the concentration of lignin degradation products in the C_5 feed solution and the filtrate C_5 feed solution after AC dose was compared in Figure 27. It is seen that nearly all the organic compounds in the AC filtrate, except 5-HMF, furfural and cinnamic acid are negligible in concentration. Even the concentrations of 5-HMF, furfural and cinnamic acid are significantly lower than that in the C_5 sugar solution. The reduction of 5-HMF and furfural is advantageous for downstream fermentation as these compounds are inhibitors for microbial fermentation. Literature studies have also shown the capability of AC to remove lignin degradation products such as vanillin, 4-hydroxybenzaldehyde, and p-coumaric acid [82]. COD analysis also showed the decrease in organics from 143 g O_2/L to 112 g O_2/L.
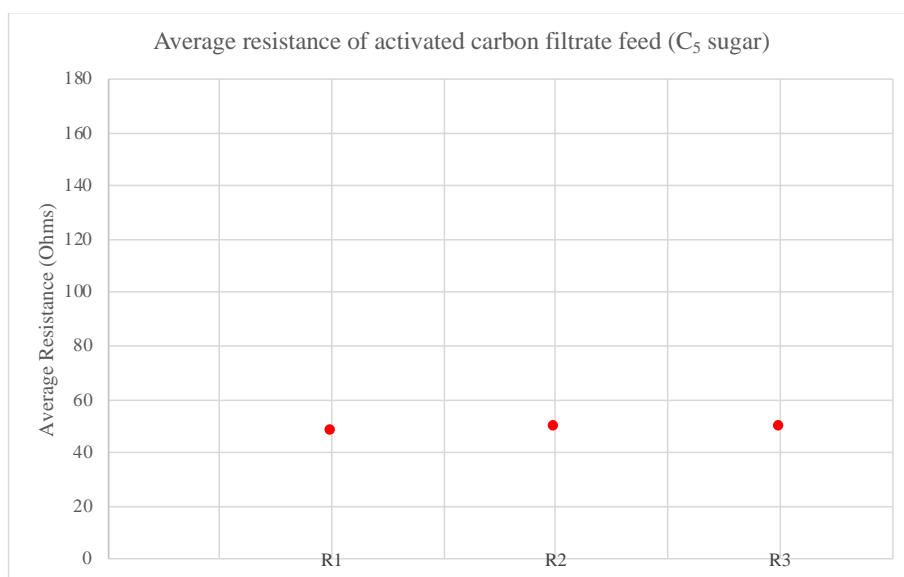
Figure 26: Average resistance of the activated carbon filtrate feed.
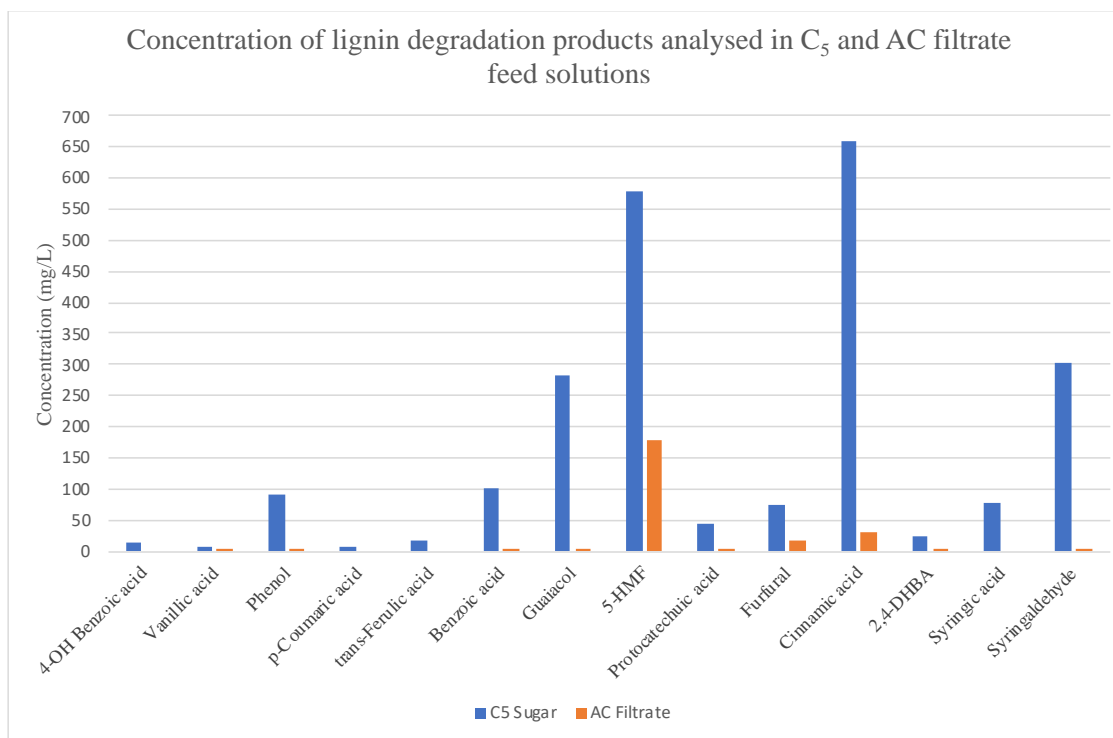
Figure 27: Comparison of lignin degradation products in C₅ feed and the AC filtrate feed solutions. The AC filtrate feed is the C₅ sugar solution dosed with 30g/L of AC and filtered to remove the organic foulants. 5-HMF is 5 Hydroxymethylfurfural; 2,4-DHBA is 2,4-Dihydroxybenzoic acid.

Figure 28 illustrates visually the difference in the C_5 sugar solution and the filtrate of the AC-treated-C_5 sugar solution. The AC filtrate C_5 sugar is significantly lighter in colour as compared to the original C_5 sugar. The dark colour in the original C_5 sugar is attributed to the formation of by-products during hemicellulose degradation when lignin is subjected to pre-treatment [83]. The adsorption of these compounds by activated carbon leads to the reduction in colour.
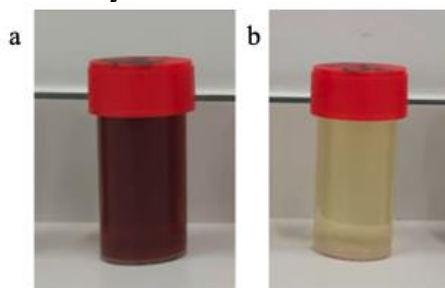
Figure 28:Visual differences between (a) C₅ feed sugar solution and (b) the activated carbon filtrate feed solution.

4.2.5   Effect of addition of acid

2% sulfuric acid was dosed in increments to ensure that the acidic nature of the feed (pH 2.5) could be maintained constantly. The desalting targets were reached with 65.79% desalting of sodium and 68.02% desalting of sulphate. The average resistance could also be constantly maintained at a low value of around 40 ohms over four runs as seen in Figure 29 and the time taken for these experiments averaged around 30 minutes for each run. As the addition of acid changed (increased) the conductivity of the feed solution and its composition, the values of average resistance of the C_5 solution with and without acid may not be directly compared. However, by comparing the duration of time taken to achieve 60% desalting, it can be concluded that addition of acid could maintain the run time at around 30 minutes whereas the run times increased steadily in the experiments without acid addition.

The main phenolic lignin degradation compounds (benzoic acid, cinnamic acid, ferulic acid, syringic acid) and acetic acid all have a pK_a value of around 4.5 and hence at an acidic pH of 2.5, these compounds would exist in its protonated form. Being protonated, the negative charge on these compounds will be neutralised and have lesser attraction to the AEM and hence can mitigate the fouling by avoiding a deposition or adsorption in the membrane. V. Hartwig has shown that the acidification of solution below pH of 2.9 could aid in the separation of low molecular weight organics and inorganics with ED [84]. Wang et al. have reported that a decrease in the degree of protonation could lead to severe fouling with high degree of irreversibility [85].
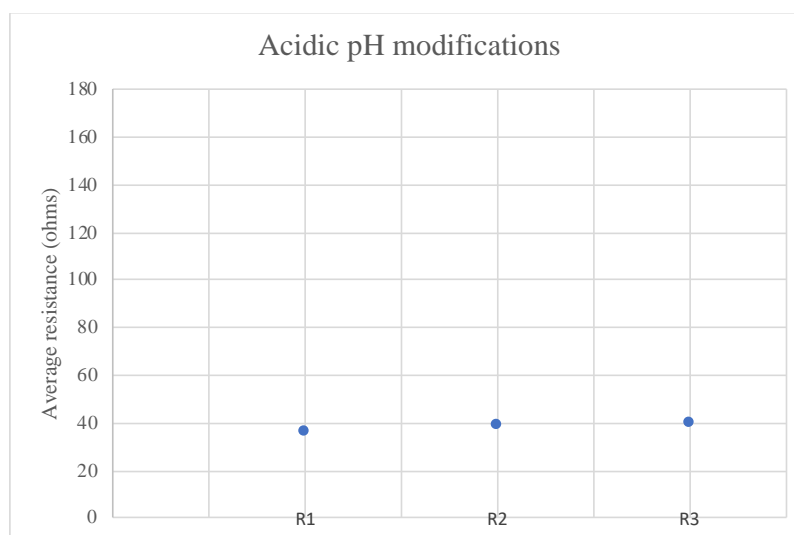
Figure 29: Average resistance of the feed maintained at a constant pH of 2.5.

The steep drop in resistance when using a different feed solution (AC filtrate and acidified feed) and the same membrane shows that it is not a spent membrane (i.e., need to be discarded). Although the membranes were irreversibly fouled and showed steadily increasing resistance with the C_5 sugar solution, changing the feed solution characteristics allowed the membrane to be used. The different properties of the AC filtrate and acidified feed solution due to the reduced concentration of organic foulants and protonated organics respectively could imply that different feed solutions interacted differently with the membrane.

Activated carbon adsorption is a physical process whereas acidification of the feed is a chemical process. AC can retain a wider variety of organic foulants on its surface by adsorption, due to its large surface area, but has some disadvantages such as designing an additional step for addition of AC and its related costs, the disposal or regeneration of spent AC carbon etc. On the other hand, acidification is simpler and inexpensive to implement. However, as acidification relies on the values of pH of the solution and pK_a of the organic compounds to protonate, not all organic foulants can be removed by this method.

To summarize, both the AC pre-treatment and addition of acid as a mitigation strategy had its advantages:
- The AC adsorbed a significant amount of lignin degradation compounds from the C_5 sugar feed without adsorbing the sugars. This was a prerequisite as the sugars were necessary for downstream fermentation.
- The resistance dropped steeply to 48 ohms and enabled the usage of ED to desalt the C_5 sugar feed.
- The desalting target was successfully reached.

- The membrane is not a 'spent membrane' as even though it was irreversibly fouled with the C_5 sugar feed, the AC filtrate could be used for desalting at a low resistance. This is due to the different properties of the AC feed.
- By maintaining an acidic pH, the desalting targets could be reached with a constant run time of 30 minutes.

5
Conclusions

Electrodialysis is increasingly being considered in other applications apart from desalination such as separation. ED as a separation technology works on the principle of electric exclusion. It can separate charged inorganic ions from uncharged organics by the transport of ions across the membrane under the influence of electric potential. This concept is used to investigate the feasibility of desalting highly organic lignocellulosic sugar solutions from a biorefinery. The solutions contain organic sugars and organic by-products (degradation products) apart from a high load of inorganic ions from an acidic pre-treatment. As high inorganic ion concentrations act as inhibitors to downstream fermentation, it is imperative that the ions are desalted from the organic sugars. However, the organic by-products are generally negatively charged at neutral pH and hence can interact with the positively charged AEM causing membrane fouling. The high concentration of organic by-products in the lignocellulosic solution is hypothesized to cause issues with fouling and the performance of the ED unit. Hence, the main scope of this thesis is to investigate whether the fouling of organic by-products can be overcome to desalt the lignocellulosic sugar solutions using ED.

By experimentally analysing two sugar solutions (C_5C_6 and C_5) for a target of 60% desalting, the fouling patterns were compared. Two different types of fouling were observed with reversible fouling in case of C_5C_6 solution and irreversible fouling in case of C_5 solution. The fouling could be dealt with by filtration in case of the C_5C_6 solution whereas the C_5 solution required an additional treatment with activated carbon or by acidification. Thus, to effectively reach 60% desalting, an anti-fouling treatment was required.

The different fouling patterns were due to the difference in solution compositions. The C_5C_6 sugar solution contained a significantly lower fraction of the organic lignin degradation compounds. This lower concentration of organic by-products explains the reversible fouling in case of the C_5C_6 sugar solution, whereas the C_5 sugar solution with a significantly higher concentration of lignin degradation compounds fouled irreversibly. Due to the difference in composition, is also likely for the foulant to interact differently with the membrane surface. The reversible fouling pattern is hypothesised to be due to a cake-layer fouling layer as visibly seen on the anion-exchange membrane. In comparison, adsorption is assumed to be the fouling pattern for C_5C_6 sugar due to the low concentration of foulants in the CIP. Moreover, all the identified lignin degradation products were aromatic in nature. According to literature, these compounds could be adsorbed on the membrane and could also undergo hydrophobic-hydrophobic interactions with the membrane to cause severe fouling. An intermediate water rinse between the experiments did not reduce the fouling, implying that most compounds had hydrophobic interactions with the membrane.

Although the target desalting was reached with the C_5 solution, the continuous increase in average resistance and time (due to irreversible resistance) was deemed unsustainable as the ED performance efficiency declined and additional treatment was considered. After a pre-treatment with PAC, the average resistance dropped from 130 to 50 ohms and the run time of the experiments reduced from an hour to 22 minutes. The positive results were achieved due to the adsorption of the organic lignin degradation compounds onto the activated carbon, which in turn reduced the organic loading on the ED membrane and hence led to lesser fouling. By

removing the foulants, both the charged interactions and the pi-pi interactions were reduced. By acidification of the feed C_5 solution to a pH of 2.5, the organic lignin degradation compounds were protonated as the compounds mostly all had a pK_a of 4.5. This reduced the attraction between the compounds and the AEM and in turn the fouling propensity.

Overall, it can be concluded that ED is feasible to desalt highly organic solutions provided a few anti-fouling steps are taken. Fouling can be overcome in this case either by removing the foulants from the feed, or by changing the property of the foulants.

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6

Recommendations

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This chapter gives recommendations for any future studies and further research on the topic of desalting highly organic, lignocellulosic process water solution by circumventing organic fouling.

The irreversible fouling observed when desalting the C_5 sugar solution should be confirmed with a scientific analysis. Comparing a pristine and a fouled membrane would show whether accumulation of organic compounds have occurred by a change in the membrane's chemical structure (adsorption) and better explain the fouling mechanism. Destructive techniques such as ATR-FTIR can fulfil these requirements. Analysing the membranes can also confirm the hypothesized type of fouling mechanism (pore blocking, cake layer, adsorption etc.) in the C_5 sugar solution and the C_5C_6 sugar solution. If the type of fouling mechanism is identified, mitigation strategies particular to that mechanism can be applied.

Upon changing the characteristics of the C_5 feed solution either by removing the organic foulants (AC adsorption) or by changing the charge on the organics (acidification), the intensity of fouling on the AEM could be mitigated. However, the thesis doesn't explain the sharp decrease in resistance of the irreversibly fouled AEM (due to adsorption) when used with the AC feed or after acidification. Further study of the AEM and membrane interaction with the different feed solutions is needed.

The acidification of the feed should also be studied further to explain the effect on the sugar solutions and the organic by-products as the discussions in this thesis were merely a hypothesis based on experimental results. Addition of acid can cause a change in feed composition and may influence the desalting. Very acidic levels can also cause the sugar to breakdown into products such as HMF and furfural which needs to be avoided.

The properties of the CIP can be investigated further by changing the solvent and its duration. With the lack of lignin degradation compounds in the basic rinse of the CIP and the inability of the CIP to reduce irreversible fouling when desalting the C_5 sugar solution, it was concluded that most of the compounds were adsorbed on the membrane. However, a different or more concentrated CIP of a longer duration may resolve the issue. Changing the flow velocity could also be investigated.

In this study it was assumed that the increasing resistance was due to organic fouling and not due to concentration polarization. This conclusion was reached due to the properties of the highly organic feed solutions, and the steep reduction in membrane resistance after the organic foulants were removed. However, future studies can use potentiometry to determine the effect of ohmic and non-ohmic resistance.

This thesis was merely a feasibility study with respect to desalting the sugar solutions. In actual practice, it would be necessary to quantify and minimize the transfer of sugars through the membrane, for optimum sugar fermentation downstream.

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Appendices

A1

Composition of raw sugar solutions

Appendix A1 describes the inorganic ion concentrations of the raw C_5C_6 and C_5 sugar solutions. This analysis was done using an IC (Ion Chromotography) on the raw solution procured from the supplier. The solutions were diluted to 10w/w during the experiments.

Parameter	Unit	C_5C_6 raw solution	C_5 raw solution
pH	-	5	3,8
EC	mS/cm	6,5	8,7
Ammonium (NH4)	mg/L	<0,1	<0,4
Nitrate (NO3)	mg/L	154	676
Chloride (Cl)	mg/L	193	268
Potassium (K)	mg/L	778	768
Sodium (Na)	mg/L	23627	15540
Calcium (Ca)	mg/L	759	282
Magnesium (Mg)	mg/L	221	712
Phosphate (PO4)	mg/L	354	357,2
Silica (Si)	mg/L	8,7	78,8
Sulphate (SO4)	mg/L	22325	20992
Iron (Fe)	µg/L	1106	8744
Manganese (Mn)	µg/L	21721	32340
Zinc (Zn)	µg/L	10499	31116
Borium (B)	µg/L	7146	4148
Copper (Cu)	µg/L	<0,1	464
Molybdenum (Mo)	µg/L	4088	15,2

Figure A1. 1: Inorganic ion concentrations of the raw C_5C_6 and C_5 sugar solutions.

Salt composition of final diluate and concentrate

Appendix A2 describes the entire inorganic ion profile of the final concentrate and diluate which was used to calculate the percentage of desalting.

Compound	Units	Final Solution-Without water rinse	
		Concentrate	**Diluate**
Ammonium	(mg/l)	< 0,8	< 0,5
Nitrate	(mg/l)	94,4	40,5
Chloride	(mg/l)	28	51,5
Potassium	(mg/l)	106,4	80
Sodium	(mg/l)	2568	930
Calcium	(mg/l)	54,4	32
Magnesium	(mg/l)	13,6	11
Phosphate	(mg/l)	22,4	23,5
Silica	(mg/l)	6,4	5,5
Sulphate	(mg/l)	2512	1260
Iron	(μg/l)	4,8	22,5
Manganese	(μg/l)	1240	1265
Zinc	(μg/l)	418,4	1370
Borium	(μg/l)	603,2	525
Copper	(μg/l)	25,6	63,5
Molybdenum	(μg/l)	15,2	5

Table A2. 1: Inorganic profile for C_5C_6 sugar solution without an intermediate water rinse-Final diluate and final concentrate.

Compound	Units	Final Solution- With water rinse	
		Concentrate	**Diluate**
Ammonium	(mg/l)	< 0,8	< 0,5
Nitrate	(mg/l)	69,6	34
Chloride	(mg/l)	31,2	19,5
Potassium	(mg/l)	59,2	70,5
Sodium	(mg/l)	1600	1760
Calcium	(mg/l)	22,4	82
Magnesium	(mg/l)	5,6	25,5
Phosphate	(mg/l)	15,2	33
Silica	(mg/l)	6,4	5,5
Sulphate	(mg/l)	2064	1530
Iron	(μg/l)	27,2	30,5
Manganese	(μg/l)	430,4	2600
Zinc	(μg/l)	261,6	1835
Borium	(μg/l)	532,8	560
Copper	(μg/l)	25,6	63,5

Compound	Units		
Molybdenum	(µg/l)	< 0,8	< 0,5

Table A2. 2: Inorganic profile for C₅C₆ sugar solution with an intermediate water rinse-Final diluate and final concentrate.

Compound	Units	Final solution	
		Concentrate	**Diluate**
Ammonium	(mg/l)	7,2	<0.5
Nitrate	(mg/l)	689,6	25
Chloride	(mg/l)	59,2	39
Potassium	(mg/l)	178,4	88
Sodium	(mg/l)	1840	1110
Calcium	(mg/l)	6,4	18
Magnesium	(mg/l)	17,6	61
Phosphate	(mg/l)	22,4	38
Silica	(mg/l)	6,4	11
Sulphate	(mg/l)	3024	845
Iron	(µg/l)	40	1400
Manganese	(µg/l)	848	2970
Zinc	(µg/l)	664	3285
Borium	(µg/l)	495,2	820
Copper	(µg/l)	10,4	98,5
Molybdenum	(µg/l)	38,4	

Table A2. 3: Inorganic profile for C₅ sugar solution -Final diluate and final concentrate.

Compound	Units	Final solution	
		Concentrate	**Diluate**
Ammonium	(mg/l)	0.5	<0.1
Nitrate	(mg/l)	461	30.4
Chloride	(mg/l)	72.0	6.0
Potassium	(mg/l)	108	32.8
Sodium	(mg/l)	2206	1245
Calcium	(mg/l)	12.8	41.7
Magnesium	(mg/l)	19.2	110
Phosphate	(mg/l)	349	217
Silica	(mg/l)	0.8	9.5
Sulphate	(mg/l)	4182	604
Iron	(µg/l)	4.5	408
Manganese	(µg/l)	1050	4865
Zinc	(µg/l)	523	3029
Borium	(µg/l)	62.7	444
Copper	(µg/l)	7.6	8.3
Molybdenum	(µg/l)	<0.1	6.7

Table A2. 4: Inorganic profile for AC filtrate C₅ sugar solution -Final diluate and final concentrate.

A3

Pre-treatment: Lignin precipitation

Appendix A3 describes the attempt to precipitate lignin in the C_5 sugar solution by lowering the pH to an acidic value. Literature studies described the ability of acid precipitation to precipitate lignin from kraft liquor which was obtained from alkaline pre-treatment of lignocellulose as described in Section 2.1. In a study, 90% of lignin and sodium were separated from kraft liquor with a combination of acid precipitation and ED part [86][87]. Although the pre-treatment in this case is different (dilute acid hydrolysis pre-treatment), a precipitation batch study was carried out.

50mL of C_5 sugar solution sample was taken and acidified at different acidic conditions using 2% sulfuric acid. The solutions were left to stand for 24 hours, and the final images are shown in Figure A3. 1. Figure A3. 2 shows the expected precipitation of lignin compounds according to literature (Gundupalli et al.[88]) but could not be observed in this study.
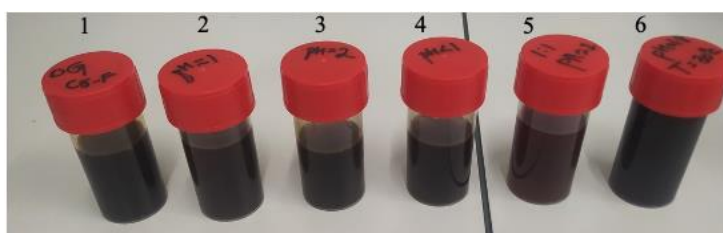

Figure A3. 1: Acidified sample of C_5 sugar solution after 24 hours. 1- Original C_5 sugar solution; 2-Acidified pH at 1; 3-Acidified pH at 2; 4-Acidified pH between 0.5-1; 5-Diluted C_5 sugar solution with demiwater at pH 2; 6-Acidified pH at 2 and sample heated at a constant temperature of 30 degree Celsius for 24 hours.
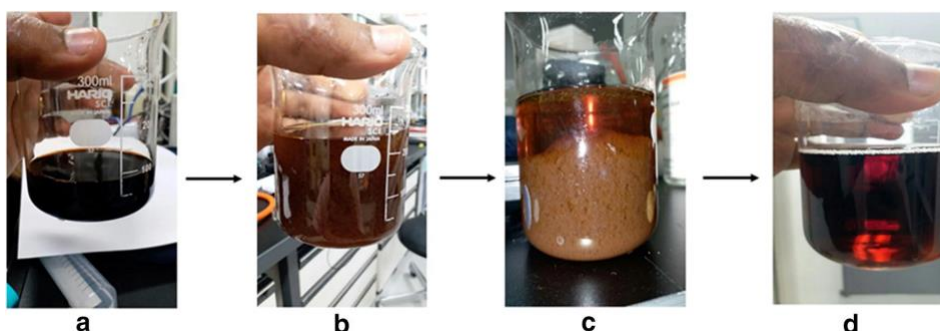

Figure A3. 2: Retrieved from Gundupalli et al.[88]. Image depicts the precipitation of lignin from kraft liquor using sulfuric acid after undergoing an alkaline pre-treatment.

The lack of precipitation could be attributed to the difference in the pre-treatment of the lignocellulose (dilute acid versus alkaline). Lignin in kraft liquor obtained from the alkaline pre-treatment existed in the form of lignin phenolate. Upon acidification, the lignin phenolate becomes insoluble in the acid and can be precipitated. However, the dilute acid pre-treatment can result in partial lignin breakdown into lignin degradation products- some of which may be soluble in acidic conditions. The lignin by-products cannot be isolated through a change in pH in case of acidic pre-treatment.

Hence, this method was deemed unsuccessful.

Appendix A4 describes the batch test experiments carried out to determine the dosage of activated carbon (AC). The hypothesis was that the AC would adsorb the lignin degradation compounds and other organics in the C_5 sugar solution, thereby reducing the likelihood of fouling.

Two types of PAC were used: Chemically activated PAC (C-PAC) and vapour activated PAC (V-PAC). Dosage values of 10 g/L, 20 g/L and 30 g/L were tested for chemically activated PAC and 20 g/L and 30 g/L of dosage values for vapour activated PAC. These value ranges were chosen from a literature study by Wang et al. on the purification of hemicellulose-derived saccharides from non-saccharide compounds [89]. The samples were kept in a shaker at 240 RPM overnight and filtered with a 0.45 syringe filter. The filtrate samples are shown in Figure A4. 1. As the removal of organics was seen visually as colour reduction, option (5)- 30g/L of C-PAC was chosen as the dosage value which was also in accordance with the value of 33g/L noted in literature.
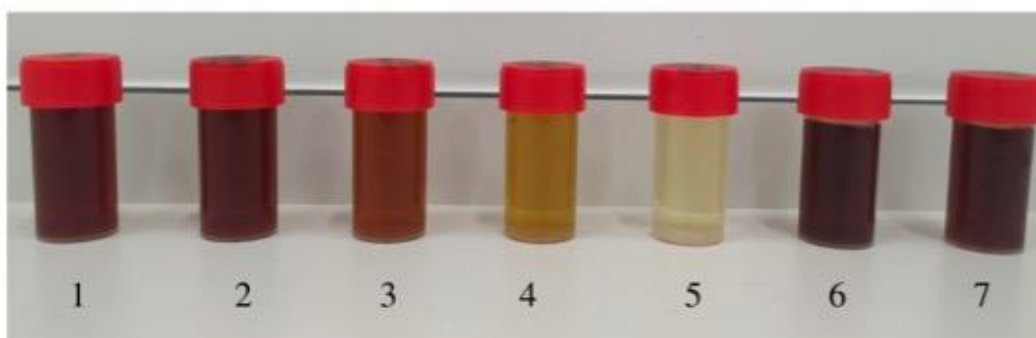

Figure A4. 1: Activated carbon filtrate from various batch tests to determine dosage value; 1-Raw C_5 filtered sample; 2-C_5 10w/w ED feed; 3- 10g/L (C-PAC); 4- 20g/L (C-PAC); 5- 30g/L (C-PAC); 6- 20g/L (V-PAC); 7- 30g/L (V-PAC).