Clarification and Concentration of Sugarcane Juiceusing Membrane Process: Study on Fouling, Cleaning, Modelling and Process Simulation

Thesis submitted in partial fulfilment
of the requirements for the degree
of
DOCTOR OF PHILOSOPHY

Submitted by

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Dedicated to

my Parents and family members

for their

unconditional love, support, and encouragement

Indian Institute of Technology Guwahati
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Department of Chemical Engineering

STATEMENT

This is to certify that I have carried out the research work presented in this thesis entitled **"Clarification and Concentration of Sugarcane Juice using Membrane Process: Study on Fouling, Cleaning, Modelling and Process Simulation,"** at the Department of Chemical Engineering, Indian Institute of Technology Guwahati, under the supervision of **Prof. Senthilmurugan Subbiah** and **Prof. Kaustubha Mohanty**. The results documented in this thesis are achieved by me and have not been submitted to any other university or institute for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgment has been made wherever the work described is based on the findings of other investigations.

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CERTIFICATE

It is certified that the work contained in this thesis entitled **"Clarification and Concentration of Sugarcane Juice using Membrane Process: Study on Fouling, Cleaning, Modelling and Process Simulation,"** being submitted by **Aanisha Akhtar** (Reg. No. 156107015) for the award of Ph.D. degree, is a record of bonafide research carried out by her at the Department of Chemical Engineering, Indian Institute of Technology Guwahati, under our guidance and supervision. The work embodied in this thesis has not been submitted to any other university or institute for the award of any other degree or diploma.

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Abstract

Membrane technology is an ever-growing field as it has several advantages over other traditional processes. Typically, membrane processes such as Ultrafiltration (UF) and Forward Osmosis(FO) have several functional applications including water treatment and food processing (clarification and concentration). Food industries play a vital role in the economic development of a country. One such industry is sugar industry which faces few problems and it is of utmost importanceto address these problems by providing technically sustainable solutions. Among the various processes in the sugar industry, clarification and concentration of sugarcane juice suffers from several technological limitations and is thus taken up as the area of this research work. During the sugarcane juice processing (clarification, concentration) and storage following technical limitationsare observed: gel formation at high concentration, browning (enzymatic) of juice, loss of vitamins and the components responsible for the juice flavour, taste change due to the thermal and chemical pre-treatment. The conventional method of sugarcane juice processing involves the pre-treatment with lime, sulphur dioxide and heat treatment above 100 °C. Considering the issues as mentioned above as well as scalability and process simplicity, membrane technology can be considered to be the most viable technology for the clarification and concentration of juice.Low costLanthanum phosphate($LaPO_4$) coated ceramic UF membrane was used for clarification of sugarcane juice and later FO membrane was used as an alternative to the conventional method of concentration of sugarcane juice. In addition to the excellent properties of the ceramic membrane, they are always proven to be susceptible to fouling. Further to analyse and mitigate the membrane fouling mechanism associated with sugarcane juice clarification and concentration process,different type of cleaning mechanisms was employed. In this work, we have developed an innovative physical cleaning mechanism to remove cake deposition from the UF ceramic membrane surface in realtime.

Similarly,the following challenges are reported while concentrating sugarcane juice by FO process: low water flux, CP, selection of appropriate draw solution (DS), and fouling. It has been also reported that clarified liquid food has reduced fouling intensity and provides stable FO operation. Therefore, this study was focused on

maximizing the design of FO experiments to minimize the optimal intensity while concentrating sugarcanejuicepre-treated by the UF process. In this work, the optimisedhybrid membrane separation process for sugarcane juice concentration was establishedto mitigate membrane fouling of the sugarcane juice concentration process.

In this research, the entire work carried out was divided into four major parts as given below,

- Feasibility study of the clarification of sugarcane juice by $LaPO_4$ coated ceramic UF membrane andits fouling and cleaning analysis.
- Feasibility study of the concentration of sugarcane juice by Aquaporin HFFO membrane and corresponding bottlenecks to be addressed to implement same in the industrial scale.
- Development of a batch FO process mathematical model forconcentration of sugarcane juice by Aquaporin HFFO membraneand its validation.
- Process simulation and performance optimization of Aquaporin HFFO membrane to minimize the SEC with maximum yield.

As part of the first objective, the application of the $LaPO_4$ ceramic membrane for the clarification of sugarcane juice was explored to avoid the use of lime and to produce chemical free sugarcane juice. Subsequently, the effect on the polyphenol oxidase (PPO) enzyme removal efficiency, bacteria removal efficiency, permeate flux decline profile, and membrane cleaning efficiency wasevaluated. Again, the result of a long termsugarcane juice storage study revealed that the UF clarified juice couldbe stored in refrigerated condition for sevenweeks without significant change in the quality of the juice. Moreover, the importance of the inline physical cleaning and its operating mechanism is evaluated to understand the fouling and cleaning phenomena of the ceramic membrane.

As part of the second objective, the performance of a commercially available Aquaporin HFFO membrane for the concentration of sugarcane juice by adopting an appropriate UF pre-treatment technique was studied.The effect of various process parameters such as DS flow rate, DS concentration and its direction of flow (co-currentor counter-current) on waterand reverse solute flux in batch mode was studied.

In this study NaCl is used as a draw solute.The experimental results showed that counter-current flow configuration between FS and DS was able to provide 7% high water flux than co-current flow configuration. In the case of counter-current mode batch FO operation, sugarcane juice was concentrated to a maximum of 1.6 times of initial concentration in just 12 min by using an initial DS concentration(NaCl)of 100 gL^{-1}(with negligible draw solute back diffusion). The maximum average water flux of 5.22 ± 0.08 L h^{-1} m^{-2} was observed for a higher DS flow rate (45 L h^{-1}). Both water flux and reverse specific salt flux (SRSF) improved by 15% and 39% for the counter-current mode compared to the co-current mode at 45 L h^{-1} DS flow rate. The effect of UF clarified and raw sugarcane juice on FO membrane fouling was studied. The pure water permeability of the FO membrane is reduced after 16 h in the case of UF clarified sugarcane juice. When unclarified juice is used the pure water permeability of FO starts reduces after 60 min. For example, it was observed that the pure water permeability of the FO membrane was reduced by 53.3% when fouled by unclarified juice. However, while using the UF clarified juice, it was 11.2%. It was observed that raw sugarcane juice led to severe membrane fouling. The cleaning study concluded that the fouled membrane could be regenerated easily by DI water wash for 30 min for UF clarified juice. However, regeneration of membrane for the case of raw juice was not possible with DI water wash alone, and it required 0.1 M NaOH wash.Further to improve the performance of the FO process, an osmotic backwash was also used, but the regenerated flux was not closer to the new membrane flux. Thus, it required an additional washing with 0.1 M NaOH.After cleaning the membrane was regenerated 100% by simple DI water wash when clarified juice was used. On the other hand, for the case of regenerating the membrane fouled by unclarified sugarcane juice 9.8%, 8.2% and 82% improvement in permeability were observed for DI wash, osmotic backwash and NaOH wash, respectively.

Under the third objective, modelling, validation and process simulation of the batch FO process was carried out. A mathematical model of the batch FO process was developed by integrating the FO membrane module, FS and DS storage tank. The model for the FO membrane module was developed by integrating mass, momentum and membrane mass transfer equations. The unknown model parameters of FO

modulewere estimated by minimizing the error between FO batch experimental data and model output. The estimated parameters were used to predict the performance of the model using the remaining experimental data. The developedmodel was able to predict experimental output within an error of 5% for permeate flux and reverse solute flux. The estimated value of model parameters such as pure water permeability (A), solute permeability (B), structural parameter (S), $\alpha_f$and $\alpha_d$were found to match the reported values in the literature. As part of the fourth objective, three case studieswere carried out viz. case I: FS and DS both are recycled, case II: FS recycle and DS in continuous mode and case III: both FS and DS were in continuous mode. From these three cases of the simulation study, it was observed that case III was more effective in terms of concentration, reverse solute flux and specific power consumption. The SECwas 78.85 W L^{-1} for Case III(both feed and DS in continuous mode),which was the lowest among all three cases. Again, a simulation study was carried out for the two FO modules in a series system and compared with other DS flow rates to find the optimal DS flow rate.A 60:40 DS flowrate ratio gavethe best results in low SEC, low RSF, and high concentration. Overall, the obtained results will serve as a useful solution for future use of membrane technology in sugar industries.

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Abbreviations and Nomenclature

Abbreviations

ALDS	: Active layer facing draw solution
ALFS	: Active layer facing feed solution
CECP	: Concentrative external concentration polarisation
CICP	: Concentrative internal concentration polarisation
CP	: Concentration polarization
CST	: Continuous stirred tank
CTA	: Cellulose triacetate
DECP	: Dilutive external concentration polarisation
DI	: De-Ionized water
DS	: Draw solution
ECP	:External concentration polarisation
FO	: Forward osmosis
FS	: Feed solution
HF	: Hollow fibre
HFFO	: Hollow fibre forward osmosis
HPLC	: High performance liquid chromatography
IC	: Ion-chromatography
ICP	: Internal concentration polarisation
NF	: Nano-filtration
PES	: Polyester
PFR	: Plug flow reactor
PSF	: Polysulfone
Re	: Reynolds number

RID : Refractive index detector

RO : Reverse osmosis

Sc : Schmidt number

SD : Solution diffusion

SEC : Specific energy consumption

Sh : Sherwood number

TFC : Thin-film composite

UF : Ultrafiltration

Nomenclature

A_m : Membrane surface area (m^2)

B : Solute permeability coefficient (L $m^{-2}h^{-1}$)

C : Concentration (g L^{-1})

D : Diffusivity coefficient (m^2h^{-1})

E : Energy consumed

$d_{i,fiber}$: Inner diameter of hollow fibre(m)

$d_{o,fiber}$: Outside diameter of hollow fibre (m)

J_s : Reverse solute flux (g $m^{-2}h^{-1}$)

J_w : Water flux (L m^{-2} h^{-1})

k_d : Mass transfer coefficient on draw side (m h^{-1})

k_f : Mass transfer coefficient on feed side (m h^{-1})

L_p : Water permeability (L m^{-2} h^{-1} bar)

M : Mass (g)

M_w : Molecular weight

P : Pressure (Pa)

P_{DS} : Draw side pressure (Pa)

P_{FS} : Feed side pressure (Pa)

Pw_{inp} : Power consumption

Q : Flowrate (Lh^{-1})

R : Gas constant

S : Structural parameter (μm)

T : Time (h)

T : Temperature (K)

V_{DS} : Volume of draw solution (L)

V_{FS} : Volume of feed solution (L)

V_p : Processed volume

U : Velocity ($m\ h^{-1}$)

Greek Letters

α, β, γ :Mass transfer correlation constants

ρ : Density ($Kg\ m^{-3}$)

Δ : Film layer thickness

π : Osmotic pressure (Pa)

μ : Viscosity (Pas)

i : Van't Hoff facto

Chapter: 1

Introduction

This chapter presents sugarcane juice processing technologies and their advantages and disadvantage in terms of operational challenges towards reaching desired juice quality. The advantages of using the membrane separation process for sugarcane juice clarification is analysed to intensify the benefits of using them in place of conventional technologies. Finally, the aim of the thesis work and its structure is presented.

1 Introduction

Rapid urbanization as well as the growth of population especially in developing countries has led to the setting up of various industries. Among these, food processing industries play a vital role to meet demand and supply between source and end-users, and also to minimize the wastage of food. In recent years, the potential utilization of juice produced from various fruits and vegetables has shown significant improvement in its shelf-life and reduced wastages. For example, sugarcane juice is one of the essential juices from which sugar is produced. Sugarcane juice is extracted from the sugarcane plant. The sugarcane plant (*Saccharumofficinarum*) is a perennial fibrous plant thatis rich in sucrose content. India is the second largest producer of sugarcane globally by contributing 18.4% of the world's total sugar production, i.e., 348 million metric tons (Horticultural statistics at a glance 2018, Ministry of Agriculture and Farmers' Welfare, Government of India). Sugarcane juices are concentrated in the food industries for further use. Generally, sugar crystals, jaggery and other similar products are manufactured by concentrating the sugarcane juice. 28.35 g of sugarcane juice contains 26.56 kcal energy, 27.51 g carbohydrate,11.23 mg calcium, potassium 41.96 mg, 0.27 g protein, iron 0.37 mg and 17.01 mg sodium [1].

In the sugar industry, conventional methods are used, which involves crushing of cane fibres and extraction of raw juice, clarification using lime and flocculants, sulphitation, evaporation and crystallization. Around the world, a wide variety of sugarcaneis produced and mostly they are seasonal. Due to this, the preservation of sugarcane juice is very important for sugarcane processing industries. The extracted sugarcane juice contains a significant (75-90%) quantity of water and microbes, and they will be creating enormous challenges during preservation, storage, and transportation. The conventional process of clarification and concentration of sugarcane juice offers many

challenges and disadvantages. Since sugar industries are using traditional technologies, thus it faces various challenges during the processing of sugarcane juice.Another common problem during sugarcane juice concentration and storage is gel formation at high concentration, browning (enzymatic) of juice, loss of vitamins and the components responsible for the juice flavour and taste loss during evaporation (due to heat).

To mitigate some of these problems, clarification of sugarcane juice is carried out by using lime. It is pre-treated by lime to remove suspended solids, colour, to clarify and to prevent degradation. Multiple effect evaporators are commonly used for the concentration of clarified sugarcane juice to 50-60% by weight [2] and vacuum filtration is used for further concentration. The bagasse is mostly used as the source of thermal energy in the evaporator for juice concentration. Therefore, replacing thermal energy-based sugarcane juice concentration technology with non-thermal technology may enable alternate usage of the bagasse, i.e., papermaking, power generation, animal feed, etc.

Many researchers have investigated emerging technologies to replace or complement the conventional processes in food processing, including membrane technology, ohmic heating, microwave heating, gamma irradiation, pulsed electric field, and ultrasound. Membrane technology is applied in juice processing for clarification as well as the concentration of juice. The principalneed of these advanced technologies is to fulfil product safety during food processing (i.e.clarification, concentration) by preserving nutritional characteristics, microbial stability, flavour etc. To address problems like aroma retention, taste, flavour, vitamins, and gel formation during liquid food processing, researchers have suggested using membrane technology to provide good quality liquid food cost-effectively. For example, the membrane assisted process of clarifying and concentrating sugarcane juice provides microbial stability and minimizes the costs of transportation, packaging, and storage of juice by reducing the water content. However, fouling is one of the inherent phenomenain the membrane separation process and its impact has to be minimized to achieveenergy-efficient membrane separation processes[3].

1.1 Research motivation

1.1.1 Importance of sugarcane juice clarification by membrane processes

The origin of sugarcane cultivation in India is reported in many literature as in between the period from 1400 to 1000 BC. It is extensively accepted that Saccharum species originated in India [1]. Sugarcane juice is the primarysource of the sugar industries of India. The sugarcane juice can be processed to concentrate for further use. After extraction of juice, it contains small particles of bagasse, different soluble substances like polysaccharides, proteins and salts of acids. The presence of substances such as flavonoids, polyphenolics, and organic acids is responsible for the sugarcane juice's dark colour[4]. It also contains other impurities like reducing sugars, organic acids, amino acids, starches and other colouring matter that imparts dark colour and high turbidity to the juice. From a commercial perspective, these impurities need to be removed to get clear and light syrup, leading to pure sugar crystals that look appealing throughthe clarification process. Many studies confirmed that during clarification and decolourization of sugarcane juice, lime is added in sugar industries. Some reported that carbonation, sulphitation or activated carbons are also used to clarify sugarcane juice [4]. Moreover, the juice remains acidic unless purified, which is undesirable. Also, partial clarification and purification inhibit enzyme action and stop the oxidation of some of its components, leading to the darkening of the juice and its subsequent degradation.

It is reported that the sugarcane juice must undergo clarification because it gets darken after extraction due to the oxidation of chlorophyll and polyphenolic compounds which are responsible for the dark colour. The unclarified juice contains unwanted components such as starch, polysaccharides, gum and suspended impurities etc. The presence of unwanted solids in the sugarcane juice leads to poor quality end products derived from unclarified sugarcane juice. Many researchers reported the adverse effect of unclarified juice during the concentration process. The unclarified juice is having a detrimental impact on the concentration and storage of sugarcane juice. Thus, we see that clarification of the raw extracted sugarcane juice is of utmost importance by

enablinglong-term storage without degradation and producing white sugar crystals for commercial use. Lime is used to clarify the sugarcane juice in the sugar industry. But it should be added tothe juice for maintaining pH at a desired level. Excess lime may lead to an adverse effect on turbidity and the colour of the sugarcane juice [5].

On the other hand, the addition of lime to clarify the sugarcane juice impacts human health due to long term consumption. Therefore, a technology that can clarify the sugarcane juice without much chemical addition may help to produce sugar crystals without lime traces. The health issues relevant to the presence oflime trace in sugar crystals isnot yet well studied. This trace of lime cannot be removed with conventional methods and there is no report available on this. Therefore, an alternative method of clarification of the sugarcane juiceis the need of the hour. The membrane separation process can be used to clarify the sugarcane juice without adding lime. Membrane technology promises better quality as well as lower viscosity and recognizable colour removal. "Need of ceramic membrane process is also not captured".

1.1.2 Importance and need of costeffective process forconcentration of sugarcane juice by membrane processes

It is well known that most sugar industries are moving towards sustainable operation by minimizing energy consumption and pollution without compromising product quality. Continuous discharge of a pollutant to the environment, especially air pollution due to the burning of bagasse to get thermal energy required for the concentration of sugarcane juice are expected to cause long term damage like global warming and increased PM levels in the air[6]. Therefore, there is a need for alternate technology against conventional processes. Modern technologies such as membrane separation/purification can provide a solution to the problems faced by the food industry. Researchers have recently proven that membrane technology is a standard and proven process for food industry, dairy, wastewater treatment, etc. Membrane technology has potential in the sugar industryto achieve minimum energy consumption and chemical elimination in pre-treatment with high quality product.

Further, to achieve improvedenergy efficiency in the sugar industry, there is a need for energy-efficient technology to concentrate sugarcane juice without losing its nutrients. Though the conventional evaporation process of concentration removes a significant portion of the water, it is still in use at the commercial level. It is time to introduce new technology like membrane processes to concentrate the sugarcane juice at the industrial level. Sugarcane juice concentration using membrane process is one of the areas where a lot of interest has been generated due to its efficiency. Researchers reported that the energy consumption of multiple-effect evaporator could be reduced by 33% by integrating membrane processes such as Nano filtration (NF),Reverse Osmosis (RO) for juice pre-concentration from 5° to 20° Brix [7].Membrane assisted processes for food processing and wastewater treatment have proven the feasibility of the technology and cost effectiveness. For the concentration of the clarified juice, membrane processes can provide a great solution in terms of cost compared to the conventional processes that use bigger equipment and higher energy. High pressure membrane processes are used in the concentration process of fruit juice. However, the high pressure assisted membrane processes are mostly not recommended for the concentration of fruit juice.Recently, Forward osmosis (FO)has beenfound to be one of the most promising membrane process for concentration of beverages, organic and inorganic acids and alcohols without product degradation. FOhas an advantage over RO and thermal-based separations in terms of operating pressure and temperature [8]. The FO process has more privileges over the RO process in respect of less energy consumption in the presence of an effective draw solute regeneration [9–11], high product recovery, low reverse solute flux and less fouling [3].

Therefore, selecting a suitable membrane process can minimise the cost of liquid food processing (concentration of juice).Many researchers used FO based separation process for liquid food concentration [12,13]. The viability of using the FO process for sugarcane juice was tested by Shalini et al. [14] and Mondal et al. [2]using test cell experiments. Both studies were limited to FO experiments to measure water flux for sugarcane – NaCl/seawater system using both commercial and lab prepared FO membrane. Mondal et al. [2] have achieved 4 fold concentration of sugarcane juice by adopting the feed recirculation mode. Some challenges have to be faced during the

concentration of sugarcane juice by FO processes such as low water flux, CP, and selection of suitable draw solution (DS). The DSselection plays a vital role in cost minimisation, high osmotic pressure requirement, toxicity, water solubility, etc. [15].

Another inherent issue with membrane separation techniques is fouling at the dense membrane surface as well as at the porous support layer. Hence, one of the main challenges during the concentration of sugarcane juice by FO membrane is the mitigation of membrane fouling. That requires a detailed analysis of the fouling phenomenon with a more extended period of FO operation with real sugarcane juice. The supply of pre-treated sugarcane juice can be a solution to the membrane fouling issue [16]. Aquaporin Hollow Fibre Forward Osmosis (HFFO) membrane is one of the promising FO membrane available in the market for concentrating food products with low energy consumption[17]. The less fouling prone nature of this membrane lead to longterm use in the concentration process. Another advantage is cost-effective cleaning process of the membrane. This can reduce the operational cost of the process by up to 50%. Therefore, the HFFO membrane process is viable in terms of cost and providing quality concentrated sugarcane juice.

1.2 Background of membrane

1.2.1 Definition

A membrane is a thin barrier, placed in between two phases/mediums which allows one or more constituents to selectively pass from one direction to another in the presence of an appropriate driving force while retaining the rest. It is an advanced separation technique. The rejected portion is known as retentate and the portion which flows across the membrane is called permeate. Fig.1.1 illustrates the membrane separation process, showing retentate and permeate regions. The membrane separation processes are classified based on the driving force applied on either side of the membrane to achieve the desired separation level.The driving forces in the membrane separation process may be pressure gradient, concentration gradient, electric potential gradient and temperature gradient. The separation efficiency of the membrane is found to be a function of following physical and chemical properties of

the membrane/solvent/solute: (i) pore size and its distribution, charge (e.g. electro dialysis, ion exchange, and electrophoresis) (ii) affinity between the membrane and solvent/solute (i.e.hydrophobic, hydrophilic), (iii) vapour pressure of the solvent, (iv) chemical properties of solvent and solute (i.e.molecular weight, pH, turbidity, solute particle size etc.) and (v) flow configuration across the membrane (i.e. dead end, cross flow). Membrane filtration technique is a process in which the membrane acts as a barrier to provide resistance to solute transport and simultaneously allows the solvent to transport across the membrane. The permeation of solvent alone leads to solute concentration polarization near the membrane surface, and solvent flux declines. Further, to maintain the consistent solvent flux, the driving force is increased till to its threshold value. Beyond the threshold value, the membrane will undergo maintenance activity.

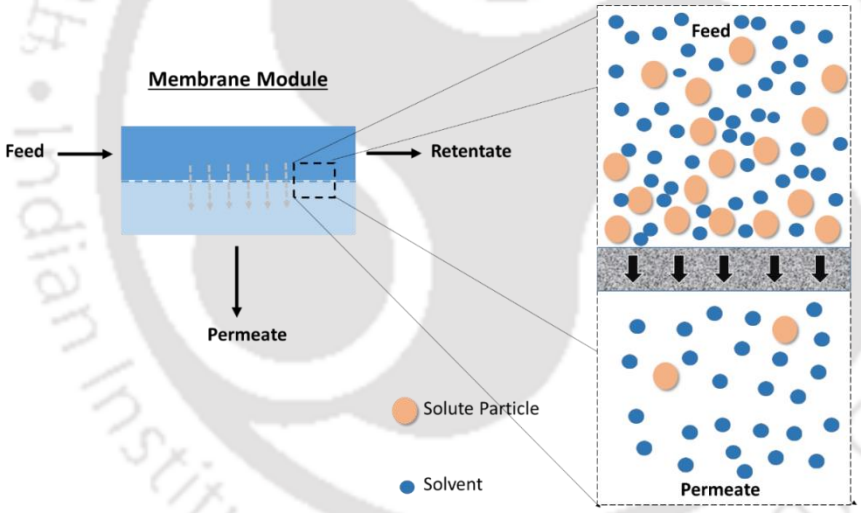


Fig. 1.1 Membrane filtration

1.2.2 Classification of membranes

Based on the material, the membrane can be classified into the biological and synthetic membrane. In living cells, the biological membranes present (e.g., nephron present in kidney act as a biological membrane to separate undesirable components) and the synthetic membrane are made from various materials. Again, the biological membrane can be further classified into non-living and living membranes.

The membrane can be further classified as solid membrane and liquid membrane. The solid membranes are further classified into dense, porous and electrically charged. Again, based on the morphology, membranes are classified into the symmetric and asymmetric membrane. Symmetric membranes are single layer and homogenous in structure, but asymmetric membranes consist of two or more porous layers that are heterogeneous in nature. Again, synthetic membranes are classified into inorganic and organic membranes. Membrane classification according to morphology is shown in Fig.1.2.The liquid membranes are subdivided basically into an unsupported liquid membrane and supported liquid membranes.

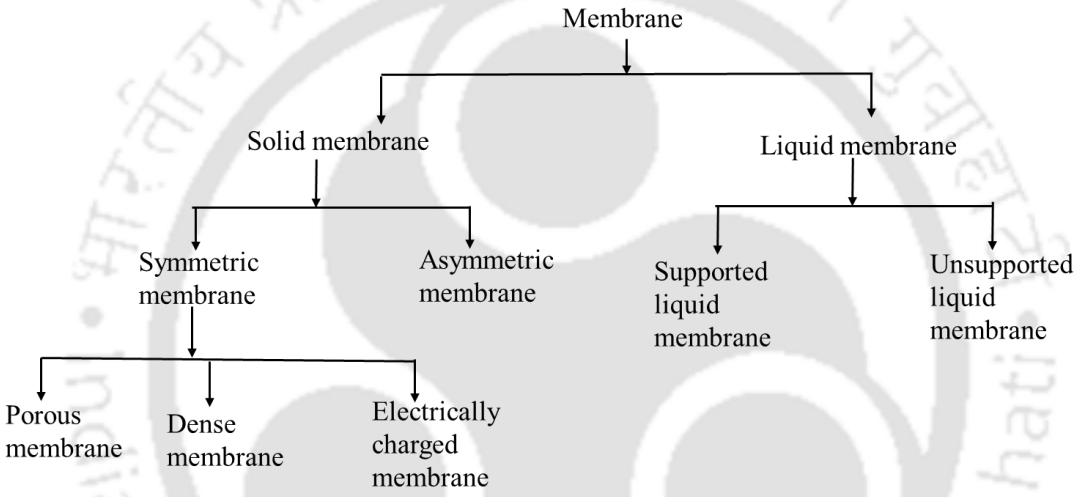


Fig. 1.2 Classification of membrane[18]

1.2.3 Classification of membrane separation processes

Based on the driving forces and transport mechanisms, membrane processes are classified into pressure-driven, concentration-driven, temperature-driven, and electrically driven processes (Fig.1.3).Pressure driven membrane processes are further classified into Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and RO. MF membranes have a pore size of 0.1-10 µmwhere pressure is 0.1 - 2.5 bar and the retentate or concentrated solution contains suspended particles and bacteria. UF membranes have a pore size of 10-100 nm where pressure is 2 -10 bar and in the retentate large molecules, various proteins, viruses are present. NF membranes have a pore size of 1-10 nm where operating pressure is 10-30 bar, and in the retentate or concentrated solution,small moleculesand divalent salts are present, whereas RO

membranes have a pore size of 0.1-1 nm where pressure is 30-100 bar and in the retentate or concentrated solution all solutes are present which are retained by the membrane[19].

Another category is the concentration driven membrane process. Here,the concentration gradient is the drivingforce during the separation process (FO, dialysis). Temperature driven membrane processes use temperature gradient as a driving force during the separation process (membrane distillation and pervaporation). Electrical potential driven membrane processes are electrolysis, electro-filtration, electrochemical ion exchange etc.

Depending on the mode of operation, membrane processes are further classified into dead-end filtration, cross-flow filtration and hybrid-flow filtration (works with combination of both dead-end and cross-flow filtrations.

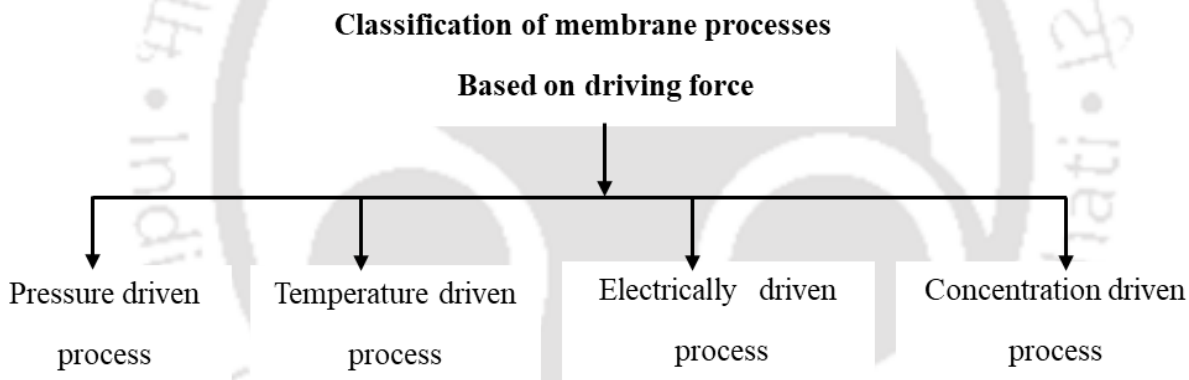


Fig. 1.3 Classification of the membrane separation process[20]

1.2.4 Ceramic membrane

The ceramic membrane is made of a combination of inorganic materials such as zirconia, α-alumina, ϒ alumina, silica, kaolin, titania etc. The thickness of the ceramic membrane is in the range of 2-5mm, and it can vary beyond this limit based on the requirements of a specific application. Mostly asymmetric ceramic membranes constitute a thin layer of 10-100 μm of ceramic coating over a thick porous symmetric support. In general, ceramic membranes are broadly classified into two types: porous ceramic membrane and dense ceramic membrane, based on the membrane's pore size.

Again based on the transport mechanism of the species through the membrane, the classification can be defined. When the separation mechanism is controlled by sieving of the species (molecules and ions etc.), it isgenerally called a porous membrane. On the other hand, when the membrane follows the solution diffusion mechanism for transportation of the species, the membrane is known as a dense membrane. Generally, NF, UF and MFceramic membranes are considered porous membranes. The physical characteristics of these membranes, such as size, shape, porosity and tortuosity etc., will be varying with respect to the fabrication process of the membrane[21]. Two major types of dense ceramic membranes are based on solid electrolyte and metal. These are used for the gas separation processes. For hydrogen separation and purification application, a dense ceramic membrane made of palladium and its alloys was very useful[22]. Because of many advantages like high porosity, chemical and thermal stability, narrow pore size distribution, high flux, mechanical strength (which enables high pressure backwash and flushing), micro biological resistance, and durability of ceramic membranes over the polymeric membrane, its demand has increased. Cleaning ceramic membrane is easier than polymeric ones due to higher chemical and thermal stability. This provides added advantage for the application of this membrane under harsh conditions. The main limitations of the ceramic membrane which limit its full scale application are high manufacturing cost and brittleness. Advantages and disadvantages of ceramic membranes are given in Table1.1.

Table 1.1 Advantages and disadvantages of ceramic membrane [23]

Membrane	Advantages	Disadvantages
Ceramic Membrane	1. High thermal stability (up to 350 °C) 2. Wide pH limit (0.5 to 14) 3. High chemical stability 4. High corrosion resistance 5. Wide operating pressure range (0 to 30 bar) 6. Less fouling tendency 7. High mechanical strength 8. Long life 9. Biocompatibility (food and pharmaceutical industry) 10. High pressure back wash for regeneration 11. Easy regeneration and dispose	1. Brittleness 2. Comparatively High capital costs 3. Scaling issue 4. Low membrane surface area per module volume 5. Risk for packing and transportation as membrane module

The inorganic ceramic membrane is the most promising technology due to their excellent resistance to thermal, chemical and mechanical strength (useful for backflushing/back washing), narrow pore size distribution, high flux, durability over polymer. These properties of ceramic membrane help in its application in various fields. The application of membrane and corresponding separation processes are shown in Fig. 1.4. At present, in the membrane industry, ceramic membranes are used for applications such as microfiltration (50 nm–1 μm), ultrafiltration (2 nm –50 nm) and nanofiltration<2 nm).

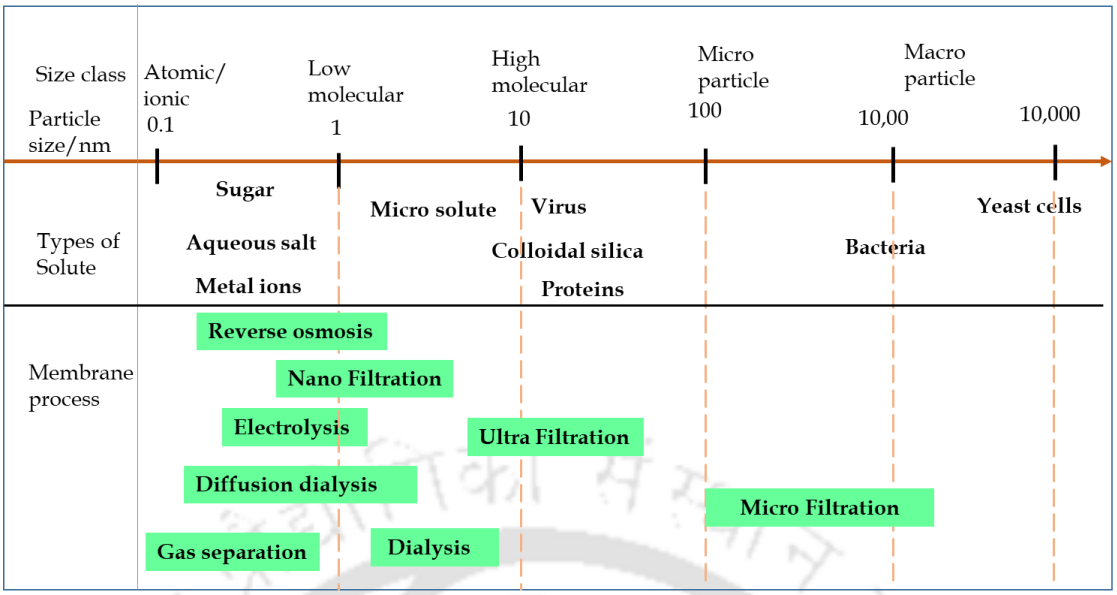


Fig. 1.4 Application of membrane and corresponding separation processes[24–26]

In gas separation processes, microporous or dense (silica or zeolite) membranes were used where the chemical potential gradient is the driving force for gas transport. The application of ceramic membranes are numerous such as chemical industries (recovery of pigments and dyes, concentration of polymer substances, desalination, catalyst separation etc.), metal industries (heavy metal recovery, treatment of wastewater glass production), food and beverage industries (purification of water, clarification and concentration of fruit juices, milk and whey), biochemical industries (protein recovery, antibody purification,concentration, isolation and sterilization of enzymes, antibiotics and vitamins etc.). Usually, the commercial ceramic membranes are based on ZrO_2, TiO_2 and Al_2O_3. In recent times ceramic components are provided from different vendors of various countries such as Tami, France (manufacturer) provide α-Al_2O_3 (0.14–1.4 µm MF), ZrO_2/TiO_2 (3000–300,000 Da UF) and TiO_2 (1000 Da NF); Pall, USA (manufacturer) provide α-Al_2O_3 (0.14–1.4 µm MF), ZrO_2 (20–100 nm Da UF) and TiO_2, SiO_2 (600–1000 DaNF); NGK, Japan (manufacturer) provide α-Al_2O_3 (0.1–1.2 µm MF), TiO_2, SiO_2 (10–150 kDa UF); Atech, Germany (manufacturer) provide α-Al_2O_3, TiO_2, ZrO_2 (0.1–1.2 µm MF)and TiO_2, ZrO_2, Al_2O_3 (1–150 kDa, 50 nm UF); Jiuwu, China (manufacturer) provide α-Al_2O_3, ZrO_2 (0.1–0.8 µm MF)and α-Al_2O_3, TiO_2, ZrO_2 (5–50 nm UF) and TiO_2, ZrO_2 (1000 DaNF) [27]. Recently, theceramic membrane has been fabricated from ionic conductors and used to separate oxygen from the air at high

temperature. The ionic ceramic membrane are also used to separate elements such as hydrogen and gallium. These are mainly used for laboratory and scientific curiosity studies. But due to the industrial interest,a Japanese group in 1985 studied a dense oxide membrane that can separate oxygen at temperature 800–1000°C (100% selectivity). Due to the high demand for oxygen in medical, aerospace, manufacturing industries and petrochemical, the ionic conductor ceramic membrane has been achieving interest for commercialization production.

1.2.5 Forward Osmosis

Osmosis is the natural process where water diffuses across the semipermeable barrier or membrane from a high water concentration to a low water concentration side. At equilibrium, the water concentration on both sides is equal. The flux across the FO membrane is a function of solute concentration/osmotic pressure difference across the semipermeable membrane. As a result, the solvent is transported from the low solute concentration solution (FS) side to the high solute concentration (DS) side. The comparison between FO and RO process is shown in Fig. 1.5 (a). In FO process, hydraulic pressure at both sides of the membrane is nearly equal at atmospheric conditions, i.e. no hydraulic pressure and rise in temperatureisapplied, and water is transported from high water concentration to low water concentration side. But in the case of the RO process, the water is transported from the low water concentration side to the high water concentration side by applying hydraulic pressure at the low water concentration side to overcome the osmotic pressure difference across the membrane. The FO process is attractive over the RO process due to its advantages such as low hydraulic pressure, lower fouling tendency, less energy requirement in the presence of efficient DS, higher water recovery and high solute rejection.

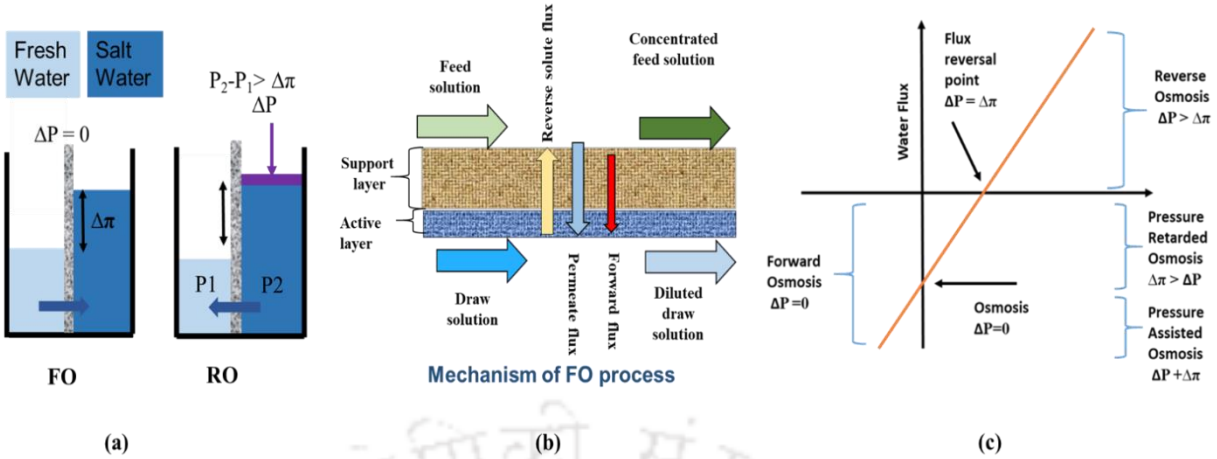


Fig. 1.5 (a) Illustration of comparison between FO and RO processes and(b) mechanism of FO process, (c) representation of the solvent flux in osmotic driven membrane separation process with respect differential hydraulic pressure across the membrane separation layer, adapted from [22]

The definition of the osmotic membrane process based on driving potential is presented in Fig 1.5 (c).For example, the ΔP is zero in the FO process, and the net driving force for water flux is Δπ. In pressure-assisted osmosis, the ΔP is less than zero, and the net driving force for water flux is Δ(+ΔP.In the case of Pressure Retarded Osmosis (PRO), the driving force is Δπ - ΔIn such a way that Δπ > ΔP. But when Δπ < ΔP, then water flux will be in theopposite direction,and that process will beRO.

Due to internal concentration polarization in the FO process, the design and optimization of the FO membrane support layer arevery important for achieving economically viable water flux in the FO process. The dense separation layer then can provide low reverse solute flux. Therefore, the availability of high flux is acritical issue for the FO process.Following companies are producing commercial FO membranes (i) aquaporin A/S, (ii) toyobo Co Ltd. and they are configured as (i) spiral-wound, (ii) axial and radial hollow fibre. The merits and demerits of both module configurations are summarised in Table 1.2.

Table 1.2The merits and demerits of hollow fibre module and spiral-wound[28]

Hollow fibre(HF)module		Spiral wound module	
Merits	Demerits	Merits	Demerits
1. HF module offers high membrane area 2. Low hold up volume 3. Energy consumption is low 4. Osmotic backflushing will be effective. 5. Compared to other modules it is cost effective	1. Susceptible to end–face fouling 2. If single fibre damage, the entire module has to be replaced 3. It is higlysensitive for fouling	1. It has a good packing density 2. Energy consumption is acceptable 3. Capital/ operating cost islow	1. Difficult to clean 2. Not suitable for very viscous fluid 3. Osmotic backwashing will not be uniform due to channel flow

Hollow fibre modules are compacted with thin hollow fibre membranes and they can withstand high back pressure. Some of the characteristics of hollow fibre modules are: (i) these modules are operated in laminar flow region (with Re numberbetween 500-3000), (ii) they can be operated under low pressure, (ii) these modules are most economical in terms of energy consumption due to low crossflow rate and low pressure drop and (iv) hollow fibre modules have highest surface area to volume ratio among all other modules with good backwash capacity and these modules are easy to clean. But the disadvantage of thismodule is that the thin fibres are susceptible to blocking by the larger particles present in the feed stream and, therefore, required pretreatment of feed to reduce the particle size to 100 μm in most of the applications. Flat sheet modules are operated in the laminar flow region and pre-treatment (pre-treatment to 150 μm) of feed is required in these types of modules. In terms of energy consumption, cost and packing density flat sheet membrane modules are between tubular and spiral wound membrane modules. In the spiral wound membrane module, spacers enablethe turbulent flow region to minimize concentration polarization and fouling.The pressure drop of spiral wound module ishigh due to the

additional drag force generated by the spacer. The spiral wound membrane modules have fair high surface to volume ratio with low capital cost.These membrane modules can be used for the feed with minimum suspended particles. Depending on all these properties, appropriate membrane modulesare selected for a particular application process.

1.2.6 Application UF and FO process for food processing

In food processing industries, membrane technology has been widely recognised as a standard tool for processinga variety of foods and beverages. In food and beverage processing, membrane filtration processes are gaining more attention as alternative processes for traditional concentration and separation operations. The application of UF membrane separation technology in the food and beverage processing industry has resulted in the availability of a wide variety of products.

For more than two decades, the UF process has been considered an essential tool for concentration and clarification in food processing industries. This membrane process offers advantages such as gentle product treatment, higher selectivity, and lower energy consumption. Considering in terms of juice clarification, the UF process has reportedly been commercially used to separate the fibrous pulp from the juice. Apart from clarification, reportedly, the effect of UF has been proven to recover essential bioactive components from fruits and vegetable juice. However, despite the high efficiency and moderate investment and maintenance expenses of membrane filtration processes, CP and fouling phenomena remain the main obstacle for the definite implementation of this technology in food and beverage processing. Therefore, the development of fouling control membranes and the modification of current membrane filtration processes (e.g., pre-treatment, module design, operation mode, and cleaning process) is crucial for membrane technology to increase further its importance in the food and beverage processing industry, as well as other processing industries.

FO process can be defined as a low-pressure operated membrane technology that takes advantage of the osmotic pressure gradient between two aqueous solutions separated by a hydrophilic perm-selective membrane. Unlike the RO and NF process, the FO process can be effectively used to concentrate liquid food without

significantmembrane fouling. The ambient operating condition of the FO process allows retention of thermo-labile sensory and nutritional qualities. The practicability of the FO process for concentrating fruit juice, milk, and whey has been successfully studied and demonstrated by various researchers. However, the impact of the reverse solute flux of draw solute on fruit juice and energy efficient root for regeneration draw solute is a critical aspect that has to be taken care of before the commercialization of FO for food processing. In food processing industries, the FO process has been widely investigated for the concentration of thermolabile aqueous solution such as juice (fruits/vegetables) such as grape [29], passion juice[30,31], coffee[32], orange[33], kokum[34,35], xylose[36], rice straw [37],jaboticaba juice[38], sucrose solution [39], fructose [40] and tomato juice,and tea. Although many potential applications of FO membrane processes have been indicated and investigated for a variety of liquid foods, it is still facing some serious and vital challenges. These challenges are issues related to CP, membrane fouling, reverse solute diffusion, and the need for membrane development and the designing of draw solute.

As per the literature review, membrane technology is an alternative to the conventional processes of clarification and concentration of sugarcane juice. An extensive literature survey on these has been carried out and is reported in the next chapter

Chapter: 2

Literature Review and Objective

This chapter provides detailed literature on the membrane separation process for sugarcane juice clarification and concentration. More specifically, the application of ceramic membrane for clarification of sugarcane juice and itsfouling challenges are summarised. Similarly, the application of modelling and simulation of FO process development for sugarcane juice clarification is summarised. Based on state of the art, the scope for further research has been identified and the aim of the present work has been summarized. From the outcome of the literature survey, the objectives of the present research work are defined at the end of this chapter and finally, the organization of the thesis has been presented.

2.1 State of the art

In this work, an investigation of sugarcane juice clarification and concentration by ceramic UF membrane and aquaporin FO membrane is reported. Further to identify the research gap and to improve the proposed membrane separation process, the following three sections are presented below: (i) application of ultrafiltration in clarification of sugarcane juice and membrane fouling, (ii) application of FO in concentration of sugarcane juice and membrane fouling and (iii) modelling, validation and process simulation study of FO membrane.

2.1.1 Application of ultrafiltration membrane in clarification of sugarcane juice

Sugarcane juice hasan immense nutritional value which constitutesvarious components that are beneficial for human health. However, impurity contents are high after extraction of the sugarcane juice which restricts its direct use in the downstreamprocesses of sugar industries. The raw sugarcane juice contains a small amount of cane fibre (called bagasse) and soluble substances such as salts of acids, base, proteins and polysaccharides.The traditional method of sugarcane juice processing involves the pre-treatment with lime, sulphur dioxide and heat treatment above 100 °C. Unfortunately, during these processing, a vital part of the juice component that contributes to the juice's quality, such as flavour, aroma declines due to the thermal and chemical pre-treatment. In the sugar industry, sucrose loss and colour formation with time is an issue. Lime pre-treatment is usually carried out to reduce sucrose loss and colour loss [41]. Variation of colour with time as pertained in sugar industries can be solved by different methods such as chemical addition, heat

treatment etc.In this regard, membrane technology is found to be beneficial compared to other conventional methods. In sugarcane juice clarification, membrane-based separation is seen as an alternative to traditional technologies as such methods are less efficient and involve high operating costs.Therefore, many researchers employed membrane-based technology to avoid the use of chemicals. The aim of clarifying sugarcane juice using membrane filtration is to remove high molecular weight materials and retain low molecular weight solutes necessary for human consumption such as sucrose, glucose, fructose, aroma, salt, and flavour components in the clarified sugarcane juice. The colourless juice can be achieved by removing starch vegetable fibres, gums and other unwanted components [42].

Numerous literature reported the application of microfiltration (MF) [43–45] and UF [42,43,53–57,45–52]on the removal of impurities from the juice. Due to high viscosity and high osmotic pressure, large volume is very difficult to handle [42]. For this, mostly polymeric membranes are widely used for sugarcane juice clarifications [45,47,50,54,58]. Ceramic membranes by virtue of their high stability (chemical, mechanical and temperature), and long life are being increasingly used for a variety of separation applications [59–61]. These membranes consist of a macroporous support layer (pore sizes >1μm) with an intermediate microporous layer (average pore size in the range of 0.2 μm to 0.5 μm) in between and a separation layer (< 100 nm) at the end [62].

Jegatheesana et al. [43] studied the performance of ceramic membranes with pore sizes of 0.02, 0.05 and 0.10μm in clarifying limed and partially clarified raw sugarcane juice under different operating conditions. They concluded that ceramic microfiltration and ultrafiltration membranes could effectively clarify the limed and partially clarified sugarcane juice. The membranes werecapable of producing average fluxes in the range of 46–66 L h^{-1} m^{-2} for an operating period of 4 h when processing the above juice at 60°C. In this study, they pre-treated the raw juice before UF process.

Verma et al. [45] studied the separation efficiency of hollow fibre polysulphone ultrafiltration membrane(MWCO 20,000). They reported that the turbidity of sugarcane juice reduced from 200-250 NTU (raw juice) to 0.5 NTU (clarified juice).

They performed a fouling experiment for raw and lime pre-treated sugarcane juice and reported that maximum flux and less foulingwere observed while feeding pre-treated juice. The clarified sugarcane juice was found to be free from microbes. In their study, the clarification of the juice was done bypolysulphone hollow fibreUF membrane where,lime pre-treatment was also done to reduce the fouling effect.

Hamachi et al. [49] studied the effect of UF membrane pore size (20 nm, 5 and 1 kDa MWCO)for clarification as well as decolourization of raw brown sugar solution of 28 °Brix and 46 °Brix at different operating conditions. The result showed that colour removal percentage was limited to 58.67% even with the use of a membrane of MWCO of 1 kDa where permeating flux was 29 $Lh^{-1}m^{-2}$ at steady state condition.

Luo et al. [58]investigatedthe filtration behaviour of polymeric membranes at high temperature for refining raw sugarcane juice. They studied an integrated membrane process (Tubular UF, spiral-wound tight UF and spiral-wound NF) and reported that the colour removal percentage was more than 95%. They proposed a novel cascade mode of operation for diafiltration, which could save 25% water compared to a normal mode of operation.

Vaillant et al. [63] conducted an experiment for clarification and concentration of melon juice using ceramic microfiltration membrane and observed that the clarified melon juice was highly similar to the initial juice properties byrejectingthe insoluble solids and carotenoids and with a relatively high average permeation flux 80 L $h^{-1}m^{-2}$.

Rei et al. [64]reportedthe application of polymeric membrane for the clarification of mosambi juice. They also observed that permeate flux increased tenfold with pore diameter variation from MWCO of 10 kDa to 0.2 µm without affecting the juice quality.

Barros et al. [65] studied the performance of polysulphone hollow fibre membrane of pore diameter 100 kDa and alumina titania ceramic tubular membrane of pore dia 0.01 µm to clarify the pineapple juice. They observed that both the membrane resulted in similar quality juice. They also reported that the ceramic membrane exhibited higher flux (90-150 kg h^{-1} m^{-2}) than the polymeric membrane (30-50 $kgh^{-1}m^{-2}$) due to high pore size.

To date, membrane fouling is a challenging phenomenon to be tackled while clarifying highly viscous and turbid FS in membrane processes. As a result of fouling, the permeate flux reduces during the separation process. Another challenge with sugarcane juice clarification is handling the stream with high viscosity, high osmotic pressure andlarge volume[42]. For this, mostly polymeric membranes are widely used for sugarcane juice clarifications [45,47,50,54,58].

Ghosh et al. [54] studied the performance of UF spiral wound membranewith varying channel sizes (20 kDapolyethersulphone and polysulphone) for clarification ofsugarcane juice.They observed that higher flux was obtained from narrow size flow channel with a lower fouling rate. They also reported that higher temperature could improve and maintain juice flux.

Sarkar et al. [64] conducted electric field assisted ultrafiltration using polyethersulfone membrane for mosambi juice. They observed that membrane fouling was reduced due to the application of electric field with a significant increase in permeate flux. The main key factors that influence the permeation of the membrane are particle size of the feed material and pore size of the membrane. The authors investigated the importance of selecting optimal membrane pore size for the polymeric and ceramic membrane-based clarification process.

Zita et al. [51] demonstrated the application of tubular ceramic (pore diameter of 5 nm) UF process to separatethe non-sucrose compound from raw brown sugar syrup. They observed the use of a static mixer in the UF process and its benefits. They concluded that low concentration polarization as well as fouling of the UF membrane equipped with static mixer.

Sim et al. [66] investigated the performance of ceramic (pore sizes of 0.05 mm and 0.10 mm) membrane for purifying lime and partially clarified sugarcane juice under different operating conditions.They studied the fouling of the membrane. They concluded that at a lower trans-membrane pressure (TMP) (0.5 bar), the 0.10 mm membrane gets fouled due to the deposition of cake on the membrane rather than progressive internal fouling. They also observed that at a higher TMP (1 bar), the 0.05 mm membrane fouled due to the deposition of cake on the membrane surface, but the

0.10 mm membrane fouled due to both cake layer formation and internal fouling at the membrane pores.

With the presence of foulants such as protein, polysaccharide, starch, gums, suspended impurities, sediments of Ca, Mg, Al, Fe, and phenolic compounds, a robust membrane cleaning technique was used by many researchers for sugarcane juice purification [3,4,26,27]. Most membrane cleaning methods were focused on chemical cleaning using a high concentration of NaOH, NaOCl, HNO_3, enzymatic detergents and hot water [42,43,58]. On the other hand, limited studies are reported on physical cleaning methods that use turbulence or mechanical force[43]

2.1.1.1 Summary and possible scope for further research

A critical review of the above literature conveys the following conclusions for the clarification of juice with membrane technology. It has been observed that due to high viscosity, osmotic pressure and large volume sugarcane juice is very difficult to handle. As a result, researchers focused on using polymeric membranes for sugarcane juice clarification. However, ceramic membranes by virtue of their high stability (chemical, mechanical and temperature), and long life are being increasingly used for a variety of separation applications. It has been observed that ceramic membranes for sugarcane juice has been proven to be one of the most important separating mediums. The scope of the membrane clarification in these aspects might be quite promising since it will reduce the use of chemicals to clarify juice. Due to the presence of starch, vegetable fibres, gums and other unwanted components in the sugarcane juice, high fouling tendency was observed during the clarification of sugarcane juice by a membrane. However, improvements in the study of fouling and cleaning process are needed. Chemical cleaning is widely usedto remove foulants from the membrane, andthe physical cleaning method wasused with limited scope. So, there is a scope to exploit different physical cleaning techniques that can reduce the use of chemicals to remove foulants. Therefore, to mitigate the fouling issue, there is a scope for an innovative physical cleaning of the fouled membrane during the clarification of sugarcane juice probably which can scrap the foulants from the membrane surface. In

literature, inline scraping during ultrafiltration was not explored at all for the regeneration of membranes.

Hence,the current research is targeted towards (i) the use of the low cost $LaPO_4$ coated ceramic membrane processes, (ii) fouling study and a hybrid cleaning technique to be developed especially using physical cleaning in combination with chemical cleaning if required depending on the fouling mechanism, (iii) comparative study of combined physical and chemical cleaning (physico-chemical cleaning) methods to develop a commercial ceramic UF system for sugarcane juice purification.

2.1.2 Application of forward osmosis in concentration of sugarcane juice and fouling

In the literature,numerous studies are reported focusing onthe concentration of liquid foodsto end products such as concentrated juice and solid crystals. Simlar aspect, the sugarcane juice is generally converted to sugar crystals, jaggery and other similar products by concentrating them. In the sugar industry, conventional multiple-effect evaporation technology is widely used to concentrate clarified sugarcane juice. The energy consumption of multiple effect evaporator can be reduced by 33% by integrating membrane processes such as NF, RO for juice pre-concentration from 5° to 20°Brix [7]. Also, effective water removal or juice concentration with retention of nutritional values and flavour is a critical requirement to achieve better quality end products from sugarcane. Therefore, there is a need for energy efficient technology that can concentrate sugarcane juice without losing its nutrients. Among various conventional processes, FO membrane process is a promising technique for the concentration of sugarcane juice. The integration of RO/NF and FO process was found to be one of the energy efficient approaches to produce a concentrated liquid for the crystallization process [69–71].

The FO is a membrane-based separation process for water removal from a FS using DS of high concentration. It is proven to work for liquid food applications using membrane test cell experiments [12,13]. For example, the feasibility of FO was studied by many researcher for following applications using test cell experiments: grape, passion juice [30,31], coffee [32], orange [33], kokum [34,35], xylose [36], rice straw

[37],jaboticaba juice [38], sucrose solution [39], fructosesolution[40] and tomato juice [72]. FO studies on the commercial membrane module were reported after 2018 [73–75], before that the FO experiments were performed in commercial microfiltration (MF) hollow fibre (HF) membrane module using $CaCl_2$ as DS;such process is also called as osmotic distillation/evaporation [30,76–78]. In another attempt, a commercial RO membrane module having two inlets and two outlets for the draw and FS circulation was used for liquid food concentration application [79].

Kim et al. [29]conducted FO for dewatering the grapefruit juice. The objective of using the thin film FO commercial membrane is to concentrate the nutrients and retention of valuable constituents of the juice. They observed that severe membrane fouling occurred due to the presence ofpectin (particles size larger 0.45 µm). They also observed that the quality of the grape juice can be enhanced either by applying pressure to the feed stream or using a sugar-based DS. They studied the fouling control too.

Vaillant et al. [30] studied the osmotic evaporation process forthe concentration of passion juice, which was pretreated by using 0.2 µm ceramic membrane. Using a polypropylene hollow fibre membrane, they could concentrate the juice up to 60 g/100 g total soluble solid content in the osmotic evaporation process. They identified that temperature, tangential velocity and solutionconcentration played a significant role in the evaporation flux. They reported that the membrane lasted for 28 h continuous operation without fouling and losing the sensory quality and vitamin C content.

Shaw et al. [77] used 0.2 µm pore size HF MF membrane to concentrate orange and passion fruit juice in batch mode. They achieved the desired concentration factor set by the food industry without compromising juice quality by using NaCl (5.3 M) and $CaCl_2$ (4.6 M) as DS.

Later in 2007, Cassano et al. [78] demonstrated the feasibility of pear juice concentration using a commercial Liquid-Cell® microporous membrane contactor. 60 w/w% $CaCl_2.2H_2O$ was used as theDS.

Even though MF HF module is proven to achieve the desired concentration for food application, the impact of reverse solute flux (RSF) in concentrated feed quality has not been reported in the above listed pilot studies. Further, the MF membrane without a separation layer is expected to provide both RSF and forward flux. Maybe because of such issues, after 2007, studies on the osmotic evaporation/distillation process was not widely reported in the literature for industrial food applications.

Further, the FO membrane made of both the support and separation layers is expected to improve the water flux,RSF and forward flux. Thelow pore size separation layer is expected to induce different typesof CP in FO process, namely internal, external, dilutive and concentrative CP. Even though FO is proven to be a less fouling process compared to other pressure-driven membrane processes, many studies also observed a decline in FO flux for food applications due to concentrated feed and DS solution [33,80–82]. The membrane orientation is also another important aspect to minimize the fouling intensity.

Tang et al. [80] experimentally identified that the active layer facing FS (AL-FS) configuration was able to provide stable water flux in comparison to active layer facing DS(AL-DS) in the presence of humic acid in the feed. Similarly, pectin is one of the molecules present in liquid food, and it induced high fouling in the presence of $CaCl_2$ during the FO process.

Also, the clarification of liquid food before FO concentration reduces fouling intensity and stable FO operation [2,83]. For example, X. An et al. [81]reported high quality (preservingjuice nutrient and flavour) concentratedapple juice using integrated forward osmosismembrane distillation (FO-MD) where potassium sorbate preservative was used as DS. They also reported that very less quantity of potassium sorbet was found in the concentrated juice which was within the permissible limit for food industry. They also observed a relatively small (~15 %) water flux decline after 240 h of continuous operation while concentrating clarified apple juice.

Garcia-Castello et al. [82] studied FO process using polymeric cellulose acetate membrane for dewatering of the orange peel press liquor. NaCl with varied concentration (2 M and 4 M) was used as DS. They reported a maximum of 1.44 times

concentration factor in the presence of pectin and $CaCl_2$ and 3.67 times without pectin.It was observed that permeate flux was reduced almost by 50% due to the presence of pectin and concluded that pectin was the dominant component for fouling of the membrane.

Many researchers have investigated the impact of organic fouling on the FO membrane processes in the last decade[84–87]. Mi and Elimelech [85] studied the organic fouling of FO membrane and stated that fouling was governed by the influences of both hydrodynamic and chemical interaction. They observed that the key factor for the fouling occurrence were calcium binding, permeation drag and hydrodynamic shear force. They reported astrong correlation betweenorganic fouling and intermolecular adhesion force. They also showed that organic fouling where they used alginate as foulant caused reversible fouling that can be easily cleaned without chemicals.

Valladares et al. [87]investigatedthe effect of natural organic matter (NOM)deposition on the active layer of FO membrane. They observed that fouling caused by NOM were showing high reversibility and the air scouring cleaning method showed up to 90% recovery within 15 min.

She et al. [88]investigated the effect of DS on fouling of the FO membrane. They investigated the fouling by using four DS viz NaCl, $MgCl_2$, $CaCl_2$, and $Ca(NO_3)_2$. They concluded that the selection of appropriate DS and a membrane with higher selectivity couldcontrol the fouling of the FO membrane.

Kim et al. [89] evaluated different cleaning strategies reported in the literature for different types of FO membrane fouling and scaling applications. They reported that both physical and chemical cleaning approaches could clean the fouled membranes. The physical cleaning methods used were hydraulic flushing, osmotic backwashing, air scoring, and a combination of these methods were applied to study their membrane regeneration efficiency. The osmotic backwash was able to provide 95% regeneration efficiency; however, they failed to regenerate the FO membrane fouled by colloidal particles. The chemical cleaning methods such as EDTA, low pH, and high pH were also tested individually. Finally, a combined hybrid cleaning process by integrating

both physical and chemical methods was also tested. The combination of Air/CO_2 scouring and hydraulic flushing was able to remove colloidal fouling induced by silica but not inthe case of organic fouling. But in the case of liquid food application, organic fouling is expected to be more severe than inorganic fouling.

Chanukya et al. [90]investigated ultrasonicwavesas an advanced physicalmembranecleaning process. They studied the impact of ultrasonic waves (30 kHz) during FO normal operation for fruit juice concentration, and observed significant improvement in water flux for liquid food application. However, no impact was observed if liquid food with 0.5% pectin.

Ibrar et al. [91] studied the fouling mechanism and controlling or minimising techniques for FO membrane processes. They concluded that for most of the FO membrane, cleaning studies hadadopted hydraulic flushing, osmotic backwash, and chemical cleaning (such as citric acid/chlorine/hypochlorite/hydrochloric acid/ sodium hydroxide/EDTA/surfactant) for membrane regeneration with few regeneration cycles. Membrane fouling is caused by the deposition of suspended particles/colloids, organic macromolecules, sparingly soluble inorganic compounds, microorganisms or their mixtures on the membrane surface (or even inside the pores of the membrane). Fouling not only reduces the osmotic power output, water recovery, and permeate quality but also causes increased operating cost and shortened membrane life. Recent studies reported that water permeability and water flux of the membrane were decreased by 22.9% and 24.8% respectively due to membrane fouling [92]. Fouling can be mainly of two types, external fouling (on the surface of membrane) and internal fouling (in the pore structure of membrane). Again fouling can be classified into

a) Organic fouling
b) Inorganic fouling
c) Bio fouling

In the literatures, it was reported that membrane fouling is caused by organic macromolecules, inorganic materials (Na, Mg, Al, Si, P, and K) and microorganisms. Depending on foulant type different fouling are occurred due to cake formation, pore

blocking, concentration polarization, organic adsorption, inorganic precipitation and biofouling. According to another classification of fouling, the fouling can be particulate fouling, organic fouling, inorganic fouling and bio fouling. Particulate fouling stars with deposition of single particle on cleaned surface and it agglomerate with time and leads to pore blocking. Particle of equal size to pore size leads to pore blocking and that of larger size of pore will form cake layer. The organic foulant causes cake layer formation, pore blocking, pore narrowing. It is observed that fouling rate is affected by hydrodynamic and intermolecular forces on organic particle. It is seen that hydrophilic membrane gets more fouled compare to hydrophobic. Both particulate fouling and crystallization occurs due to inorganic salt. Phosphate, carbonate salts are dominant for fouling and it also depends on membrane properties, feed characteristic and operating conditions. Biofouling may cause due to the formation of macromolecules, protein, and chemical like flocculants, scale inhibitor. Limited use of phosphate can reduce biofouling. SEM, FESEM, FTIR, EDX, AFM are used to identify fouling mechanism qualitatively. The scaling is also known as precipitation or inorganic fouling. The scaling of membrane is caused by the crystalline salts, hydroxide and oxides that are present in the feed solution. When the dissolved constituents get precipitated from the feed solution and deposited on the membrane surface or lodge in the pores of the membrane scaling occurs.

Membrane fouling in the FO process is an inherent phenomenon and its impact on membrane performance is evaluated by many researchers in terms of flux reduction and membrane life. The membrane fouling due to FS is found to be more severe than the DS. The foulant present in the FS may decide the severity of the fouling in the FO process. For example, if the feed contains more organic particulate matter, then that leads to organic fouling on the membrane surface. Similarly,an inorganic component such as silica, $CaCl_2$ may cause inorganic fouling. Finally, microorganism growth on the membrane surface alsolead to bio-fouling.The cleaning of the membrane fouled by the above three fouling sources can be cleaned by using the appropriate cleaning protocol. The fouling phenomena in the FO membrane can also bedifferentiated based on surface fouling and fouling inside the porous support layer. Surface fouling alone is expected when the separation layer is exposed to FS. But when feed is exposed to

the support layer, then the fouling is expected to happen in both the support layer and surface. The membrane fouled at the surface can be cleaned easily by physical cleaning methods such as osmotic backwash, flushing etc. If it is fouled in both surface and support layer, then the combination of physical and chemical cleaning methods is found to be effective. The selection of cleaning chemicals will be purely based on the type of foulant present in the fouling layer. For example, organic content is cleaned by using citric acid, NaOH etc. The inorganic content is removed by acids such as H_2SO_4, HCl etc.Similarly, microorganisms present in the membrane is removed by using an appropriate disinfectant.

Therefore, for a given FO-based concentration process, selecting a suitable membrane cleaning process and the chemical to be used requires a systematic study of membrane fouling and the cleaning process.

2.1.2.1 Summaryand possible scope for further research

A critical insight into the above literature infers that FO membrane process have been studied for the concentration of liquid food though not extensively. The viability of using FO process for sugarcane juice was tested by Shalini et. al. [14] and Mondal et. al. [2] using test cell experiments. Both studies were limited to FO experiments to measure water flux for sugarcane-NaCl/seawater system using both commercial and laboratory prepared FO membrane. They achieved a fourfold concentration of sugarcane juice by adopting feed recirculation mode. One of the main challenges during the concentration of sugarcane juice by FO membrane is the mitigation of membrane fouling, and that requires a detailed analysis of the fouling phenomenon with a more extended period of FO operation with real sugarcane juice. Therefore, this study focused on the design of FO experiments to achieve optimal operating conditions to maximize the water flux and mitigate FO membrane fouling for the sugarcane juice concentration process. The impact of membrane fouling with respect to following FO process parameters was studied experimentally using high flux Aquaporin FO membrane module available in the market: (i) feed and DS flowrate, (ii) DS concentration, (iii) flow orientation (i.e. counter and co-current operation) and (iv) juice pre-treatment. There is a need to propose the fouling mitigation plan to achieve

minimal membrane fouling based on experimentally observed optimal FO operating conditions for sugarcane juice application. There is a scope for the optimised FO process conditions that can be used to study the fouling behaviour of the FO membrane. Another scope is to study the membrane regeneration techniques adopted in food application such as osmotic backwash and NaOH cleaning.

2.1.3 Modelling, validation and process simulation study of forward osmosis membrane

The performance of the FO process can be optimised by selecting appropriate operating parameters such as FS and DS flow rate and DS concentration. To calculate optimal operating conditions of the FO process, the following two approaches can be adopted (i) experimental study to find optimal operations, (ii)combinations of experimental, modelling and simulation study. In a pure experimental study, the experiment has to be performed for multiple operating conditions. This approach may lead to a large number of experiments when the number of operating variables is more than two, andthe process is nonlinear. In the second approach, experiments will be performed selectively in the given operating range and used to validate the model and experimental data. The validated model will be used for simulation and optimization study to find optimal operating conditions. Alsothe second approach will provide cost effective solution to find an optimal point for a given process. To implement the same inthe FO process for sugarcane juice concentration, the mathematical model of the FO process is important. This section provides an overview of different models reported in the literature, especially for the Hollow fibre FO module.Recently, several studies have found that FO membrane process is a cost-effective technology for liquid food concentration. The FO processes have more privileges over the RO process regarding less energy consumption in the presence of effective draw solute regeneration process [9–11], high product recovery, low reverse solute flux, and less fouling[3].

Lee et al.[92] have made early attempts to model mass transfer for FO membrane process. They developed the mathematical model to predict the performance of the pressure retarded osmosis membrane process where Active Layer (AL) facing DS was considered for the experiments.

Loeb et al. [93] developed a mathematical model for the FO membrane process by following Lee et al. approach. Later on,Mc Cutcheon et al. [94] introduced boundary layer film theory to predict the effect of ECP on AL and ICP in porous support layer for PRO and FO membrane processes.

Suh and Lee [95] developed a mathematical model where dilutive ECP on the draw side was considered. They reported that ECP must be considered for low cross-flow velocity and high water flux.

Most of the literature reported on FO modelling studies are based on the solution diffusion (SD) model by integrating model for external concentration polarisation (ECP) and internal concentration polarization (ICP). Researchers have worked on both experimental as well as modelling for both membrane orientation AL-DS and AL-FS.

Tan et al. [96]investigated the impact of CP. Considering the boundary layer concept, they developed a modified film model. They calculatedthe diffusion coefficient by using convective–diffusion equations. With experimental data, the model validation was established. This study has enlightened the effect of concentration polarization and gave the opportunity to modify the FO membrane structure.

Shim and Kim [97]studied the performance of the FO membrane process using 1-D model where ICP and ECP were considered. They examined the effect of operating condition on water flux in the FO membrane process. They also concluded that the increase in water flux could be observed if the FS is in series and DS are in rows.

Gu et al. [98] investigated themodelling and simulation of the FO membrane process. by using spiral wound and plate and frame membrane modules. They carried out simulation studies by varying fourdifferent operating conditions and concluded that this model is useful to design FO module and optimised the operating conditions.

Phuntsho et al. [99] studied the FO modelling based on SD model and they consideredboth the effect of ECP and ICP. They observed the influences of various operating parameters through a simulation study. They proposed a modified equation where they considered the osmotic equilibrium concept and mass balance and

concluded that there is a need for process optimization for FO operation on a large scale.

A number of HFRO mathematical model have been investigated with validation but HFFO module performance by considering DS and FS in batch mode have not been reported.

2.1.3.1 Summary and possible scope for further research

Many researchers have studied on HFRO mathematical model with experimental validation [97,100,101]. In literature, no mathematical model is reported for the FO process by considering DS and FS in batch mode with tank model equation to estimate the performance of the batch process. There is a scope for the development of a mathematicalmodel for the FO process to analyse the effect of DS flow rate in co-current and counter-current mode and validation of experimental result along with analysis of different process flow sheet simulationfor finding the optimal result with respect to sugarcane juice concentration, energy consumption and reverse solute flux.

2.2 Summaryof Research gap

The discussion over the ceramic membrane process for clarification of sugarcane juice reveals that there are still enough possibilities for studying the various challenges this process faces.The scope of membrane basedclarification might be quite promising since it will reduce the use of chemicals for clarification of juice. However, improvements in the study of fouling and cleaning processesare needed. Mostly to remove foulants from the membrane, chemical cleaning is preferred with almost nil physical cleaning. So, there is scope to study variousphysical cleaning processes that can reduce the use of chemicals to remove foulants. After confirming the fouling mechanism,a hybrid cleaning technique can be suggested especially using physical cleaning in combination with chemical cleaning depending on the fouling mechanism.

The literature shows that FO membranes for sugarcane juice concentration is one of the promissing solutions. However, improvements in the study of fouling and cleaning processesare needed. At present, many reported works are still at laboratory or pilot scale level, and further works would be required. However, there is a need to

investigate the performance of FO experiments using HFFO aquaporinmembrane in counter-current and co-current mode. There is also need to investigate the performance of the high flux aquaporin membrane with different DS flow rate as well as at different DS concentration. The study of membrane fouling by sugarcane juice has to be done systematically. The study of suitable cleaning systems for the HFFO aquaporin membrane has to be done in order to achieve higher permeability and minimise membrane fouling on long-term operation.

Another scope of this work is to develop a new mathematical model for the FO process. In literature, no mathematical model is reported by considering DS and FS in batch mode to estimate the performance of the FO batch process. Also, so far no mathematical model has been developed for axial flow high flux HFFO membrane with tank model equations to analyse the performance in batch, continuous, feed-in - batch mode and draw-in-recycle mode. Therefore, there is scope for the development of a mathematical model for the FO process and validation of experimental result along with analysis of different process flowsheet simulations for finding the optimal result with respect to sugarcane juice concentration, energy consumption and reverse solute flux.There is a scope for optimization ofthe continuous operation of pilot plant and intensive investigations on the long-term performance of HFFO membranes.

2.3 Objective of research work

From the above research gaps, the objectives of this doctoral thesis are identified as follows:

- To study the characteristic change in properties of the sugarcane juice while clarifying that by UF ceramic membrane.
- To study the effect of conventional and unconventional physical cleaning mechanism on ceramic UF membrane system for sugarcane juice clarification.
- Experimental study of the concentration of sugarcane juice by high flux Hollow Fibre Forward Osmosis (HFFO) membrane along with fouling and cleaning study.

- Development of a mathematical model, validation and process simulation for concentration of sugarcane juice by high flux HFFO membrane.
- Performance evaluation of HFFO membrane system by process simulation study for sugarcane juice concentration to optimize the membrane system parameters while minimizing the specific energy consumption (SEC)with maximum yield.

2.4 Organisation of the thesis

This thesis is organised in six chapters, a brief summary of each chapters is presented below,

Chapter1 Introduction
Chapter 2 Literature review, research gaps and objectives of the thesis
Chapter 3 Sugarcane juice clarification by ultrafiltration membrane with fouling and cleaning study
Chapter 4 Concentration of sugarcane juice using forward osmosis membrane withfouling and cleaning study
Chapter 5 Modelling, validation and process simulation of forward osmosis membrane for the concentration of sugarcane juice
Chapter 6 Conclusion and future scope

Chapter:3

Sugarcane juice clarification by ultrafiltration membrane with fouling and cleaning study

This chapter presents the potential application of novel low cost Lanthanum phosphate coated tubular ceramic membrane for the clarification of sugarcane juice. The main aim of this work is to prove potential suitability of sugarcane juice clarification by attainting quality of the permeate without using chemicals which can directly be used for further concentration process. In this chapter design of the experimental setup and experimental procedure is illustrated. Here the application of $LaPO_4$ ceramic membrane for the clarification of sugarcane juice is explored without the application of lime by measuring polyphenol oxidase (PPO) enzyme, bacteria removal efficiency and permeate flux decline profile. This chapter includes the various methodologies and techniques used for characterisation of membrane, sugarcane juice and membrane fouling. Moreover, a hybrid cleaning strategy involving an innovative brushing action on the membrane surface for physical cleaning combined with chemical cleaning was implemented in this study.

3.1 Material and methods

3.1.1 Extraction of Sugarcane juice

Sugarcane juice was collected from a local vendor. The juice extracted was filtered through a 100 mesh screen and used without any pretreatment (with lime). The pH was not adjusted. This juice was stored properly to be used as feed for the purification process.

3.1.2 Membrane

The $LaPO_4$, α-alumina supported ceramic membrane of 50 cm length, 3.4 cm diameter,membrane active area (0.24 m^2)and containing 19 channels of ~3 mm diameter was used in this study. The tubes were supplied by HR-Johnson, Mumbai.

3.1.3 Membrane physical cleaning setup

A physical cleaning method was introduced during juice filtration in the UF membrane module. It consists of a cylindrical cast iron hollow pipe with a nylon brush on the inner surface of the cylinder. The cleaning setup pipe with brush inside is of 50 mm length and 45 mm diameter. A hollow circular magnet of inner diameter 61 mm and outer diameter of 100 mm is used to drag the cleaning brush along the membrane

surface manually. At an interval of every one minute, the cleaning module is dragged from one end to another end of the membrane with the help of the circular shaped hollowmagnet which is attached to the outer surface of the module casing as shown in Fig. 3.1. The cost of mechanical cleaning set up is INR 350 (5 US$) which is a one-time investment. Flux declined drastically while the raw juice was filtered without using any physical cleaning method during the operation. By introducing the physical cleaning method during the juice filtration in the ultrafiltration module, permeate flux decline study was carried out.

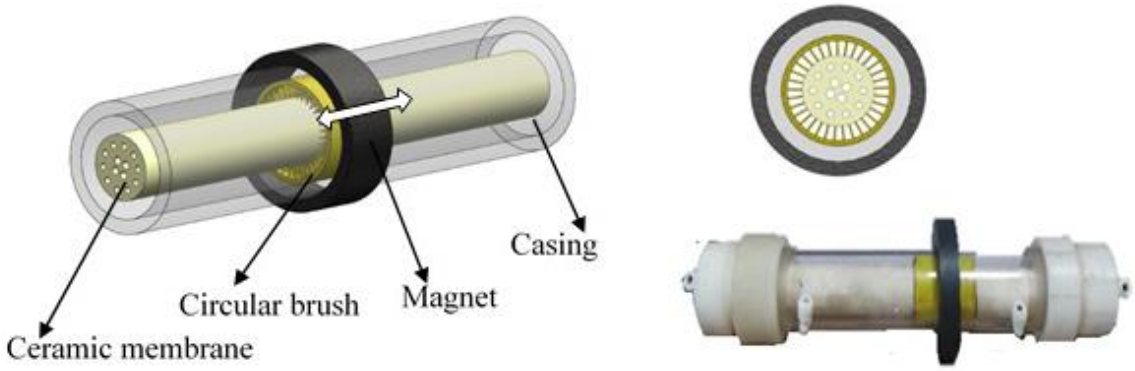


Fig. 3.1 Physical cleaning set up for UF ceramic membrane physical cleaning set up for UF ceramic membrane

3.1.4 Membrane chemical cleaning process

The fouled membrane was cleaned with 1% NaOH, 0.5%NaClO and 0.5% HNO_3 until water flux regains its original value. Membrane fouling was calculated quantitatively by using flux decline values as given below,

$$m = \frac{J_0 - J_f}{J_0} \qquad (3.1)$$

where, flux decay coefficient is m, J_o is initial flux (L h^{-1} m^{-2}) at the time of filtration and $J_f$is the fouled membrane flux at the time of filtration process. After fouling, if flux decay reached to 90%, then the membrane is recomened to be clean. Flux decay percentage increased due to the occurrence of fouling on the membrane.

The membrane cleaning process involved the following steps,

Step1: The fouled membrane was washed with tap water to remove sugarcane juice from the membrane module.

Step 2: 1%NaOH and 0.5% NaClO (w/w) mixture was circulated through the membrane in cross-flow mode for 3 h. Tap water was used for removing the used chemicals till the pH level reached 7 and pure water permeability was attained.

Step 3: If the water flux was not regained, 0.5% HNO_3 was circulated through the membrane in cross-flow mode for 30 min, and tap water was used for rinsing until pH become 7.0 and the pure water permeability was measured. Flux recovery ratio (FRR) was calculated using the equation3.2. All the processes of cleaning were done at 1 bar and at the cross-flow velocity (CFV) of 0.02 m s^{-1} at 60 °C. J_c and J_n are cleaned membrane and new membrane pure water permeability (L h^{-1} m^{-2} bar) respectively.

$$FRR = \frac{J_c}{J_n} \times 100 \qquad (3.2)$$

3.1.5 Sugarcane juice purification experimental setup

The schematic diagram of the experimental set-up is shown in Fig. 3.2. The experiment setup primarily consists of ceramic membrane, sugarcane juice tank, permeate tank, weighing balance with data logger, pumps (plunger pump), conductivity meters, control valves, pressure gauges, and dampener. The flow meter and pressure gauges were positioned on the feed and reject side of the module to measure the flow rate and pressure of feed and reject. Dampener was placed after the pumps to reduce the fluctuation in flow rate and pressure gauge reading.

The sugarcane juice was passed through the shell side, and the generated permeate was collected through the tube side of the ceramic module. One side of the tube outlet was closed throughout the experiment. The outlet from the other side was collected in the permeate tank which was placed in weighing balance. Ultrafiltration unit consists of 2 numbers of the storage tank of 10 L. A booster pump was used to circulate the feed from the tank via dampener to the membrane module. Two TDS meters and two

flowmeters were used in both feed and permeate side. Transmembrane pressure was calculated by using the following equation,

$$P = \frac{P_{feed} + P_{reject}}{2} \tag{3.3}$$

where P_{feed} is pressure in feed side and $P_{reject}$is pressure in reject side.

The transmembrane pressure (TMP) and cross-flow velocity were controlled by three valves. The permeate volume was collected in the permeate tank where, a weighing machine with a data acquisition system was placed.

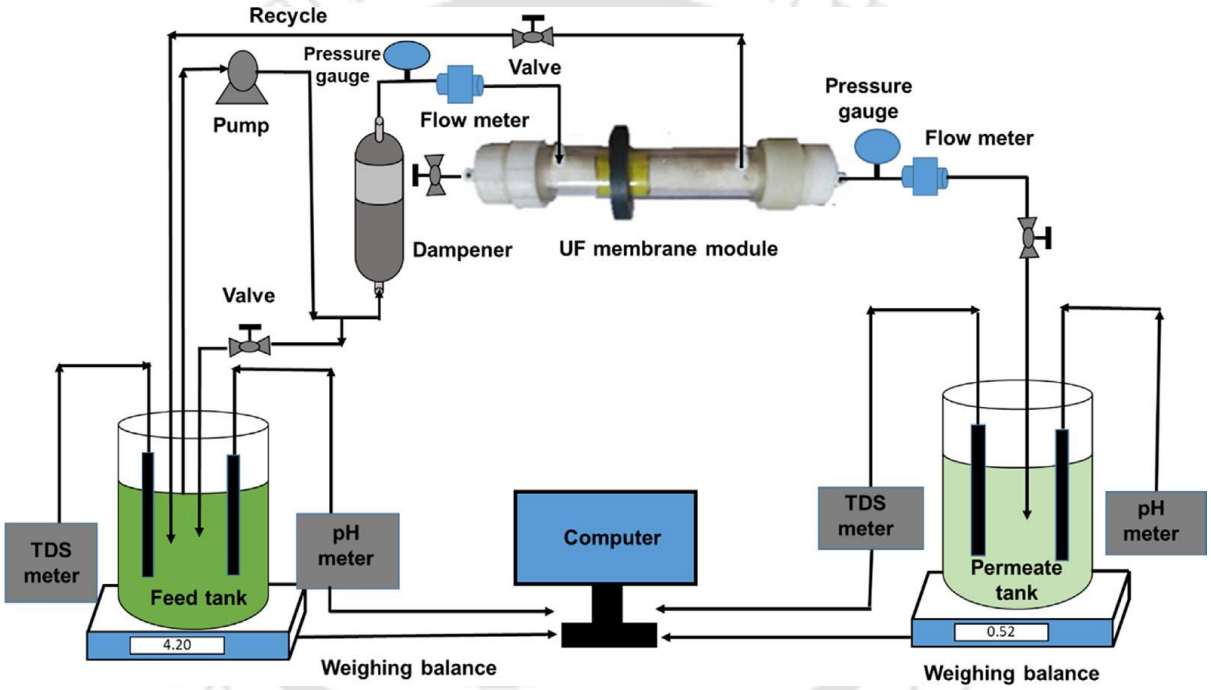


Fig. 3.2 Experimental setup for sugarcane juice clarification

3.1.6 Experimental procedure

Before performing the sugarcane juice clarification experiment, the setup was washed with deionised(DI) water to make sure that there were no foreign materials and leakage. Pure water permeability (A) of the membrane was measured using DIwater flux at constant temperature and varying pressure. The raw juice was filtered through a 100 mesh screen without any pre-treatment with lime (pH was not adjusted). The filtered juice was used as a FSand it was pumped from the feed tank to the ceramic UF module passing through the dampener. The rejected solution was recirculated back to

the feed tank under batch mode operation. The pressure 135 psi (9.3 bar), Cross-flow velocity (CFV)0.02 $ms^{-1}$and temperature 25°C were maintained throughout the experiment. The permeate volume was collected in the permeate tank and it's properties such as conductivity, pH and flow rate were recorded for every 5 min. The experiments were carried out at different feed flow rates and pressure conditions. Clarified juice and raw juice samples were collected to study the sucrose loss with time.

During the filtration process, a physical cleaning process of the membrane was introduced in the membrane module through a brushing action since it was found from the literature that cake formation is the dominant factor for flux decline in the UF of sugarcane juice [43,57]. At an interval of 1 min, the brush was moved from one end to another, with the help of a magnet to clean the surface of the membrane. The membrane was further subjected to the chemical cleaning process.

3.1.7 Membrane characterisation

The morphology of the $LaPO_4$ sols coated on ceramic membranes was evaluated using field emission scanning electron microscopy (FESEM, Sigma 300, Zeiss). Porosity and average pore size distribution were measured with the help of Hg porosity meter. FESEM analysis was carried out for both new and fouled membrane with a Field Emission Scanning Electron Microscope (Sigma 300, Zeiss). Before FESEM analysis, the sample was prepared by keeping it in the oven to remove moisture followed by gold coating. Energy Dispersive X-ray (EDX) analysis was carried out in another scanning microscope (Sigma, Zeiss) for the cleaned, fouled membranes and scrap of foulants. Foulants were scrapped from the membrane surface and dried in an oven to remove moisture.FTIR analysis was performed for evaluating the functional groups of foulants present in the membrane surface. With the help of a Fourier Transform Infrared Spectrophotometer (IRAffinity-1, M/S Shimadzu, Japan), functional groups of foulants were identified. For cleaned membrane, a sample was prepared by grinding the cleaned membrane followed by drying in an oven. Another piece of oven dried fouled membrane was ground with KBr for FTIR analysis.

3.1.8 Sugarcane juice characterisation

Different analytical methods for juice analysis were used. Juice was analyzed for turbidity by turbidity meter (TN 100, Utach), particle size distribution in Delsa Nano (M/s BeckmanCoulter, Delsa Nano C, Switzerland), brix by refractometer (Abbe Refractometer 2WAJ), viscosity by U-tube viscosity meter (U tube BS/U, ABG borosilicate) and pH by a pH meter (Eutech pH 2700) [53]. The juice colour and purity was ascertained by UV-Vis Spectrophotometer (UV 2600, Shimadzu, Singapore). At a wavelength of 420 nm, the colour of sugarcane juice was measured by optical absorbance (A) [102], and in percentage terms, juice clarity was measured by transmittance (%T). Juice purity was calculated by using equation 3.4, where, wavelength of 660 nm was considered as optical absorbance [102].

$$\%T = 100 \times 10^{-A} \quad (3.4)$$

AHigh-performance liquid chromatography (HPLC) (M/S Shimadzu, Singapore) system comprising of the auto sampler, pump, and RID with HI-PLEX H column was used to analyse the sucrose loss of clarified sugarcane juice, raw sugarcane juice and raw sugarcane juice with lime (pH 7). The sugarcane juice was diluted in 1:100 ratio and 2 µm filter was used. The mobile phase used for this study was H_2SO_4 (0.005M) at 0.5 mL min $^{-1}$ flow rate at 35°C. From the chromatogram area, the concentration of sugarcane juice components such as sucrose, glucose and fructose were calculated by comparing with the standard curves generated by using standard solutions of sucrose, glucose and fructose.

3.2 Results and discussion

3.2.1 Characterisation of ceramic ultrafiltration membrane

The specifications of the ceramic membrane support tubes are shown in Table 3.1. The ceramic membranes had an outer diameter of 3.4 cm and inner pore diameter of 0.4 cm. The porosity of the membrane is 35%, with an average pore size of ~1 µm (Fig. 3.3). The initial water permeability of the UF membrane support at 1-bar pressure was

found to be 450 L h^{-1} m^{-2} bar^{-1}. The $LaPO_4$ coated membrane showed pure water flux around 120 L h^{-1} m^{-2} bar^{-1} at 1 bar pressure. The SEM analysis of the ceramic membrane with lanthanum phosphate ($LaPO_4$) as the top layer is shown in Fig. 3.3. From Fig. 3.3 (c), the cross-sectional view of the membrane, the deposited layer of $LaPO_4$ after coating over base matrix of α-alumina could be seen. Fig. 3.3 (d) shows the cross-sectional thickness of $LaPO_4$ deposition to be 5.77 µm - 6.04 µm. An enlarged portion (Fig. 3.3 e) shows the size of $LaPO_4$ nano-rods to be in the range of 212 nm -270 nm. The nano-rods were found to cover the support tube uniformly. The absence of cracks in the coating morphology confirmed the strong adherence of $LaPO_4$ with the support tubes.

Table 3.1 Specifications of the porous alumina ceramic membrane support tubes.

Sl. No.	Ceramic Support Tube	Specifications
1	Length	50 cm
2	Number of channels	19
3	Outer diameter	34 mm
4	Inner pore diameter	4 mm
5	Active area	0.24 m^2
6	Particle size (SEM) of support tube	~ 1 µm
7	Pore size (SEM) of support tube	~ 1 µm
8	Porosity	35 %
9	Water Flux	450 L m^{-2} h^{-1}

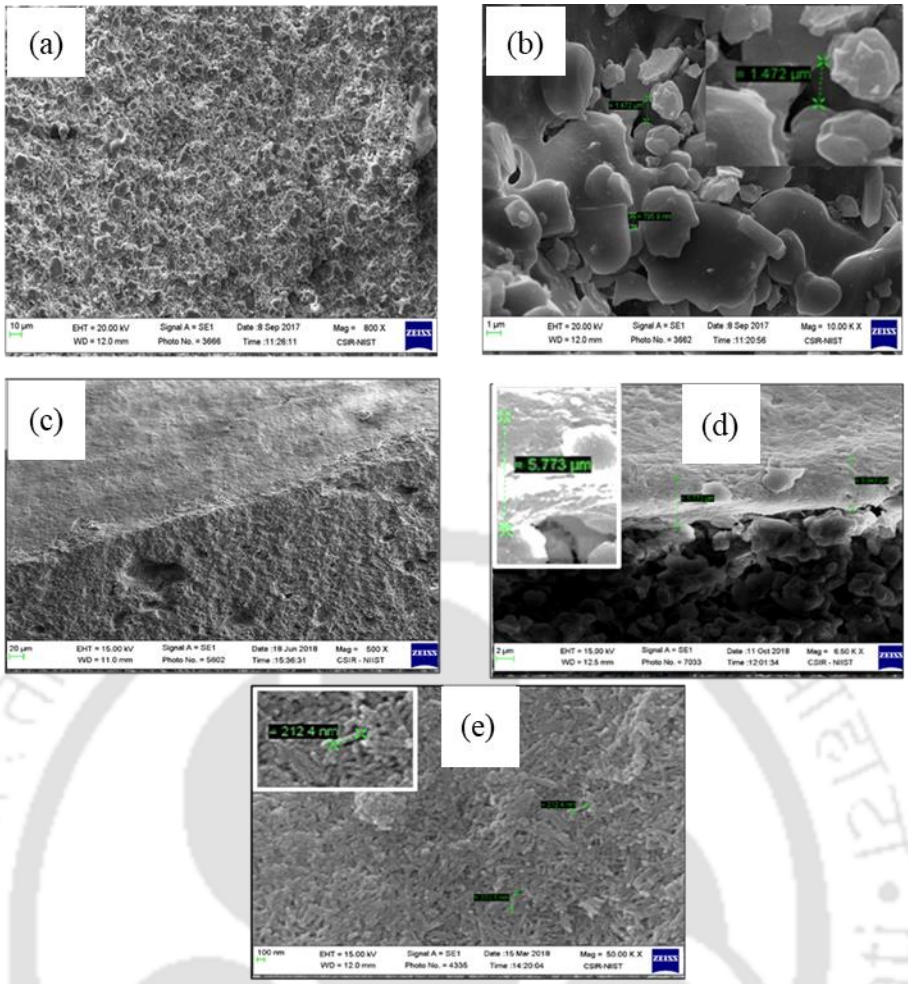


Fig. 3.3 FESEM image of support tube (a) surface morphology at low magnification, (b) pore size at high magnification and FESEM image of $LaPO_4$ coated UF membrane (c) cross-sectional view of the membrane after $LaPO_4$ layer has deposited on the membrane, (d) thickness of $LaPO_4$ coated layer and (e) uniform deposition of the $LaPO_4$ nano-rods on the membrane surface (Inset: Enlarged image of $LaPO_4$ nano-rods).

3.2.2 Performance of ultrafiltration membrane

The performance of the UF membrane with respect to different operating pressures are shown in Fig. 3.4. The permeate flux increased with an increase in TMP and decreased with time due to fouling for both coated and uncoated membrane (here in this study include only TMP of 130 psi and 135 psi). From the flux decline profile, the nature of fouling was presumed to be proceed in two stages. At the initial stage, pore blocking phenomena induced a sharp decrease in the permeate flux in the case of

uncoated membrane. In the later stage (after 25 min), cake layer start forming and this cake layer formation was the dominating fouling phenomena leading to asymptotic permeate flux profile. It was observed in our study that at initial stage (till 25 min) high flux decline rate 85.69% of uncoated membrane. On the contrary, $LaPO_4$ coated membrane exhibited comparatively less (60.85%) flux decline rate. After 25 min, effect of cake layer formation was observed. Another observation was that for both the membranes (coated and uncoated), after cake layer formation flux decline rate was nearly the same. From the analysis it could be concluded that uncoated membrane showed higher fouling rate than coated one at initial stage. Therefore, coated membrane is better than the uncoated membrane. In Fig. 3.5 (a) colour of feed and (b) permeate colour of uncoated membrane juice (c) permeate colour of $LaPO_4$ coated membrane at pH 5.86 and 135 psi (9.307 bar), CFV 0.02 m s^{-1} are shown. As reported in literature, the filtration efficiency could be quantified by measuring the particle size distribution of feed and permeate [33].

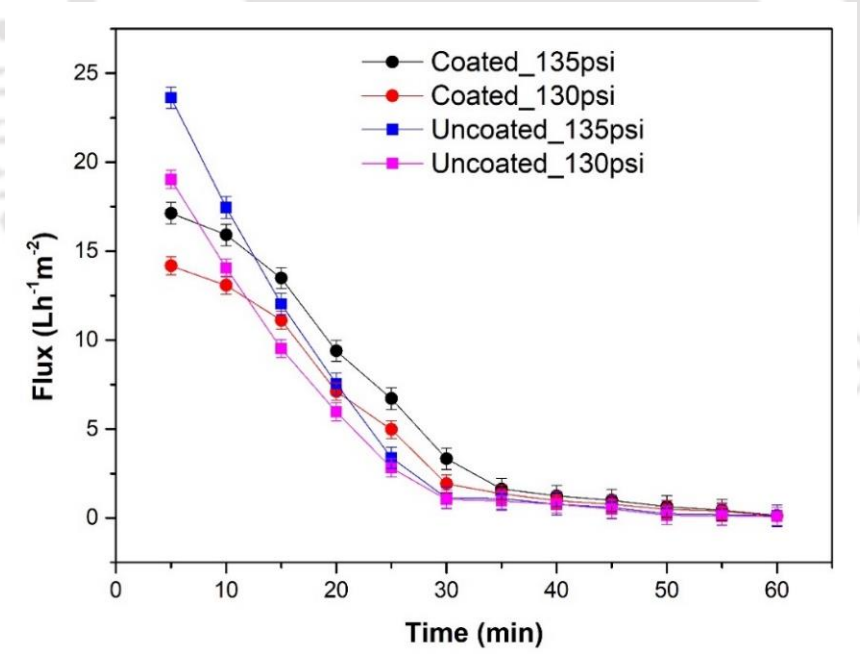


Fig. 3.4 Variation of juice flux with trans-membrane pressure at different condition at 35 °C, pH 5.86 and CFV 0.02 m s^{-1}, pressure 135 psi (9.3 bar), CFV 0.02 m s^{-1}

(a) (b) (c)

Fig. 3.5 (a) Change in colour of feed and (b) permeate of uncoated membrane juice (c) permeate of $LaPO_4$ coated membrane at 35 °C, pH 5.86 and 135 psi (9.3 bar), CFV 0.02 m s^{-1}

The particle size distribution of raw juice (feed) and clarified juice (permeate) are shown in Fig. 3.6 (a). Feed contained particles of sizes from 15.9 nm to 1438 nm while permeate contained particles of sizes from 15.2 nm to 69.2 nm. It could be concluded that the particles above 270 nm were removed by the membrane filtration. To study the stability of sugarcane juice (at storage condition 4˚C) was measured by the change in the viscosity with time. The change in viscosity values of raw (feed) and clarified juice (permeate) were observed for 7 weeks. The viscosity of raw sugarcane juice was increased in comparison to clarified sugarcane juice (Fig. 3.6 b) [103]. The increase in viscosity of raw sugarcane juice may be due to the formation of dextran (gummy substance generated by leuconostic bacteria). Since in the clarified sugarcane juice less bacteria are present this dextran production may be less and as a result change in viscosity of the clarified juice was less with time. Result obtained in this study were relevent to Yusof et al. (2000), Lotha et al. (1994) regarding storage of juice [104,105]. However, the clarified juice started degrading after 7 weeks. Therefore, the UF clarified juice could be stored for 7 weeks in a refrigerator at 4 °C without adding any preservatives. The physico-chemical characteristics of sugarcane juice of feed and

permeate of uncoated and $LaPO_4$ coated UF were studied and are summarised in Table 3.2. During clarification experiment by coated and uncoated membranes, the physico-chemical characteristics of feed and permeate were evaluated after each experiment via respective measuring instruments. For all the run, a 99.3% reduction in turbidity, 99.58% reduction in colour was observed for the permeate of $LaPO_4$ coated membrane as compared to feed. An increase in 99.84% clarity of the sugarcane juice with 49.76% reduction in TDS of the clarified sugarcane juice compared to feed sample was observed. The pH of permeate has undergone less change due to the removal of bacteria and acidic substances produced by the bacteria. Again, a separate study was performed to observe the physico-chemical characteristics of the permeate of uncoated membrane. A 92.54% reduction in turbidity, 83.29% reduction in colour was observed. A 89.77% increase in clarity of permeate with TDS reduction of 49.76% was seen. The pH of feed and permeate of uncoated membrane showed similar values. It may be due to the non-rejection of bacteria and acidic component by the uncoated membrane. The clarity of the permeate by $LaPO_4$-coated membrane is much higher than that of the uncoated membrane with same % of brix loss. Therefore, the permeate of coated membrane showed better quality of juice compared to the uncoated membrane. In Fig. 3.7, the dynamic variation of feed (raw juice) and permeate (clarified juice) stream for 90 min run are reported. In this cross-flow UF experiment, the feed juice was recirculated back to the feed tank and permeate was collected continuously in a separate tank. From the Table 3.2 it can be seen that the values turbidity of feed increased with time due to recycling of reject stream in the feed tank, however, the turbidity of permeate did not change much. Similarly, a trend of increase in TDS of feed with time was observed and corresponding TDS value of permeate also showed the similar trend.

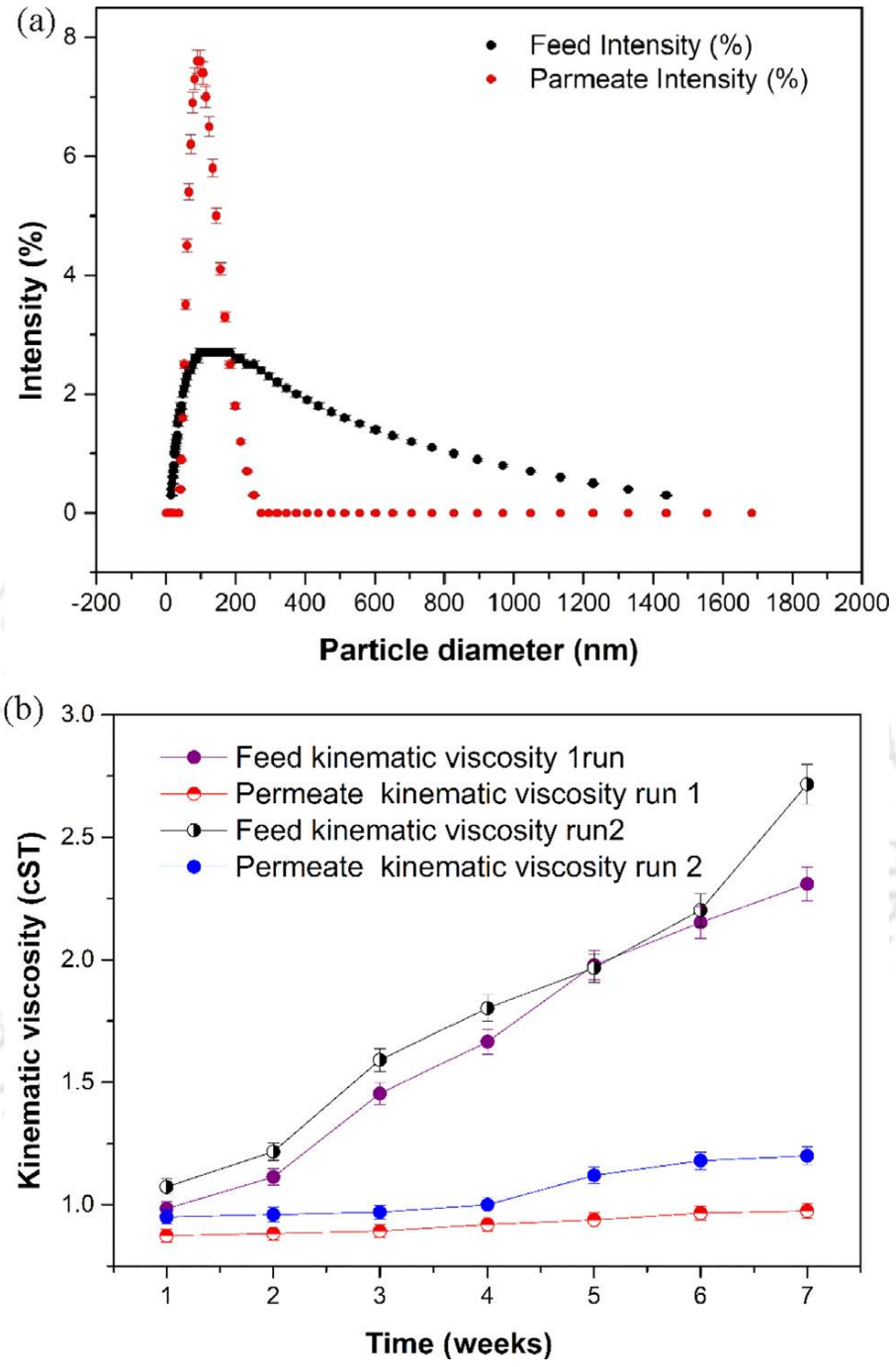


Fig. 3.6 (a) particle size distribution in permeate and feed, (b) viscosity of feed and permeate change with respect to time.

Table 3.2 Physico-chemical characteristics of sugarcane juice feed and permeate (CFV 3 ms^{-1}, temperature 35°C)

Parameters	Turbidity (NTU)	Brix (%)	Colour (A)	Clarity (T%)	TDS (mgL^{-1})	pH
Feed	738	18	4.573	3.179	860	5.8
Permeate of uncoated membrane	55	16.8	0.764	0.325	521	5.8
Permeate $LaPO_4$ coated membrane	6.4	16.8	0.192	0.005	432	6.03
Reduction/improvement % for uncoated membrane	92.54%	6.66%	83.29%	89.77%	49.76%	-
Reduction/improvement% for coatede membrane	99.13%	6.66%	99.58%	99.84%	49.76%	

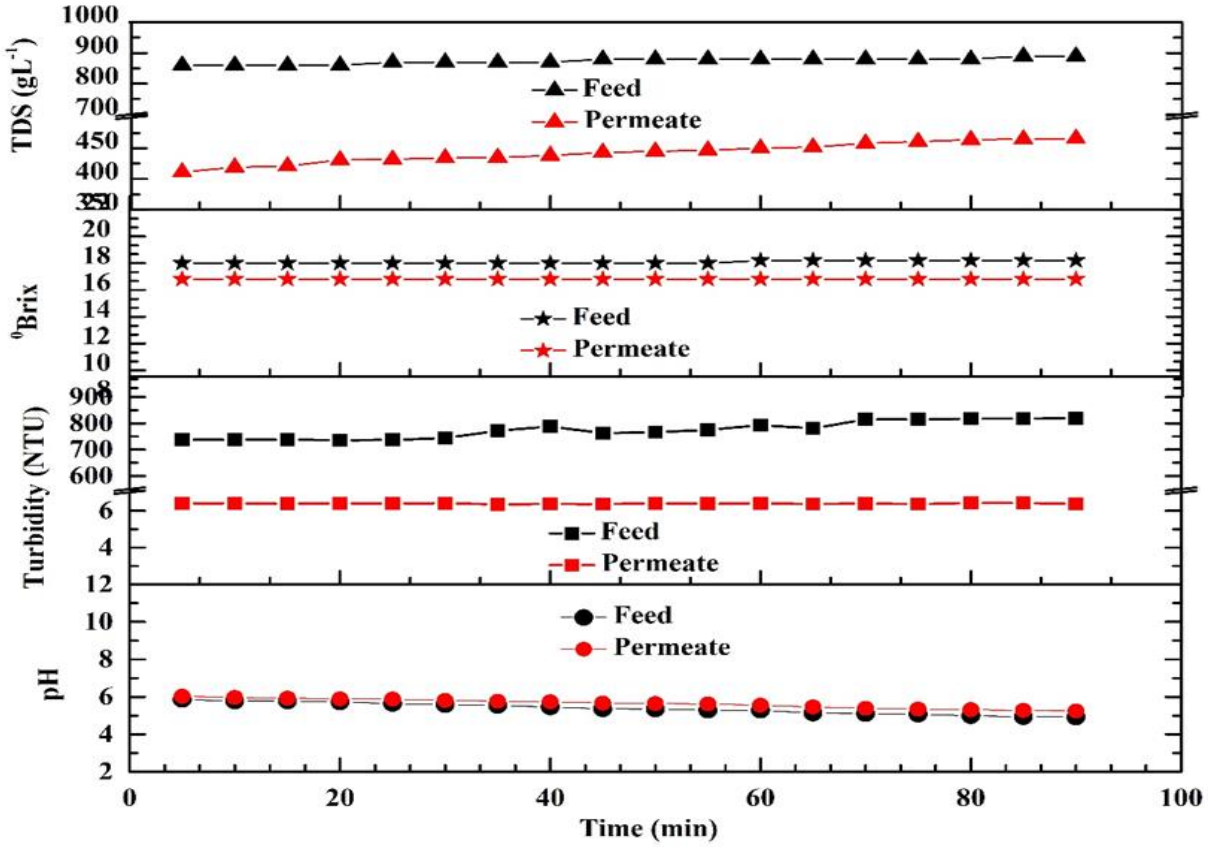


Fig. 3.7 Juice properties change with time for feed and permeate of coated membrane (CFV 3 m s^{-1}, temperature 35 °C).

The pH of the feed decreased with time due to the accumulation of acidic substance (produced by bacteria) with time. The rate of decrease of pH at 90 min was 16.03%. The permeate pH decreased with time. A variation in permeate (decrease rate 13%) was noticed due to corresponding variation of pH in feed tank. Since the acidic compounds (released by the bacteria present in the feed juice) were recycled back to the feed tank, the pH of the feed tank varied with time. Therefore, corresponding permeate pH also showed a similar trend. Indeed, this was due to the variation of feed pH with time. It would not be the case if a constant pH was maintained. Since the pH of feed was not kept constant, a variation of permeate pH was seen. However, the Brix of feed did not vary much. Moreover, permeate also showed similar result with consistent quality. The permeate conductivity increased with feed conductivity. The pH decreased with time due to accumulation of acidic substances. Increase in conductivity was due to the accumulation of acidic substances as revealed clearly from the decrease in pH.A similar result was reported for water (Leveing, 2002). Conductivity of water was reported to increase with decrease in pH from 7 to 5 (towards acidic nature) [37].

3.2.3 Removal of Polyphenol oxidase enzyme

Polyphenol oxidase (PPO) enzyme is naturally present in the sugarcane juice and is responsible for the colour change of the juice from green to yellow. Feed and permeate samples were analysed for every 5 minutes in a multimode micro plate spectrophotometer and the activity was calculated. During the activity measurements, all the process parameters such as concentration of the substrate, temperature and pressure were kept constant for both permeate and feed sample. As shown in Fig. 3.8, the measured PPO enzyme activity for feed was observed to be fluctuating from 5 to 11.

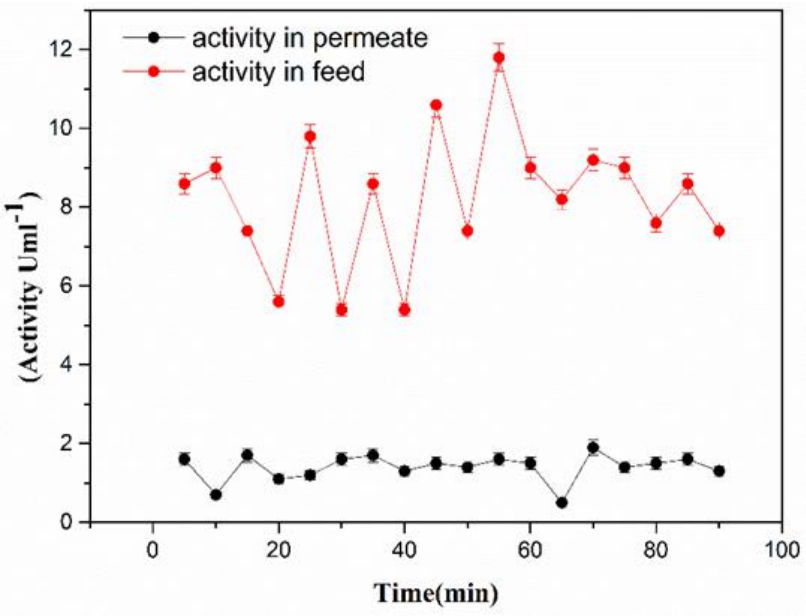


Fig. 3.8 PPO enzyme activity in feed and permeate at 4 °C

The enzyme activity is affected by environmental conditions like temperature, pH (acidity and basicity), enzyme and substrate concentration. The environment in which the clarification of sugarcane juice was performed was uncontrolled between time intervals. As a result, a fluctuation in enzyme activity of feed with high bacterial count was observed, wherein permeate which was with low bacterial count showed less fluctuations. Enzyme activity is proportional to amount of enzyme present. The enzyme concentration is the limiting factor for its activity. The activity of the enzyme decreased by 70% in permeate due to the removal of the PPO enzyme by UF membrane.

3.2.4 Juice self- life sustainability and sucrose loss study

The bacteria present in the feed were responsible for lowering the pH of juice and degrading the juice during storage. To evaluate bacterial concentration in feed and permeate, ten-fold serial dilutions was carried out. The bacterial colony growth in feed and permeate samples are shown in Fig. 3.9 and Table 3.3.Results concluded that the UF filtered juice has less number of bacterial colony growth compared to the un-filtered juice. From this study, it could be concluded that due to the removal of

unwanted bacteria present in the feed during UF, the permeate juice could be stored for a long time without adding any preservatives.

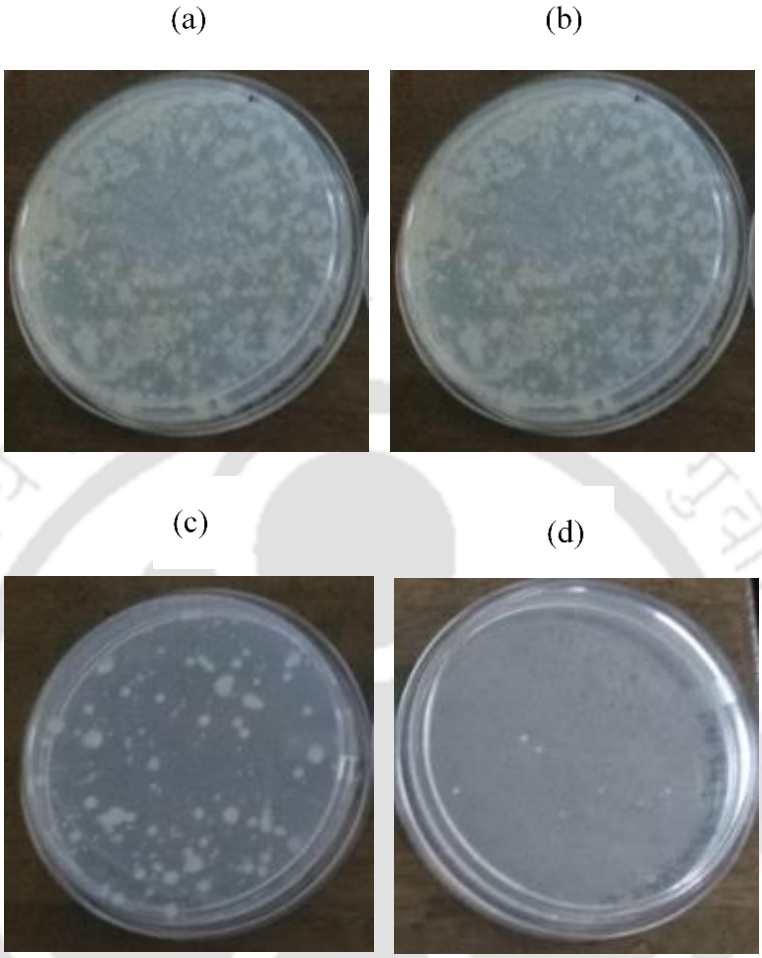


Fig. 3.9 Bacterial growth in nutrient agar plates at 37 °C for 24 h, (a) initial feed, (b) feed at 104 dilutions, (c) initial permeate of coated membrane and (d) permeate of coated membrane at 104 dilutions.

Table 3.3 Bacterial count for feed and permeate juice (temperature 37 °C, time 24 h)

Dilution	**10^{-1}**	**10^{-2}**	**10^{-4}**
Feed	TNTC*	TNTC	5,200,000
Permeate	TNTC	50,400	12

TNTC* = Too Numerous To Count

The sucrose of the sugarcane juice is lost with time due to the hydrolysis reaction under acidic condition. The sucrose degradation study was carried out by using high performance liquid chromatography (HPLC). The sugarcane juice samples which are kept for 6 h and 12 h to see the sucrose conversions at room temperature (25 °C) and humidity 75%. Here, three types of samples (raw juice pH 5.8, clarified juice pH 6.03 and raw juice with lime pH 7) were studied. The sugarcane juice was clarified at 135 psi (9.3 bar), CFV 0.02 m s^{-1}. In Fig. 3.10, sucrose loss analysis of HPLC is showed. HPLC analysis showed that the lime pre-treated raw juice had 1.62% sucrose loss, UF clarified had 2.7% sucrose loss and raw juice without pre-treatment had 43.52% after 6 h at room temperature. Clarified and lime pre-treated sugarcane juice showed minimum loss of sucrose to till 6 h at room temperature. The raw sugarcane juice is highly degraded without adding lime and exhibits high sucrose loss. Literature also reported that minimum sucrose degradation occurred between pH 6.45- 8.5 [106]. But after 12 h, the lime pre-treated and clarified juice also showed sucrose loss.

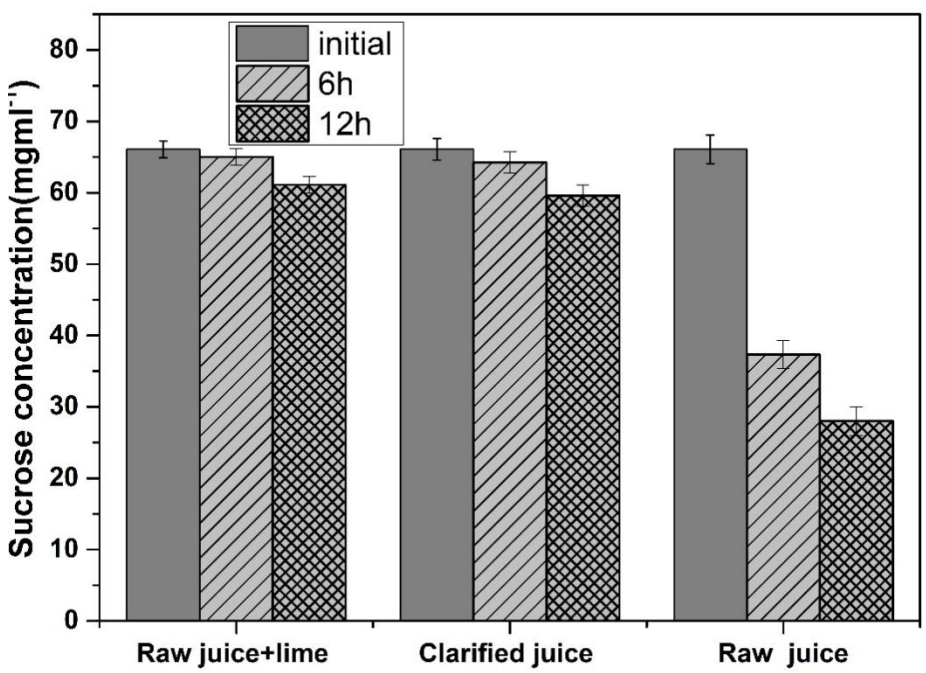


Fig. 3.10 Sucrose loss of raw juice, clarified juice and lime pre-treated juice at 35 °C

3.2.5 Membrane fouling analysis

3.2.5.1 FESEM analysis and EDX analysis

FESEM analysis was carried out to elucidate the morphological features of the membrane surfaces of the UF, fouled ceramic membrane, and foulants scraped from the membrane surface. Fig. 3.11 (a) showed porous structure and Fig. 3.11 (b) showed the FESEM image of the ceramic membrane after 3 h of filtration which indicated the formation of a dense layer of cake on the top surface of the membrane after filtration. It was also visible from the FESEM image of foulants that the membrane was coated with $LaPO_4$. The major components found in the membrane surface were C and O. A small amount of Mg, Al, Si, P, K, Ca, Fe, Na were found to be deposited on the membrane surface during sugarcane juice filtration [14]. Small amount of C was adsorbed in the transition layer which did not have any role in lowering the performance of the membrane (Fig. 3.12).

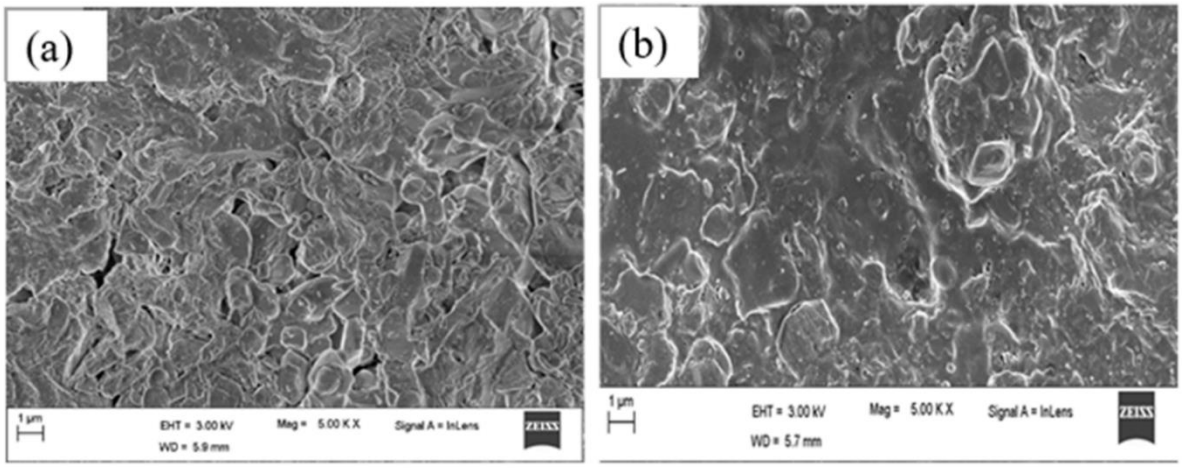


Fig. 3.11 FESEM image of (a) new membrane (5.00KX), (b) fouled membrane (5.00KX)

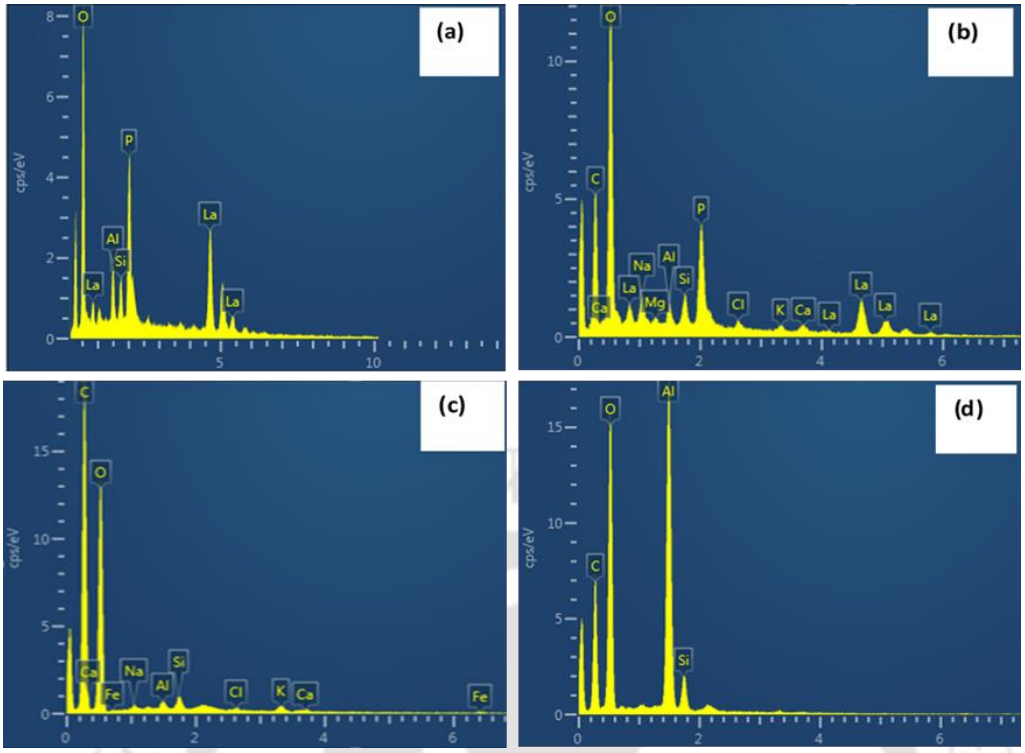


Fig. 3.12 EDX analysis of a) new membrane, b) fouled membrane c) foulants scraped from the membrane surface d) transition layer of fouled membrane.

3.2.5.2 FTIR analysis of foulants

The fouling elements responsible for reduction of flux were analysed by FTIR. The FTIR result of foulants scraped from the surface of the membrane during filtration process of sugarcane juice is shown in Fig. 3.13.

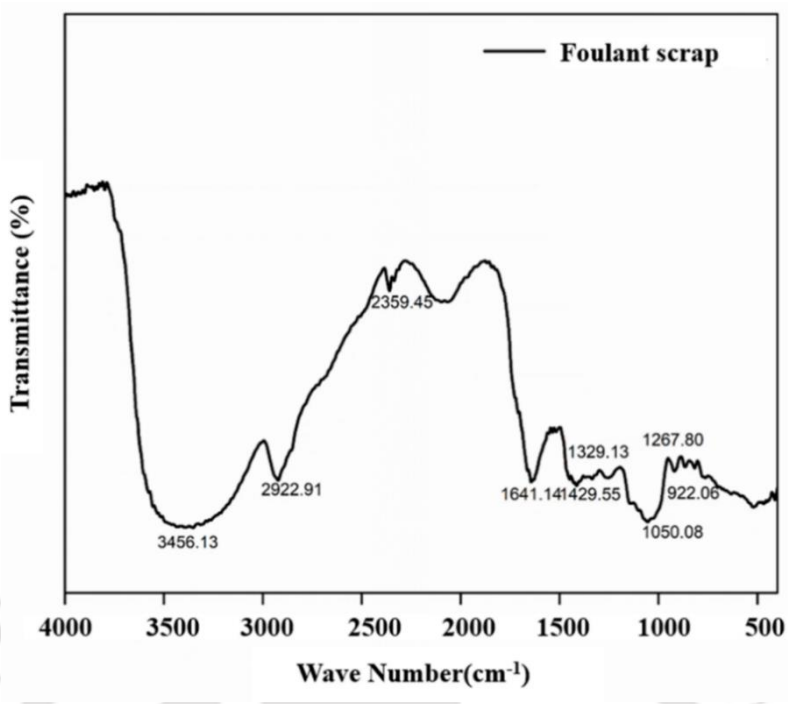


Fig. 3.13 FTIR spectra of foulants material scraped from the membrane surface

The absorption peak at 3419.23 cm^{-1} represents stretching and vibration of OH bond in hydroxyl functional group. The peak at 2922.91 cm^{-1}represent CH_3 bond due to catenated carbon. It revealed that carbonaceous materials were deposited on the surface of UF membrane. The wave number at 1641.14 cm^{-1} and 1429.55 cm^{-1} represented C=N stretching and H-N-H stretching which showed that amino group was present due to the presence of protein. Again, the peak at 1267.80 cm^{-1} and 1429.55 cm^{-1}represent C-O stretching and methyl stretching which are attributed to the presence of polysaccharides and lipids. The peak at 1050.06 cm^{-1} and 3456.13 cm^{-1} suggested CO stretching and OH stretching due to the presence of sucrose and phenol. CO was due to the presence of polysaccharide in sugarcane juice. The peak at 922.06 cm^{-1} represented OH stretching and vibration of carboxylic group and peak at 750 cm^{-1} - 400 cm^{-1} which represented the presence of membrane materials. From the above analysis, it can be concluded that polysaccharides, protein, aliphatic, phenols were the main membrane fouling materials while traces of metals were also found in EDX analysis. The results obtained in this work are similar to that reported in literature [14].

3.2.6 Membrane cleaning

3.2.6.1 Effect of physical cleaning

Fig. 3.14 shows the flux decline rate of $LaPO_4$ coated and uncoated membrane. Flux data reported for uncoated membrane showed high rate of flux (85.69%) decrease after 25min than the coated membrane (60.85%). This decrease in flux was may be due to the deposition of foulants in the pore and in the later stage flux declined further due to the deposition of all rejected particles on the membrane surface which might have form cake layer. From the analysis it was observed that uncoated membrane is not suitable (in terms of juices properties as well as flux decline) for clarification process of sugarcane.

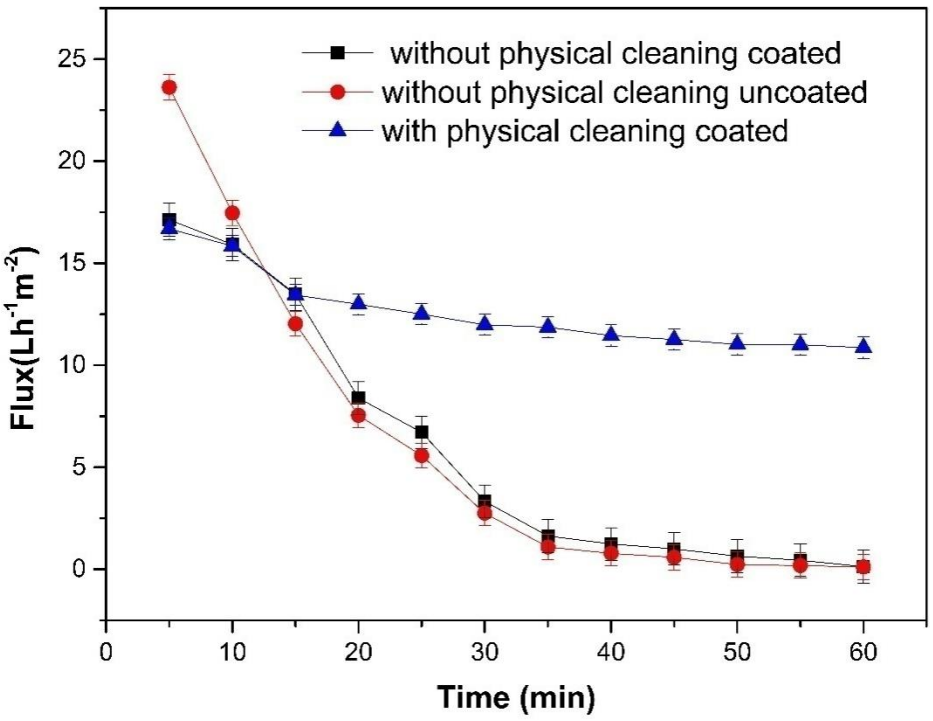


Fig. 3.14 Flux decline study of sugarcane juice a) without using a physical cleaning mechanism and b) with using physical cleaning mechanism at different condition at pH 5.86 and CFV 0.02 ms^{-1}.

Therefore, the cleaning study for the uncoated membrane was not performed. A physical cleaning study only for the coated membrane was performed during the clarification process. In the Fig. 3.14, flux declined from 17.13 L h^{-1} m^{-2} to 0.13 L $h^{-1}m^{-}$

[2]after 1 h of filtration for $LaPO_4$ coated membrane without using the brushing action during filtration process and flux declined from 16.86 L h^{-1} m^{-2} to 10.85 L h^{-1} m^{-2} within 1 h of operation with using the physical cleaning mechanism. A clearly visible difference was observed in the flux decline (Fig. 3.14), during the filtration process, with and without physical cleaning method. In literature, it was reported that the decline of permeate juice flux was primarily due to the dominant fouling mechanism of cake/gel layer formation [14]. When physical scrubbing was done, the cake layer was removed and thus, flux decline rate was less.

3.2.6.2 Effect of chemical cleaning

In this study, both chemical and physico-chemical cleaning were carried out for membrane cleaning. The flux decline rate was observed to be more when chemical cleaning alone was performed (Fig. 3.15).

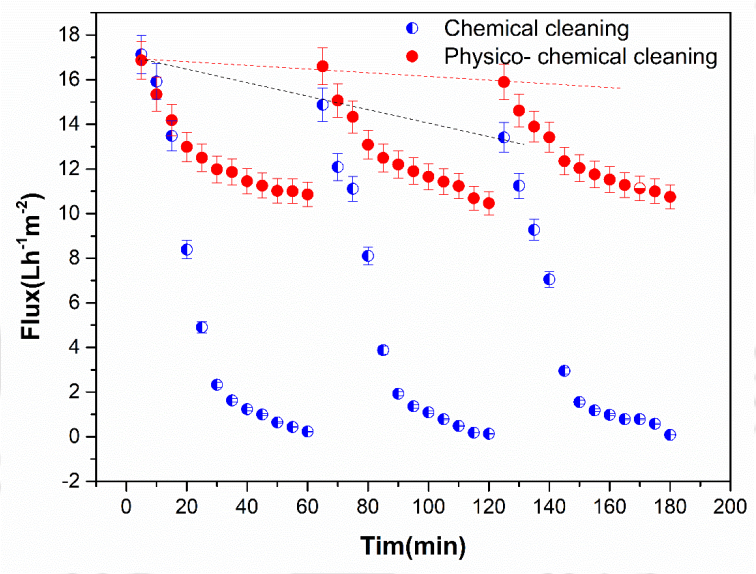


Fig. 3.15 Batch type flux decline of raw sugarcane juice after cleaning the membrane with chemical cleaning and with hybrid cleaning mechanisms

The physico-chemical cleaning proposed in this study showed less decrease in the slope of the flux. The cleaning efficiency was represented by Flux Recovery (FR) ratio. Flux recovery ratio was calculated after every cleaning to evaluate the membrane regeneration efficiency. In the chemical cleaning process, it was observed that the FR was 86.83% while, the physico-chemical cleaning process yielded a FR of 98.39%. The calculation of permanent loss in flux was done in terms of Flux Decline percent (FD)

which was observed for both chemical cleaning and physico-chemical cleaning. FD for chemical cleaning alone was 13.16% and for physico-chemical cleaning it was 3.16%. It was thus observed that in the case of physico-chemical cleaning, permanent flux loss was lesser than the chemical cleaning. The flux decay coefficient (m) was calculated for 60 min run time of experiment and it was observed that for the run where no physical cleaning mechanism was introduced, the flux decline coefficient (m) was 98.65% after 60 min of time while for the same time period, the flux decay coefficient was only 36.60% when physical cleaning mechanism was introduced. It could thus be concluded that if physical cleaning mechanism was introduced during the process of sugarcane juice clarification, the clarification can be continued for a longer duration. As a general practise, the fouled membrane should be cleaned when flux decay coefficient (m) reaches approximately 90% at operating conditions.

3.3 Summary

Novel low cost ceramic membrane of multi channelled porous alumina support coated with $LaPO_4$ nano-fibrils was successfully applied for the sugarcane juice clarification in combination with the physical and chemical cleaning processes. The importance of membrane regeneration could be attributed to the fact that membrane flux reduction could be significantly controlled with the help of physical cleaning. In the present study, membrane flux improvement up to 50 times was obtained when physical cleaning was introduced during the juice clarification process. The cake layer deposition on the surface of the UF membrane, which was observed to be the major fouling phenomena, could be tackled by the use of physical cleaning. Chemical cleaning further removed the foulants from the surface thereby improving the overall efficiency of the filtration process. Foulants analysis revealed the presence of polysaccharides, proteins, aliphatic, phenols, phosphorus, silicon and few other metals like sodium, aluminium, silicon, and potassium. The permeate properties produced by this process were observed to be of acceptable standards. The hybrid cleaning process for membrane regeneration is thus a promising solution for the sugarcane juice clarification.

Chapter: 4

Concentration of sugarcane juice using forward osmosis membrane with fouling and cleaning study

This chapter elaborated the performance of a commercially available aquaporin HFFO membrane for concentration of sugarcane juice by adopting appropriate UF pre-treatment technique. This includes preparation of DS and study the effect of draw, FS flowrate, draw concentration and its direction of flow such as co-current or counter-current on water reverse solute flux in batch mode. Also, the membrane fouling due to organics present in the sugarcane juice was studied systematically with appropriate membrane cleaning strategy.Based on the observed FO flux decline data, the effect of UF clarified and unclarified sugarcane juice on FO membrane fouling is discussed here.

4.1. Materials and Methods

4.1.1. Sugarcane juice

The raw sugarcane juice was purchased from the fruit juice centre located inside Indian Institute of Technology Guwahati (IITG) campus, India. The raw juice was prepared by crushing the water washed sugarcane after removing the skin, in manual sugarcane crusher. The extracted juice was homogenized and 100 mesh size sieves were used for preliminary filtration where large particles were removed. Further, UF ceramic membrane (0.1 μm mean pore size) was used for clarification of the sugarcane juice. Initial characterization for both raw and UF pre-treated (clarified) sugarcane juices is shown in Table 4.1. The clarified sugarcane juice was used as a feed to Forward Osmosis (FO)membrane in order to establish optimal conditions for FO process and later both raw and clarified juices were used as a feed to FO for membrane fouling characterization studies.

Table 4.1 Initial characteristics of untreated and UF treated sugarcane juice

Parameters	Brix (°)	Turbidity (NTU)	Sucrose (g L^{-1})	Glucose (g L^{-1})	Fructose (g L^{-1})
Untreated	11.4 ± 0.2	737 ± 4	114.2 ± 0.9	29.9 ± 0.5	22.7± 0.4
UF pre-treated	11.4 ± 0.2	5.57 ± 0.08	114.2 ± 0.9	29.9 ± 0.5	22.7 ± 0.4

4.1.2. Membrane material and module configuration

Aquaporin Hollow Fibre Forward Osmosis (HFFO) membrane comprising an active layer of polyamide thin film composite (TFC) with integrated aquaporin proteins was purchased from Aquaporin A/S, Denmark. These membranes were coated with aquaporin on the lumen side of the fibre with an active area (lumen side) of 2.3 m^2 having inner diameter of the fibre as 200 µm. The module diameter of 70 mm, module length of 300 mm and membrane-active length of 280 mm is used for the experiment. The packing density of the membrane is 279.2 kg m^{-3} and the number of fibres in the module is 13000. The recommended operating conditions by membrane supplier are as follows: feed flow rate inside lumen = 25 L h^{-1}, the draw flow rate = 25 to 45 L h^{-1}, temperature 10-30 ^{0}C, the maximum operating pressure is 4 bar, pH 2–11 and free chlorine tolerance <0.1 mg L^{-1}. The water and specific reverse salt flux of aquaporin membrane for NaCl (0.5 M) - DI water system is 11 ±1.5 L h^{-1} m^{-2} and 0.15 ± 0.05 g L^{-1} in ALFS (FO) mode at temperature 25 ± 1 ^{0}C, counter-current flow, feed flow rate (lumen side): 60 L h^{-1}, draw flow rate (shell side): 25 L h^{-1}, transmembrane pressure (TMP) feed to draw: 0.2 bar (2.9 psi). In this study, due to highly turbid raw sugarcane juice, the FO experiments were performed using DS facing the active layer (Pressure Retarded Osmosis mode), i.e., raw sugarcane juice was circulated in shell side and DSwas circulated through the fibre lumen side. While circulating the highly turbid sugarcane juice in the lumen side, it got choked within 5 min of continuous operation, resulting in high pressure drop across the flow path.

4.1.3. Preparation of Draw solution

Analytical grade NaCl was purchased from M/S Merck Life SciencePvt. Ltd., India. This NaCl and DI water (Milli-Q pure water) at room temperature was used to prepare DS of various concentrations (100, 200 g L^{-1}).

4.1.4. Analytical Methods

4.1.4.1. HPLC analysis of feed solution

The sucrose, glucose, and fructose concentration were measured using the HPLC system (M/S Shimadzu, Singapore) with an auto-sampler and RID detector. HI-PLEX

H column was used. Prior to each set of analysis, the sample was diluted with deionized water in 1:100 ratios and filtered with a 0.22 µm filter to remove the particulate matter. Sulphuric acid (H_2SO_4)of 0.005 M was used as the mobile phase at 0.5 mL min^{-1} flow rate and 35 °C. The auto-calibration mode was used to calibrate the HPLC by using six concentration standards (0.025, 0.25, 0.5, 1.0, 3.0, 5.0 mg mL^{-1} of sucrose solution). Then actual FO feed and draw samples were injected to measure corresponding juice component concentration.

4.1.4.2. IC analysis of feed solution

Ion Chromatography (IC) system consisting of METROSEP C2 – 250 column was used to measure the Na^+ concentration in the FS. The sample was diluted in the ratio of 1:100 and filtered through 0.22 µm syringe filter and Pyridine-2.6-dicarboxylic acid, 98% (dipicolinic acid) was used as the mobile phase. The IC auto-calibration mode was used to measure Na^+ concentration by using three/four standard solutions (0.1, 1, 50, 100 ppm), wherein initial Na^+ concentration raw sugarcane juice was subtracted from actual Na^+ concentration to calculate reverse solute flux. Finally, the actual NaCl flux across the membrane was calculated by applying the electro neutrality condition.

4.1.5. Experimental setup for clarification of sugarcane juice

A laboratory-scale FO system was established with an aquaporin HFFO membrane as described above for the concentration of sugarcane juice as shown in Fig. 4.1.

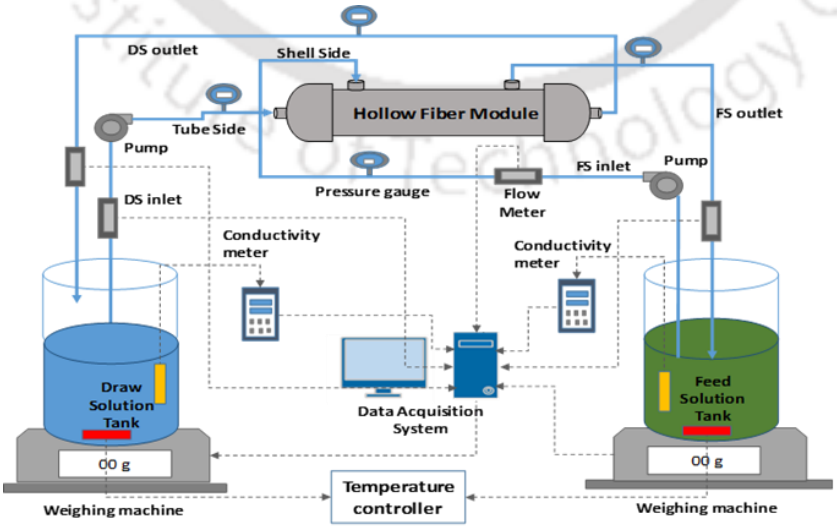


Fig. 4.1 Forward osmosis experimental setup

The experimental setup is fabricated in order to pump both FS (sugarcane juice) and DS (NaCl) by using two low pressure plunger pumps coupled with the flow control circuit (0 to 1.2 L m^{-2}, Hi-Tech booster pump, Hi-Tech Sweet Water Technologies (P) Ltd).

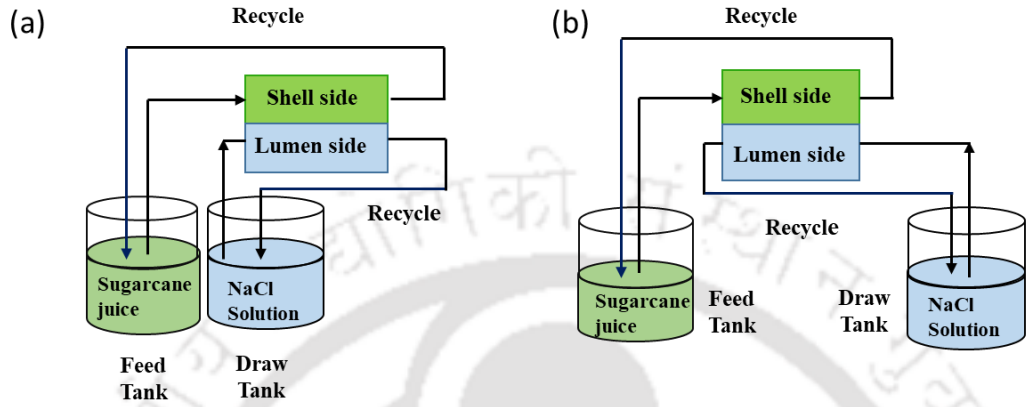


Fig. 4.2 Process flowsheet diagram for feed and draw recycle, (a)co-current and (b) counter-current.

As shown in Fig. 4.2 (a) and (b), the flow configuration, i.e., either co-current or counter-current mode can be configured by interchanging feed inlet and outlet connection and *vice-versa*. To avoid blockage of lumen side fiber by the particles of sugarcane juice, the sugarcane juice was circulated through the shell side and the NaCl solution was circulated through the lumen side, facing membrane active layer with a cross-flow velocity of 2 m s^{-1}. The draw and FS tanks were equipped with stirrer for uniform mixing. They were kept on a digital weighing machine and connected with a data logger system. The change in tank weight was recorded at an interval of 1 s. The water flux across the membrane was calculated from measured change in tank weight per unit time.

The inlet and outlet flow rate of feed and DS were monitored and recorded continuously by a digital flow meter (Remote flow indicator, ASMAIndustrial Corporation, India). The total dissolved solids (TDS) change in feed and DS was monitored by a digital conductivity/TDS meter (HANNA edge®, M/S HANNA Instruments, India) connected with the data logger system. TDS/conductivity of DS was recorded for each second. During the experiment, 1 mL of feed sample was

collected after every 1 min with micropipette (M/STarson Ltd.) to analyze the NaCl, sucrose, glucose and fructose concentration. The FO experiments were performed by varying different draw flow rate (at 25, 35, 45 L h^{-1}) at a fixed feed flow rate (at 25 L h^{-1}). The NaCl solution (100 g L^{-1}) and sugarcane juice (11.4 ± 0.2 °Brix) were used as a draw and FS respectively. Before each FO experiment, the membrane was stabilized by passing DI water in both lumen and shell side of the membrane module for 30 min. After stabilization of the membrane, the DS was passed through the lumen side to remove the DI water from the lumen side by closing the shell side inlet and outlet port. Similarly, the FS (sugarcane juice) was pumped into the shell side to remove the DI water in the shell side by closing the inlet and outlet port. Actual FO experiment was conducted by opening both shell and lumen side inlet and outlet port, then the parameters such as: (i) mass of draw and feed tank, (ii) inlet and outlet flow rate of both draw and FS, and (iii) TDS/conductivity of DS were recorded per second by using data logger. Also, the feed sample was collected every min for IC and HPLC analysis.

4.1.6. Design of FO experiments

The objective of this work is to establish the optimal FO process condition to achieve maximum water flux and minimum reverse solute flux (RSF) by mitigating the fouling potential. The FO batch experiments were designed to manipulate the FO process parameters such as: (i) draw flow rate, (ii) draw concentration (iii) flow configuration in a systematic manner to achieve optimal parameters. All the FO experiments were conducted at 25 ± 1 °C without applying back pressure to draw and feed outlet, wherein the initial solution volume of 6.1 L feed and 6.4 L draw was used for batch experiments. Initial FO experiments were conducted by manipulating draw flow rate (25 L h^{-1}, 35 L h^{-1} and 45 L h^{-1}) at a fixed feed flowrate (25 L h^{-1}) for both flow configurations. From the initial experiment, the best flow configuration and optimal draw flowrate were fixed based on water flux and RSF. Next level of FO experiment was performed by varying DS concentration (100, 200 g L^{-1}) at a fixed optimal draw and feed flow rate (25 L h^{-1}) and flow configuration.

4.1.7. Fouling and cleaning study

To study the fouling behaviour of aquaporin HFFO module, the FO continuous mode experiments were performed by using both clarified and unclarified sugarcane juice. The optimal operating parameters which were established from the batch FO experiments were used for fouling experiments. Only difference between batch and continuous experiments is that the recycled feed and DS were stored in separate storage tanks, such that the inlet feed and DS concentrations were kept constant throughout the fouling experiments. All the fouling experiments were performed in counter-current mode, active layer facing DS where DS concentration was kept at 100 g L^{-1} and a feed (sugarcane juice) of 11.4 °Brix was used. The FO fouling experiments were conducted after stabilizing the new HFFO membrane module with deionized water (DI) water in batch mode for 30 min. After stabilization, the membrane permeability was estimated by measuring membrane water flux by applying pressure at the shell side, i.e. by performing low pressure RO experiments with DI water.

First, the fouling potential of clarified sugarcane juice was studied by performing continuous mode FO experiment till 20% reduction in original water flux was achieved (i.e., ~ 16 h). Both draw and FSs were maintained at 25 ± 1°C by using the temperature controller. The fouled membrane was cleaned in three steps, (i) DI water flushing, (ii) osmotic backwash and (iii) chemical cleaning. The permeability of the membrane was calculated after each cleaning method to find its cleaning efficiency. Based on the membrane regeneration efficiency by DI water flushing, the remaining two cleaning protocol were executed. When DI water flushing was sufficient enough to regenerate the membrane to its original permeability, then the other two cleaning methods were not applied. Both FO fouling and membrane cleaning experiments were repeated for three cycles of operation for both clarified and unclarified sugarcane juice. The FO water flux was measured from the recorded inlet and outlet flow rate of the draw and FS by the data logger. Similarly, the RSF was measured by measuring the draw outlet NaCl concentration along with draw inlet and outlet flow rate. The three step membrane regeneration process was performed as follows:

(i) DI water flushing: After each cycle of FO experiment, both draw and FS were taken out from the membrane module by air scoring and then the module was rinsed with DI water for 10 min in batch mode for removal of residual NaCl solution and juice. After that, the fouled membrane was flushed with the DI water (25 ± 1 °C, 45 L h^{-1}) for 30 min to remove the foulants. Since, no back pressure was applied during the FO process, the foulants compaction with membrane surface was expected to be less, and hence flushing with DI water might have beenable to remove most of the foulants accumulated during one cycle of FO operation [84].

(ii) Osmotic backwash: The osmotic backwash was carried out for 30 min by circulating NaCl solution (50 g L^{-1}, 45 L h^{-1}) in the shell side and DI water (25 L h^{-1}) in fibre lumen side.

(iii) Chemical cleaning: After osmotic backwash, the membrane was washed with 0.1 M NaOH for 30 min in batch mode. After chemical wash, the membrane module was rinsed with DI water for 20 min for both feed and draw side to remove the residual NaOH.

4.2. Results and discussion

4.2.1. Effect of draw solution flow rate in co-current mode

The optimal DS flowrate for aquaporin HFFO module operation was calculated experimentally by performing FO batch experiments at a different DS flowrate (25, 35, 45 L h^{-1}). It has been reported that variation in FS flowrate has almost no impact in water flux in comparison to DS flowrate and that will result in increased energy consumption without yielding improved water flux[74] Therefore, in this study, while varying DS flowrate, the FS flowrate was kept at the membrane manufacturer's recommended flowrate (25 Lh^{-1}). In this work, the batch mode is chosen to minimize the NaCl usage. i.e. the continues replacement of DS with time requires more NaCl as well as more water. Another, advantage of batch process is that we can re-use the DS forward flux of juice is zero (which is confirmed by analysing sucrose presence DS by using HPLC) during the entire experiment.The effect of draw flowrate on FO process performance in co-current mode is presented in Fig.4.3 and Fig.4.4. During batch FO

experiments, the DS concentration decreases and feed concentration increases, and this resulted in nonlinear variation of volume in feed and draw tank (Fig.4.3a). The slope of the volume *vs* time curve was high at the start of the process, and it was observed to decrease with increase in time in FO batch process. This change in tank volume will continue until osmotic pressure of both FS and DS become equal.

Due to water flux from FS to DS, the positive slope was observed for draw tank volume *vs*. time, and vice versa negative slope was observed for FS tank volume. As expected, the change of FS and DS solution volume was found be exactly same without having experimental error in digital weighing balance. From the slope of the volume vs time curve and membrane surface area, the water flux for a given time interval can be calculated by using the equation 4.1.

$$J_{w,t} = \frac{V_{FS,t} - V_{FS,t-\Delta t}}{A_m \Delta t} = \frac{V_{DS,t-\Delta t} - V_{DS,t}}{A_m \Delta t} \quad (4.1)$$

Where,$V_{FS,t}$ is the volume of feed tank at time t, and $V_{FS,t-\Delta t}$ is the volume of feed tank at $t - \Delta t$, $V_{DS,t}$ is the volume of draw tank at time t, and $V_{DS,t-\Delta t}$ is the volume of draw tank at $t - \Delta t$, A_m is the active membrane area of aquaporin HFFO module, Δt is the time interval for flux measurement.

As shown in Fig. 4.3 (a), J_w was decreasing with time in batch process. The average $J_{w,Avg}$ was calculated for a single batch as per below given equation 4.2.

$$J_{w,Avg} = \sum_{t=t_1}^{t_n} \frac{J_{w,t}}{n} \quad (4.2)$$

Where, $t_i$time stamp at which water flux is calculated, n = total number intervals for which water flux calculated.

The RSF of NaCl from DS to FS for a given time interval was calculated by using the equation 4.3.

$$RSF_t = \frac{V_{FS,t}C_{FS,t} - V_{FS,t-\Delta t}C_{FS,t-\Delta t}}{A_m \Delta t} = \frac{V_{DS,t-\Delta t}C_{DS,t-\Delta t} - V_{DS,t}C_{DS,t}}{A_m \Delta t} \quad (4.3)$$

Similar to J_w, RSF was also expected vary with process time, so average RSF was calculated for a given FO batch operation by using the equation 4.4.

$$RSF_{Avg} = \sum_{t=t_1}^{t_n} \frac{RSF_t}{n} \tag{4.4}$$

Where, $C_{FS,t}$ is the NaCl concentration in FS tank at time t, and $C_{FS,t-\Delta t}$ is the NaCl concentration in FS tank at $t - \Delta t$, $C_{DS,t}$ is the NaCl concentration in DS tank at time t, and $C_{DS,t-\Delta t}$ is the NaCl concentration in DS tank at $t - \Delta t$.

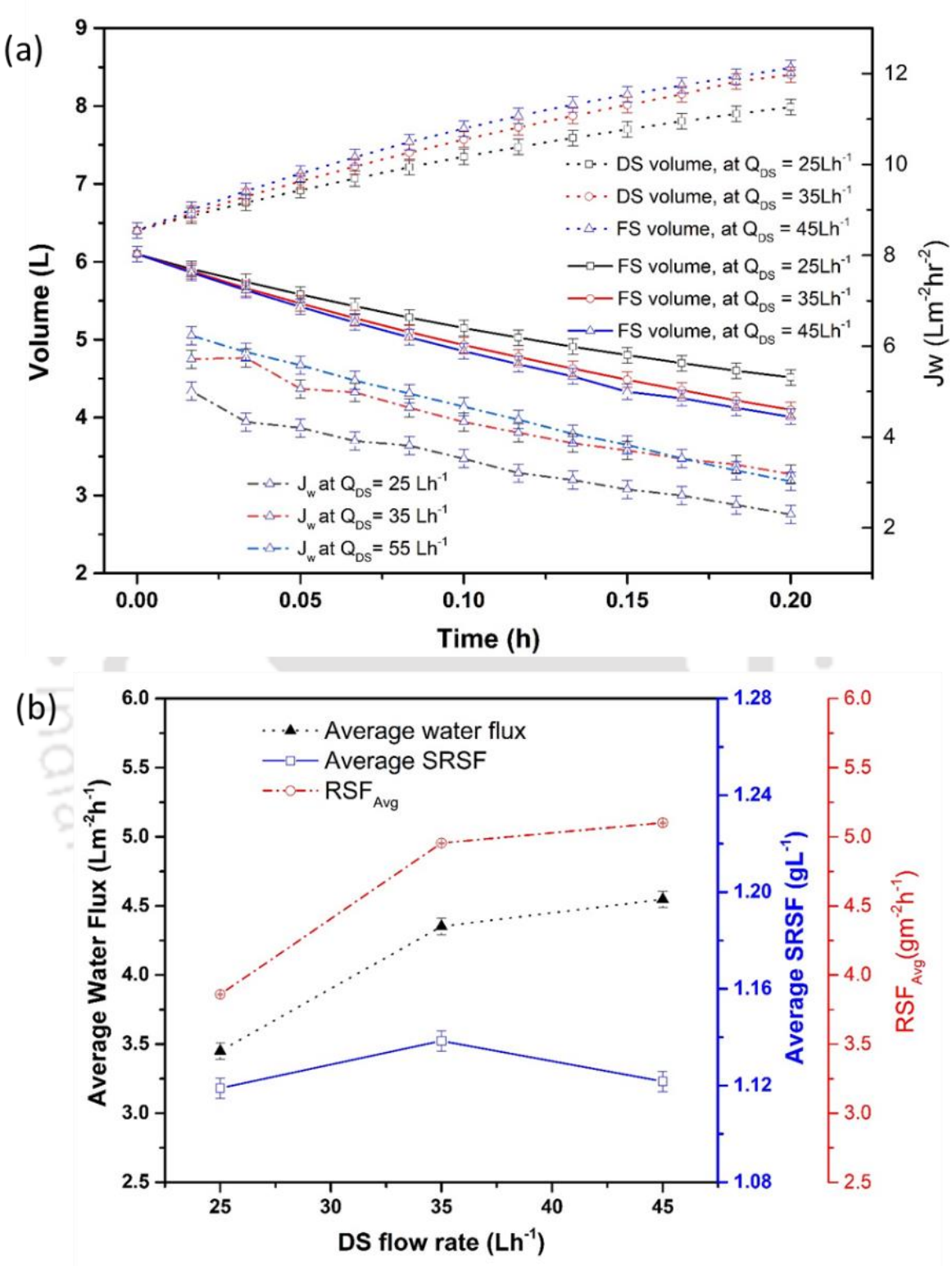


Fig. 4.3 Experimental results for co-current mode effect of DS flow rate on (a) water flux variation and change in feed and draw volume (b) average water flux, RSF and SRSF at $Q_{DS,in}$ = 25, 35 and 45 L h^{-1} and $Q_{FS,in}$ = 25 L h^{-1}, $C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$=114.2 ±0.9 g L^{-1}

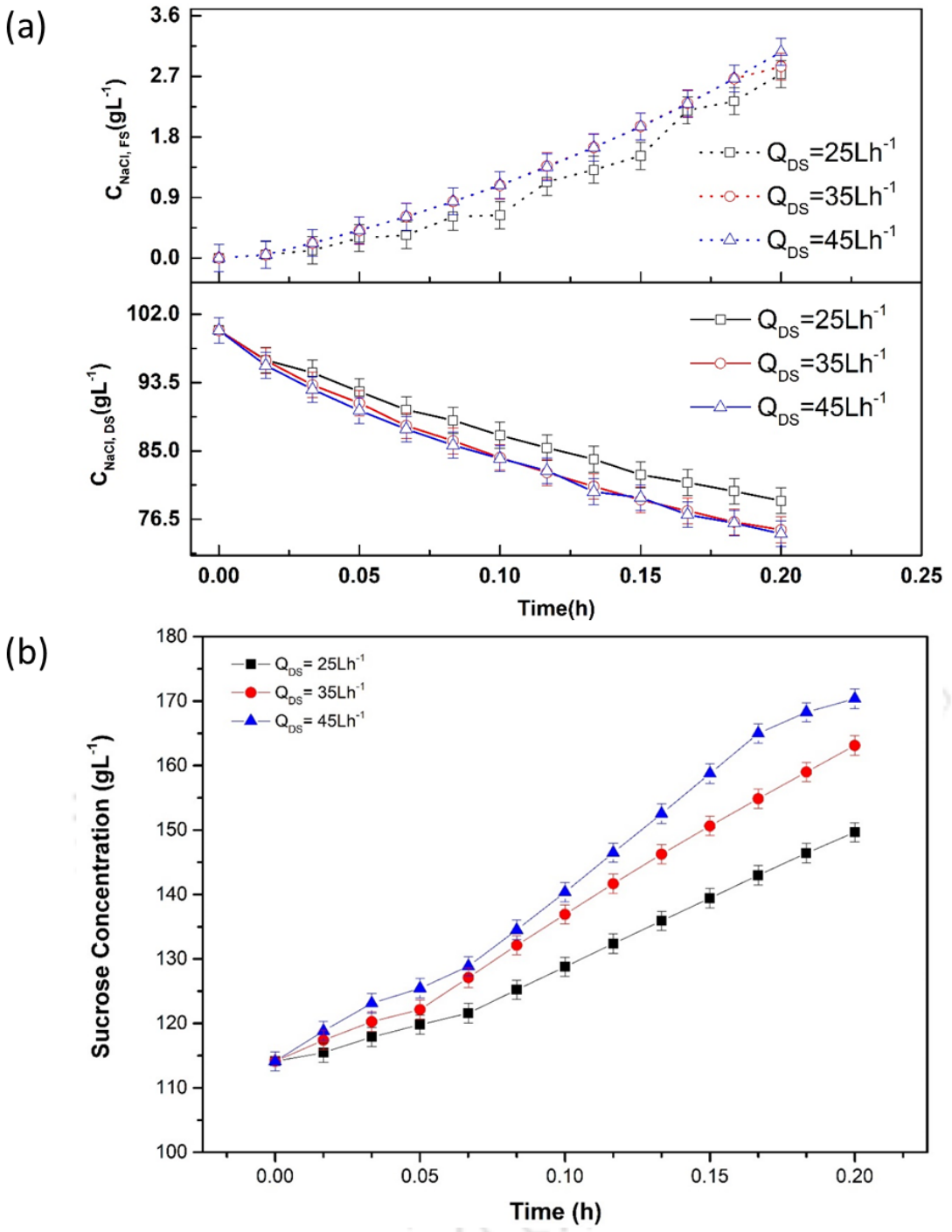


Fig. 4.4 (a) NaCl concentration in draw and feed tank at $Q_{DS,in}$ = 25, 35 and 45 L h^{-1}, $C_{DS,int}$= 100 g L^{-1} in co-current mode. (b) sucrose concentration vs process time

As shown in Fig. 4.4a, the NaCl concentration in draw tank decreased with process time due to increased DS volume, and in another side of the membrane, the concentration of sugarcane juice component (sucrose) increased (114.2 ± 0.9 g L^{-1} to 149.6 ± 0.9 g L^{-1}, 163.1 ± 0.9 g L^{-1}and 170.3 ± 0.9 g L^{-1}at DS flow rate 25, 35 and 45 L h^{-1} respectively) due to removal of water from FS (Fig. 4. 4b). Also, due to RSF, the NaCl

concentration in FS increased with process time. The final concentration of NaCl in feed is 0.3 ± 0.2, 0.5 ± 0.2 and 0.5 ± 0.2 g L^{-1}at 25, 35 and 45 L h^{-1} respectively. At the end of the batch process, the feed sugarcane juice volume reduced, and it was concentrated to a maximum of 1.35 times of the original concentration for 45 L h^{-1} DS flow rateTable 4.2 for co-current flow configuration. The average water flux corresponding to DS flowrate 45 L h^{-1} is 4.5 ± 0.06 L $h^{-1}m^{-2}$ and it was observed to be higher than average water flux with DS flowrate of 25 L h^{-1} (i.e., 3.4 ± 0.06 L h^{-1} m^{-2}). Similarly, as shown in Table 4.2, the high sucrose concentration (170.3 ± 0.9 g L^{-1}) was achieved while maintaining high DS flowrate (45 L h^{-1}) in comparison with lower DS flowrate. Due to both DS dilution and FS concentration, the osmotic driving force across the membrane separation layer got reduced with process time, and that resulted in reduced HFFO module water flux with process timeFig. 4.3a.

The improved DS velocity across the shell side will reduce the internal dilutive concentration polarization occurring at the support layer. This phenomenon will increase the actual osmotic driving force across the separation layer. The reduction in the effect of internal dilutive concentration polarization will be minimal when the cross-flow velocity reaches beyond the threshold value[74]. As an effect of that, the measured average water flux of HFFO module increased nonlinearly with respect to DS flowrate (Fig. 4.3b).

The specific reverse solute flux (SRSF) was calculated by using average water flux and RSF $\left(RSF_{avg}/J_{w,avg}\right)$. In a batch FO process, the DS concentration was reduced with increase in process time, and that results in the reduced driving force for RSF. Therefore, SRSF will reduce with process time. However, while increasing the DS velocity in the shell side, the average SRSF increased and then decreased. As reported in the authors previous work [107], this was mainly due to reduced internal dilutive concentration polarization which increased the concentration difference across the membrane separation layer. Further,J_w and RSF were also observed to increase, however, increase in J_w was observed to be much higher than the RSF when DS was higher than 35 L h^{-1} (Fig.4.3b)

4.2.2. Effect of draw solution flow rate in counter current mode

The batch FO experimental results for counter-current mode was observed to be similar to co-current experimental results presented in Fig. 4.3 and Fig. 4.4. Therefore, the experimental result of counter-current mode is shown in the Fig. 4.5, Fig. 4.6, Fig. 4.7. Further, to compare the performance of co-current and counter-current mode FO performance, both $J_{w,avg}$RSF$_{Avg}$and SRSF$_{Avg}$ were analysed and presented in Fig. 4.8. The SRSF$_{Avg}$ in counter-current mode was found to decrease from 25 L h^{-1} DS flowrate onwards and similar behaviour was also observed for co-current but beyond a DS flowrate of 35 L h^{-1}. The final concentration by aquaporin membrane in 12 min was 53% - 60% (with negligible draw solute back diffusion) in comparison to the initial concentration. This is very close to the concentration achieved by multiple-effect evaporators in industrial operations before the feed enters the final evaporator where crystallization is done.The maximum average water flux of 5.2 ± 0.08 L h^{-1} m^{-2} was observed for higher DS flow rate (45 L h^{-1}). As shown in Fig. 4.8, both water flux and SRSF improved by 15% and 39% for counter-current mode FO operation in comparison to the co-current mode at 45 L h^{-1} DS flow rate. This was mainly due to improved osmotic pressure difference across the membrane module during the counter-current mode operation. The summary of the co-current and counter-current experimental results are presented in Table 4.2. Therefore, remaining FO sugarcane juice concentration studies were performed at DS flow rate of 45 L h^{-1}, FS flow rate25 L h^{-1} and counter-current mode.

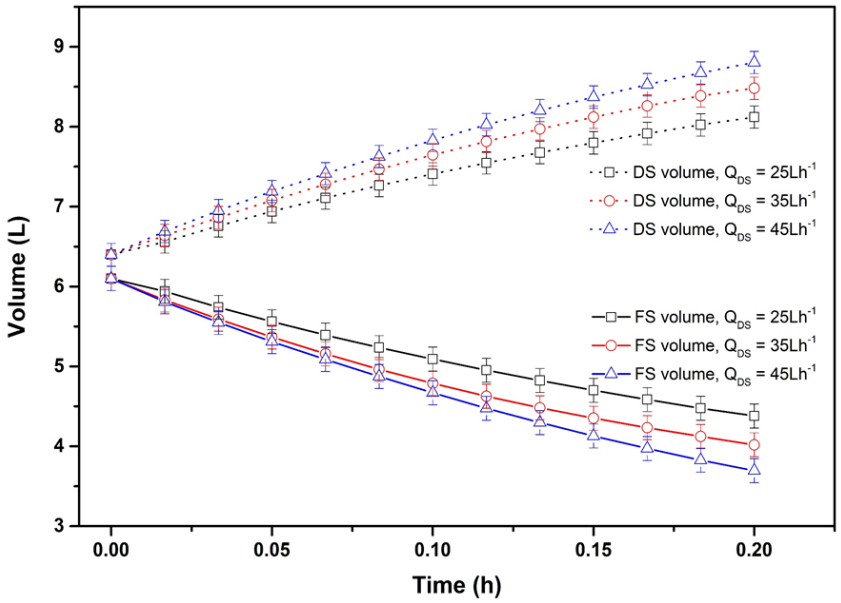


Fig. 4.5 Experimental results for counter current mode change in FS and DS volume at $Q_{DS,in}$= 25, 35 and 45 L h^{-1} and $Q_{FS,in}$ = 25 L h^{-1}, $C_{DS,int}$= 100 g L^{-1}, $C_{Sucrose,int}$= 114.2 ± 0.9 g L^{-1}

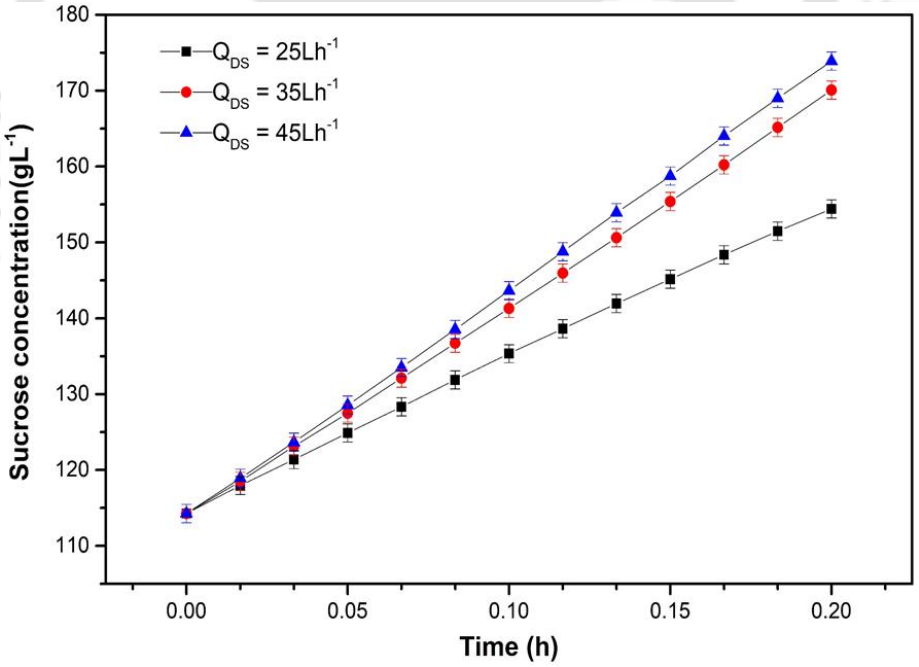


Fig. 4.6 Experimental results for counter current mode sucrose concentration $Q_{DS,in}$= 25, 35 and 45 L h^{-1} and $Q_{FS,in}$ = 25 L h^{-1}, $C_{DS,int}$= 100 g L^{-1}, $C_{Sucrose,int}$= 114.2 ± 0.9 g L^{-1}

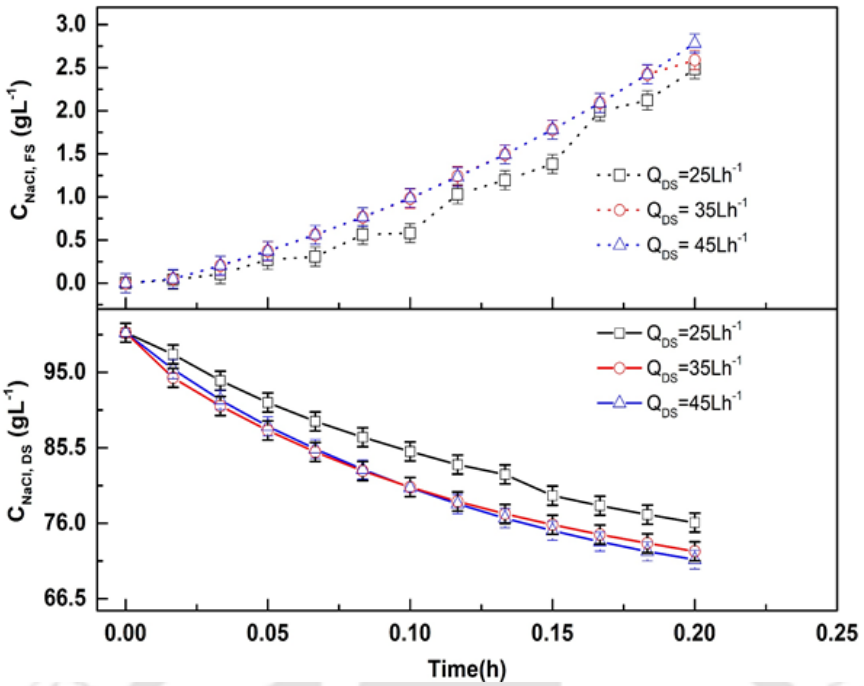


Fig. 4.7 Experimental results for counter current mode NaCl concentration in DS and FS tank at $Q_{DS,in}$= 25, 35 and 45 L h^{-1} and $Q_{FS,in}$ = 25 L h^{-1}, $C_{DS,int}$= 100 g L^{-1}, $C_{Sucrose,int}$= 114.2 ± 0.9 g L^{-1}

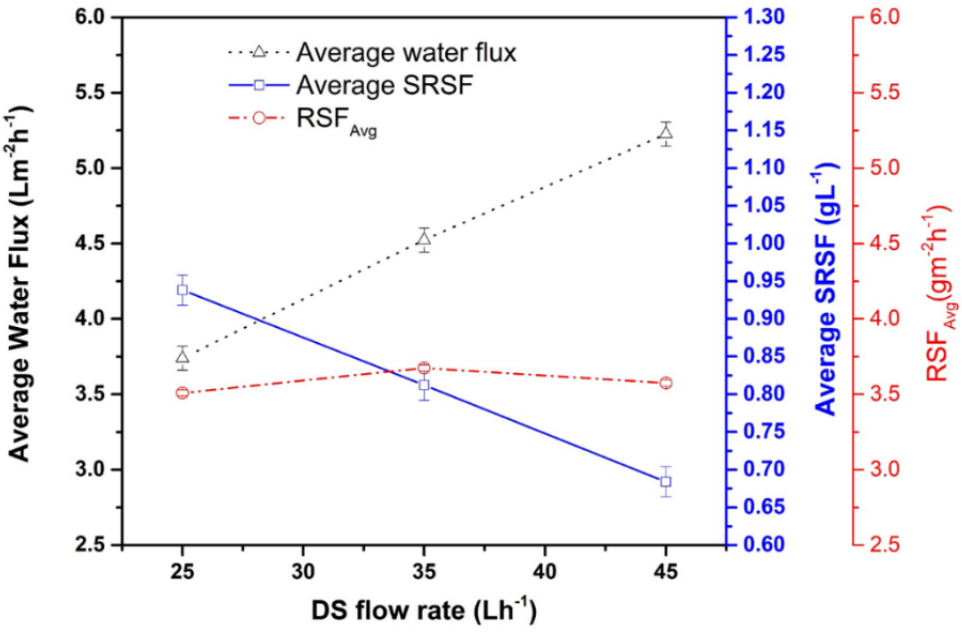
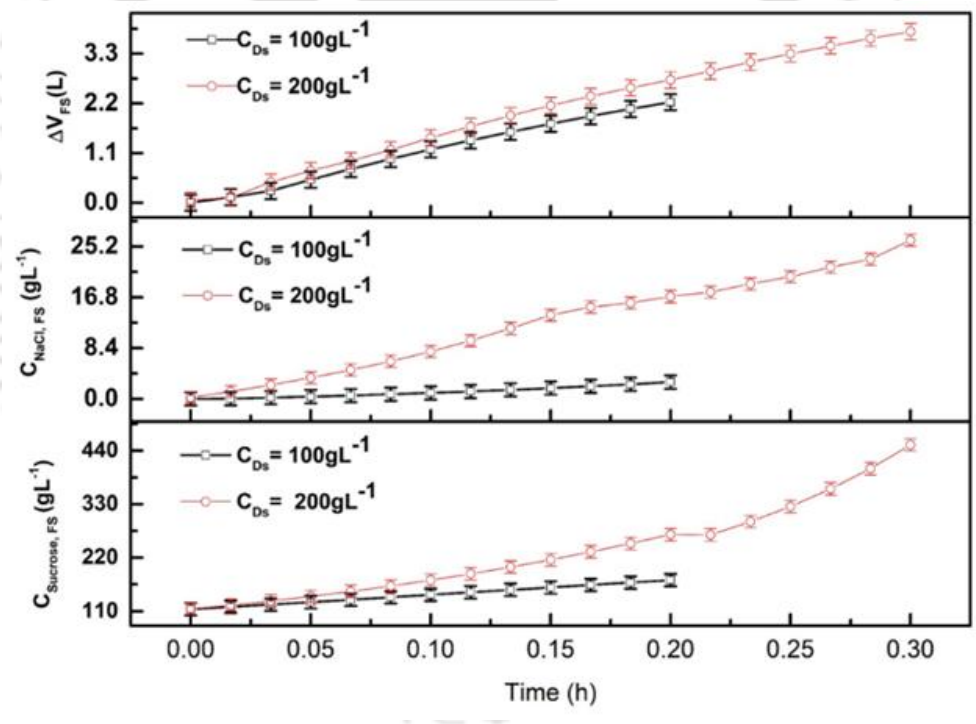


Fig. 4.8 Average water flux and SRSF vs DS flow rate for counter-current mode FO batch operation for sugarcane juice concentration at $Q_{DS,in}$= 25, 35 and 45 L h^{-1} and $Q_{FS,in}$= 25 L h^{-1}, $C_{DS,int}$= 100 g L^{-1}, $C_{Sucrose,int}$= 114.2 ± 0.9g L^{-1}

4.2.3. Effect of draw solution concentration

The DS concentration is another operating parameter that will affect the FO process performance. As shown in Fig. 4.9 and Table 4.2, both water flux and SRSF is affected by DS NaCl concentration. In the presence of high osmotic driving force, the batch experiments with 200 gL^{-1} DS was extended up to 0.3 h. The average water flux and SRSF were increasing nonlinearly with DS concentration, i.e., water flux increased by 155 %, and average SRSF increased by 1257% while increasing DS concentration by 200%. Even though high (3.9) FS concentration ratio was achieved with 200 g L^{-1} DS, due to high SRSF, the concentration of NaCl in FS was increased to 26.2 ± 0.8 g L^{-1} (at time = 0.3 h) and such high NaCl concentration in sugarcane juice is not suitable in the food industry.



4.9 Experimental results of sucrose concentration, NaCl concentration in feed tank, and processed volume for batch process with 100 gL^{-1} and 200 gL^{-1} DS concentration, $Q_{DS,in}$= 45 L h^{-1}, $Q_{FS,in}$= 25 L h^{-1}, $C_{Sucrose,int}$ = 114.2 ± 0.9 g L^{-1}

To achieve high water flux, aquaporin membrane is used for this study, however high RSF was observed while using high DS concentration. Further to achieve high recovery in FO, one has to use high concentration DS, therefore, these experimental results

conclude that the aquaporin membrane may not be suitable liquid food application that requires high recovery i.e. near to saturation concentration.The same can be concluded as "the aquaporin high flux HFFO membrane was observed to be unsuitable for food concentration application while using high concentration NaCl solution as DS".Further, membrane fouling experiments were performed with the DS concentration of 100 g L^{-1}.

Table 4.2 Experimental results of co-current and counter-current mode

Parameters	Unit	Co-current mode			Counter-current mode			
Batch time	h	0.2	0.2	0.2	0.2	0.2	0.2	0.3
Initial feed volume	L	6.1 ± 0.1	6.1 ± 0 .1	6.1 ± 0.1	6.1 ± 0.1	6.1 ± 0.1	6.1 ± 0.1	5.0 ± 0.1
Initial draw volume	L	6.4 ± 0.1	6.4 ± 0.1	6.4 ± 0.1	6.4 ± 0.1	6.4 ± 0.1	6.4 ± 0.1	5.3 ± 0.1
Initial sucrose concentration in FS	g L^{-1}	114.2 ± 0.9	114.2 ± 0.9	114.2 ± 0.9	114.2 ± 0.9	114.2 ± 0.9	114.2 ± 0.9	114.2 ± 0.9
Initial fructose concentration in FS	g L^{-1}	24.7 ± 0.4	24.0 ± 0.4	24.7 ± 0.4	24.0 ± 0.4	24.7 ± 0.4	24.0 ± 0.4	32.0 ± 0.6
Initial Glucose concentration in FS	g L^{-1}	29.0 ± 0.5	29.8 ± 0.5	29.8 ± 0.5	29.9 ± 0.5	29.9 ± 0.5	29.9 ± 0.5	32.8 ± 0.6
DS Flowrate	L h^{-1}	25	35	45	25	35	45	45
Initial NaCl concentration in DS	g L^{-1}	100 ± 0.08	100 ± 0.08	100 ± 0.08	100 ± 0.08	100 ± 0.08	100 ± 0.08	200 ± 0.06
Final sucrose concentration in FS	g L^{-1}	149.6 ± 0.9	163.1 ± 0.9	170.3 ± 0.9	154.4 ± 0.9	170.0 ± 0.9	173.8 ± 0.9	451.9 ± 3.1
Final fructose concentration in FS	g L^{-1}	32.7 ± 0.4	35.1 ± 0.4	37.6 ± 0.4	34.4 ± 0.4	36.8 ± 0.4	39.6 ± 0.4	126.7 ± 0.4
Final Glucose concentration in FS	g L^{-1}	39.6 ± 0.5	42.7 ± 0.5	46.0 ± 0.5	41.4 ± 0.5	44.5 ± 0.5	49.5 ± 0.5	130.0 ± 1.0
Final FS volume	L	4.5 ± 0.1	4.0 ± 0.1	4.0 ± 0.1	4.3 ± 0.15	4.0 ± 0.15	3.6 ± 0.15	1.2 ± 0.08
Final DS volume	L	7.9 ± 0.1	8.4 ± 0.1	8.4 ± 0.1	8.0 ± 0.1	8.4 ± 0.1	8.8 ± 0.1	9.0 ± 0.1
Final DS concentration	g L^{-1}	79.9 ± 1.6	75.9 ± 1.6	75.0 ± 1.6	78.6 ± 1.6	75.2 ± 1.6	72.5 ± 1.6	120.7 ± 1.6
Final NaCl concentration in feed	g L^{-1}	0.3 ± 0.2	0.5 ± 0.2	0.5 ± 0.2	0.3 ± 0.2	0.4 ± 0.2	0.4 ± 0.2	26.2 ± 0.8
Average water flux ($J_{w,avg}$)	Lh^{-1} m^{-2}	3.4 ± 0.06	4.3 ± 0.06	4.5 ± 0.06	3.7 ± 0.08	4.5 ± 0.08	5.2 ± 0.08	8.1 ± 0.09
Average SRSF	g L^{-1}	1.1 ± 0.05	1.1 ± 0.05	1.1 ± 0.05	0.9 ± 0.05	0.8 ± 0.05	0.6 ± 0.05	8.5 ± 0.03
FS concentration ratio ($V_{F,int}/V_{F,final}$)	-	1.3 ± 0.02	1.4 ± 0.02	1.5 ± 0.02	1.3 ± 0.02	1.5 ± 0.03	1.6 ± 0.03	3.9 ± 0.03

4.2.4. Effect of fouling

Two new aquaporin HFFO modules were used to perform the fouling study with UF clarified and unclarified sugarcane juice. Before fouling study, the pure water permeability of the new membrane was measured by performing RO experiment with DI water at 25 °C. Before performing pure water permeability experiment, the membrane module was stabilized by circulating DI water without Trans Membrane Pressure (TMP). The first set of fouling experiments with UF clarified sugarcane juice was performed in continuous mode. The method of sugarcane juice clarification with ceramic UF membrane and its characteristics are reported in authors previous work [108]. In continuous FO operation, both DS and pre-treated sugarcane juice were pumped continuously through the HFFO membrane module at 45 and 25 L h^{-1} respectively. The DS and FS pressure were maintained at 13.8 and 55.1 kPa respectively. The continuous FO operation was stopped for membrane regeneration when water flux reduced below 80% of initial water flux (at time =0) and this period operation is called one cycle of FO operation. After regeneration of the HFFO membrane module, the next cycle of the experiment was continued with fresh pre-treated sugarcane juice. Total three cycles of FO operation were conducted with UF clarified sugarcane juice, and its performance is shown in Fig.4.10. At steady-state the FO operation with single HFFO membrane module was able to concentrate the sucrose level from 114.2 ± 0.9 g L^{-1} to 173.8 ± 0.9 g L^{-1} with water flux of 6.5 ± 0.3 L h^{-1} m^{-2}. During the first cycle, the constant flux (6.5 ± 0.3 L h^{-1} m^{-2}) was observed until 9 h, after that flux started declining and reduced to 80% of the initial flux in 16 h of operation. Similar membrane fouling behaviour was observed for the remaining two cycles.

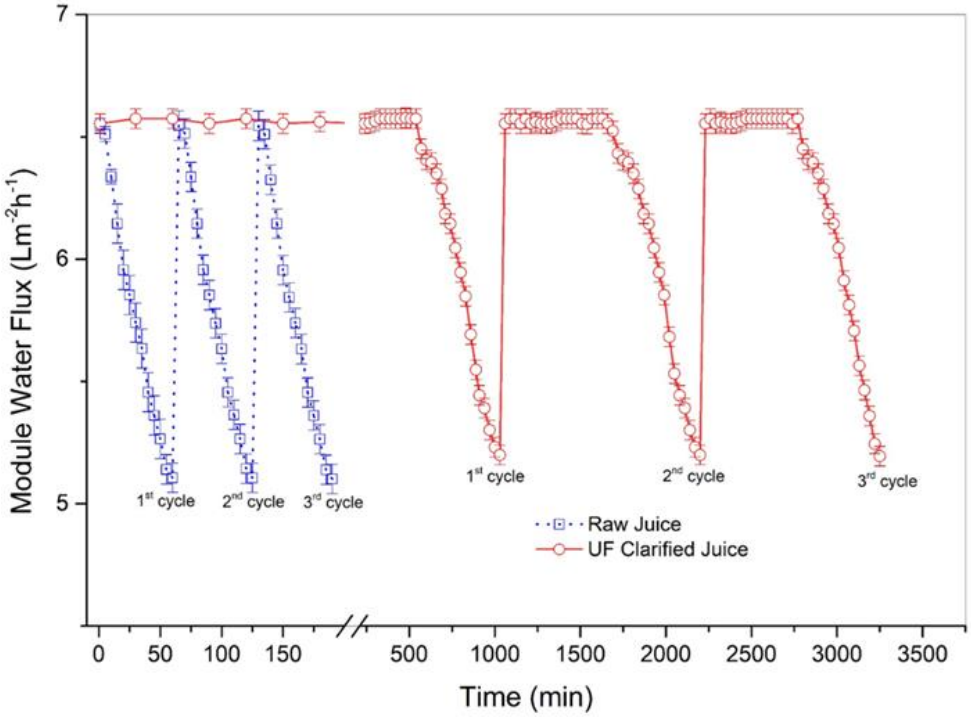


Fig. 4.10 Time-dependent flux decline study of UF clarified and unclarified sugarcane juice at $Q_{DS,in}$ = 45 L h^{-1}, $Q_{FS,in}$ = 25 L h^{-1}, C_{DS},in = 100 g L^{-1}

Further, to study the impact of UF pre-treatment on FO membrane fouling, the next level of FO continuous operation was conducted by using raw sugarcane without UF pre-treatment wherein similar FO operating conditions were maintained. The initial water flux was found be same for both the cases, but the unclarified juice resulted in quick membrane fouling. The water flux was reduced to 80% of the initial flux in 60 min. This may be due to the fouling of the membrane by large colloidal particles made of polyphenol oxidase enzyme, polysaccharides, protein, aliphatic, phenols fraction in sugarcane juice. The ceramic UF membrane removed these larger colloidal particles [108]; therefore, less FO membrane fouling was observed while concentrating UF treated sugarcane juice. The FO has advantage over RO and thermal-based separations in terms of operating pressure and temperature [8], it consumes less energy with effective regeneration of DS[9–11], low RSF, high product recovery and less fouling [3].

4.2.5. Membrane Regeneration

After each FO operation cycle, the HFFO module was regenerated by three step regeneration process described in section4.1.7. As shown in Fig. 4.11a, the membrane fouled by UF treated juice was able to regenerate 100% by simple DI water wash. But in the case of membrane fouled by raw sugarcane juice, all three regeneration techniques were applied, and finally, NaOH wash was able to bring back the membrane to its original water permeability (Fig. 4.9b). Both DI water wash and osmotic backwash were ineffective when membrane was fouled with organic colloidal particles as listed above.

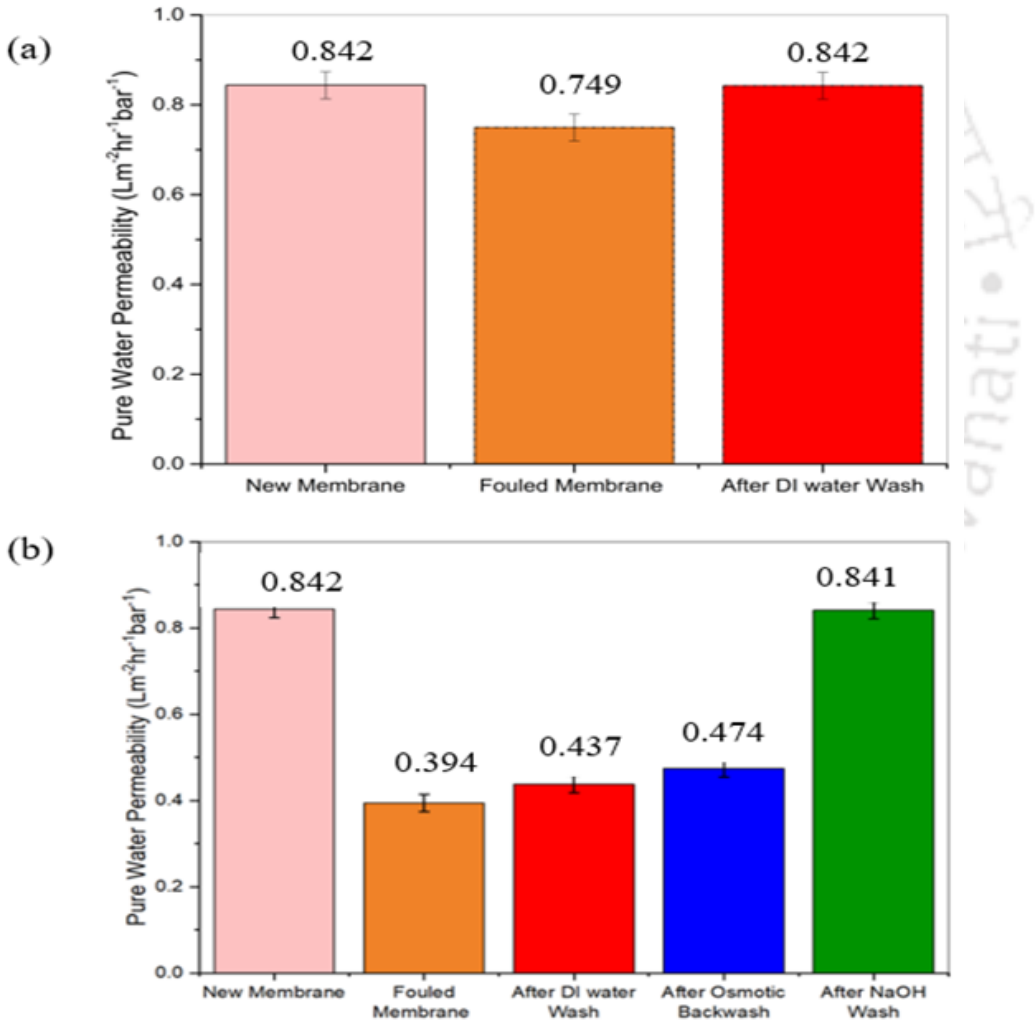


Fig. 4.11 Water permeability of the HFFO membrane with respect to membrane cleaning protocol (a) UF clarified sugarcane juice and (b) unclarified sugarcane juice

However, the NaOH solution could react with the organic molecules and detach them from the membrane surface for effective membrane cleaning. The pure water permeability of membrane fouled by unclarified juice reduced 53.3% (0.84 to 0.39 L h^{-1} m^{-2}) but in the case of UF clarified juice fouled membrane, 11.2% reduction was observed. In the case of UF clarified juice fouled membrane, DI water backwash improved 11% of permeability. In another case, 9.8%, 8.2% and 82% improvement in permeability were observed for DI wash, osmotic backwash and NaOH wash, respectively.

4.3. Summary

This study reports on the viability of implementing the FO process for the concentration of sugarcane juice by using Aquaporin commercial HFFO module are presented. Several important results can be drawn from this study. It was observed that in batch FO process, the recovery of FS can be improved by increasing DS flow rate at a fixed FS flow rate. 7% high water flux was observed in counter-current flow configuration than co-current flow configuration. By applying optimal DS flow rate and flow configuration, the aquaporin HFFO module was able to concentrate UF pre-treated sugarcane solution up to 60% of initial concentration in 12 min of batch FO operation with the initial DS concentration 100 g L^{-1}. This is very close to the concentration achieved by multiple-effect evaporators in industrial operations before the feed enters the final evaporator where crystallization is done[17]. It was observed that the aquaporin HFFO membrane was highly resistive to sugar molecules such that forward flux is zero. However, for higher DS concentration, the NaCl RSF is found to be abnormal and that limits the applicability of FO for liquid food application. The study also confirmed that the DS can be regenerated by using other processes (such as Membrane Distillation, thermal evaporation etc.). In another approach, if an innovative DS can have used, that can be regenerated with minimal energy input and zero RSF,such FO process can become an economically viable alternate process. From the fouling study, it was observed that the FO membrane fouling rate was less while concentrating UF pre-treated sugarcane juice. For example, the pure water

permeability of membrane fouled by unclarified juice was reduced by 53.3% and that for UF clarified juice 11.2%. The fouled membrane was regenerated with only DI water wash for 30 min for UF clarified juice. However, in case of untreated juice concentration, the fouled FO membrane was not able to regenerate with DI water wash and osmotic backwash, and it required 0.1 M NaOH wash. From this study, it can be concluded that aquaporin HFFO membrane can be applied at industrial level and can provide an alternate solution to the evaporation and pressure driven membrane separation processes where the sugarcane juice has to be concentrated near to its saturation concentration without losing its nutritional value for further crystallization. The novel features of the FO process such as ambient temperature and pressure are appealing characteristics for commercial applications.

Chapter 5:

Modelling, validation and process simulation of forward osmosis membrane for the concentration of sugarcane juice

In this chapter an aquaporin hollow fibre forward osmosis membrane is used in the experiments. This chapter targets the modelling, validation and process simulation of forward osmosis membrane for the concentration of sugarcane juice. It discusses the mathematical model which is developed based on the tank mass balance and concentration polarization. By minimizing the error between experimental and model data, the new model is developed using Dymola software. It also discusses the process flowsheet simulation which is performed for various flow condition for optimal process design in terms of sugarcane juice condition, energy consumption, reverse solute flux and processed volume and the flow sheets are also developed by using the same software.

5.1. Theory

In the osmosis process, natural diffusion of water occurs through semipermeable barrier due to concentration or osmotic pressure difference which act as the driving force. According to the 2nd law of thermodynamics, if chemical potential exists then energy or mass is exchanged between the systems until equilibrium is achieved. The FO process also follows the 2nd law of thermodynamics. In this process, water molecule moves from high concentration region to lower concentration regions though the semipermeable membrane until chemical potential equilibrium has reached [109,110]. In the FO process osmotic pressure difference ($\Delta\pi$) act as the driven force for the net water flux. Using the film theory, water flux (J_w) can be determined. Fig. 5.1 describes the concept of internal concentration polarisation(ICP) and ECP in FO membrane while the DS is facing the active layer (AL) and FS is facing support layer, where,δ_D and δ_F are the CP layer thickness [13]. The concentrative ECP occurs at FS side, concentrative ICP occurred at the support layer of the membrane and similarly, dilutive ECP is happening at DS side. The concentration profile of draw and feed solute across the membrane and CP layer due to RSF and forward flux is shown in Fig. 5.1. The draw and feed solute concentration are presented in Fig. 5.1 as per CECP, CICP and DECP in concentration polarization layer and membrane support layer. This chapter has focus on the development of one dimensional model under unsteady state conditions for hollow fibre forward osmosis (HFFO) process by integrating three models viz solution diffusion (SD) model for membrane active layer transport, film

theory model for mass transport in ICP and ECP layer and unsteady mass balance equation across feed and DS tank.

5.1.1 Solution diffusion model

The solute and solvent passage through the membrane is explained by using the solution diffusion model where the solvent flux is defining as water permeability co-efficient (L_p) and solute flux is defined as solute permeability co-efficient (B). The diving force to transport the water from feed tank to draw tank is pressure difference across the selective layer of the membrane. The performance of the FO membrane is evaluated by water flux (J_w) and draw solute flux (J_s). The osmotic pressure between FS and DS is to act as a driving force for water movement which is considered as water flux [80,111]. The equation of water flux is defined as:

$$J_w = L_p(\pi_d - \pi_f - \Delta P) \tag{5.1}$$

where, L_p, π_d, π_f and ΔP are water permeability co-efficient, the osmotic pressure of DS, the osmotic pressure of FS and pressure difference respectively. The osmotic pressure equation developed by Van't Hoff [101] is widely used as:

$$\pi_d = \frac{iRTC_{DS,m}}{M_w} \tag{5.2}$$

$$\pi_f = \frac{iRTC_{FS,m}}{M_w} \tag{5.3}$$

where, $C_{DS,m}$, $C_{DS,b}$ and i are DS concentration at the membrane surface in g L^{-1}, the concentration of FS at the membrane surface (g L^{-1}), ionization number of the solution orVan't Hoff equations parameter. All the values of *i*used in Van't Hoff equation and molecular weight of NaCl, sugar components are listed in Table 5.1

The governing equations for J_w, J_s by SD models, are

$$J_w = L_p\left[\frac{iRT}{M_w}\left(C_{DS,m} - C_{FS,m}\right) - \left(P_{DS} - P_{FS}\right)\right] \tag{5.4}$$

$$-J_s = B\left(C_{DS,m} - C_{FS,m}\right) \tag{5.5}$$

where, J_w, L_p, J_s, B, $C_{DS,m}$, $C_{FS,m}$, i, R, M_w and T are water flux in (L h^{-1} m^{-2}), water permeability co-efficient (L h^{-1} m^{-2} bar^{-1}), solute flux in (g m^{-2} h^{-1}), solute permeability co-efficient (L h^{-1} m^{-2}), concentration of DS at membrane surface in (g L^{-1}), concentration of FS at membrane surface (g L^{-1}), ionization number of the solution, universal gas constant in (L Pa K^{-1} mol^{-1}), molecular weight of DS in (g mol^{-1}) and temperature of solution in (*K*) , $P_{DS}$and P_{FS} are the hydraulic pressure in (*Pa*) for DS and FS respectively. Due to the concentration gradient solute transport through the membrane. As expressed in equation 5.5, the direction of reverse solute flux is opposite to that of water flux.

Table 5.1 Value of Van't Hoff equation parameter and molecular weight

Component name	Van't Hoff parameter	Molecular weight
NaCl	2	58.44
Sucrose	1	342.2965
Glucose	1	180.156
Fructose	1	180.16

5.1.2 Concentration polarization model with solution diffusion model

The CP occurs due to concentration gradient developed at the membrane/solution interface. This is an inherent phenomenon of all types of the membrane and it is a performance limiting factor for the FO process [94,98]. Here, the deposition of solute particles occurs at the membrane surface, within the pores of the membrane. Due to the CP osmotic pressure gradient increased which decreases the net driving pressure gradient [101]. This decrease in net driving force, the experimental flux is found to be lower than the theoretical flux of any FO processes. As a result of low CP, there will be less cleaning, membrane life longevity higher and it will also provide higher operational time along with a low capital cost. In the FO process, two types of ECP occurs viz concentrative external concentration polarisation (CECP) and dilutive

external concentration polarisation (DECP). The CECP occurs due to FS concentration on the membrane surface in the feed side and DECP occurs in the draw side due to DS dilution. The membrane fouling canoccur due to accumulation or adsorption of organic, inorganic and other insoluble particulate matters. The membrane surface orientation during the FO process where the DS facing the active layer (AL) and FS facing support layer is shown in Fig. 5.1. The DECP has occurred on DS side, CICP occurred at the support layer of the membrane and on the FS side CECP occurred. ECP and ICP have great influence on net water flux. The DECP will affect the osmotic pressure of DS, the concentrative ECP will affect the osmotic pressure of FS and the concentrative ICP will affect the osmotic pressure of FS for Active layer facing DS (AL-DS) orientation. The positive exponent on feed side signifies the concentrative ECP and ICP $\left(C_{FS,m} > C_{FS,b}\right)$, and the negative exponent on the DS side signifies the dilutive ECP $\left(C_{DS,m} < C_{DS,b}\right)$ at the membrane surface. The flux decline might be also due to foulant existing in FS.

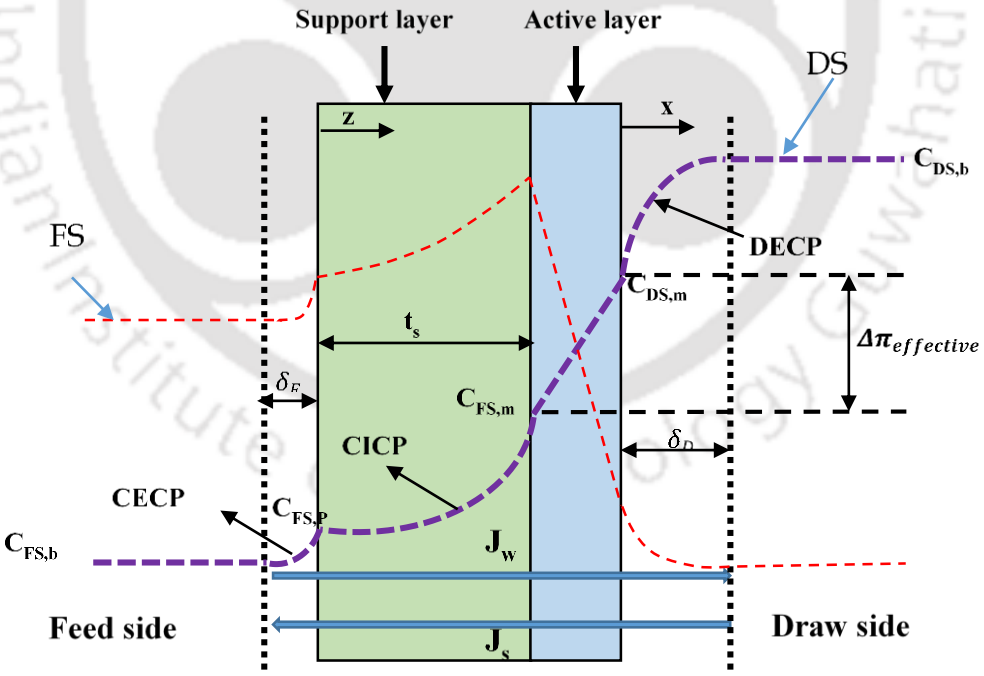


Fig. 5.1 Concentration polarization and driving force analysis for FO mode in AL-DS

5.1.2.1 External concentration polarization (ECP)

Mostly, a FO membrane is made up of thin active layer and a porous support layer. During FO membrane process, two types of membrane orientation can be used viz active layer facing FS (AL-FS) and another one is active layer facing DS (AL-DS). Because of CP, net driving force decreases at AL and SL. The DS gets diluted and FS gets concentrated in the FO process due to the ECP phenomenon.

The DECP model equation is defined according to the film theory i.e., salt flux (J_s) across the ECP can be expressed as a combination of convective and diffusive terms [111,112]:

$$J_S = -J_W C(x) + D\frac{dC(x)}{dx} \tag{5.6}$$

Boundary conditions,

$C(x) = C_{DS,m}$ at x = 0,

$C(x) = C_{DS,b}$ at x = δ_D, yields

$$C_{DS,m} = C_{DS,b}e^{-\frac{J_w}{k_d 1000}} + \frac{J_s}{J_w}\left(e^{-\frac{J_w}{k_d 1000}} - 1\right) \tag{5.7}$$

Where, $C_{DS,m}$, $C_{DS,b}$ and k_d are the concentration of draw on the membrane surface, the concentration of draw in the bulk, mass transfer co-efficient on the draw side respectively. Here the CECP effect is neglected. The CECP model equation derived from equation 5.6 using boundary equations is,

Boundary conditions,

$C(x) = C_{FS,b}$ at x = 0,

$C(x) = C_{FS,m}$ at x = δ_F, yields

$$C_{FS,m} = C_{FS,b}e^{\frac{J_w}{1000}\left(\frac{1}{k_f}+\frac{S}{D}\right)} + \frac{J_s}{J_w}\left(e^{\frac{J_w}{1000}\left(\frac{1}{k_f}+\frac{S}{D}\right)} - 1\right) \tag{5.8}$$

where, $k_f = \frac{\delta_f}{D_f}$, $C_{FS,m}$, $C_{FS,b}$ and k_f are feed side concentration of draw on the membrane surface, draw concentration of draw in bulk of feed, mass transfer co-efficient on feed side respectively.

5.1.2.2 Internal concentration polarization (ICP)

In AL-FS orientation system, during FO process, the concentration of FS is increased in the porous support layer as a result of transportation of water through a membrane from the FS tank to the DS tank. Again for the DS-AL orientation, for FO process, DS concentration is gradually decreased due to water flux movement from FS tank to DS tank [97]. Tang et al. have studied the ICP effect during filtration of humic acid and concluded that ICP effect is more for AL-FS orientation in comparison to AL-DS orientation. AL-FS orientation provides steady flux against AL-DS orientation [113]. The reasons for the severe flux decline for AL-DS orientation is due to high ICP in support layer as well as deposition of feed particles on the support layer. As shown in Fig. 5.1, water diffuses from the FS side to the DS side as a result of the osmotic pressure gradient [13]. Some solute particles accumulated on the FS side within the porous support of the membrane. DS solute also diffuses through active and porous layer to the FS side during the FO process due to the concentration gradient. Considering concentration polarization, the water flux can be calculated by convection-diffusion equation, using the following equations (5.3), (5.6), (5.7)

$$J_w = L_p\left[\frac{iRT}{M_w}\left(C_{DS,b}e^{-\frac{J_w}{k_d 1000}} + \frac{J_s}{J_w}\left(e^{-\frac{J_w}{k_d 1000}} - 1\right) - \left(C_{FS,b}e^{\frac{J_w}{1000}\left(\frac{1}{k_f}+\frac{S}{D}\right)} + \frac{J_s}{J_w}\left(e^{\frac{J_w}{1000}\left(\frac{1}{k_f}+\frac{S}{D}\right)} - 1\right)\right)\right) - \left(P_{DS} - P_{FS}\right)\right] \quad (5.9)$$

Usually the water flux and reverse solute flux can be expressed in terms of structural parameter (S), solute permeability co-efficient (B) and water permeability co-efficient as shown in equation (5.4) and equation (5.5). The mass transfer co-efficients k_d and k_f can be obtained from the correlation in which Sherwood number(Sh) is a function of two other dimensionless numbers, Reynolds number (Re) and Schmidt number (Sc) [94,97,101].

$$Sh_d = \alpha_d \, \mathrm{Re}_d^{\beta_d} \, Sc^{0.33} \tag{5.10}$$

$$Sh_f = \alpha_f \, \mathrm{Re}_f^{\beta_f} \, Sc^{0.33} \tag{5.11}$$

$$k_d = \frac{D_{diff} Sh_d}{d_{o,fiber}} \tag{5.12}$$

$$k_f = \frac{D_{diff} Sh_f}{d_{i,fiber}} \tag{5.13}$$

Here, Shrefers to the Sherwood number. D_{diff}, $d_{i,fiber}$ and $d_{o,fiber}$ are the diffusion co-efficient, inner diameter of fibre and outer diameter of fibre respectively. In this study, α_d, β_d, α_f, β_f are the tuning parameters which are determined during the validation. From the literature, the value of the term β_d and β_f are 0.7845 and Υ = 0.33 [114]. The Schmidt number(Sc) [101] for FS and DS can be expressed as:

$$Sc_f = \frac{\mu_f}{\rho_f D_f} \tag{5.14}$$

$$Sc_d = \frac{\mu_d}{\rho_d D_d} \tag{5.15}$$

Where, μ, ρ and D are the dynamic viscosity, density and diffusion co-efficient. The subscript d and f represent DS and FS.

5.1.2.3 FOHF model equations

To predict the concentration variation, reverse solute flux, forward flux mass balance equations are used. Here, the DS solution is passing through the tube side and FS is passing through the shell side of the membrane module. The output of the draw and feed tank is input for the membrane module. The flow configuration of HFFO membrane is shown in Fig. 5.2. The total volumetric flow rate equations for draw and feed side are,

$$Q_{d,in} - Q_{d,out} = -J_w A_m \tag{5.16}$$

$$Q_{f,in} - Q_{f,out} = J_w A_m \quad (5.17)$$

where, Q_d and Q_f are a draw and feed volumetric flow rates respectively, A_m is the area of the membrane and J_w is the water flux through the membrane.

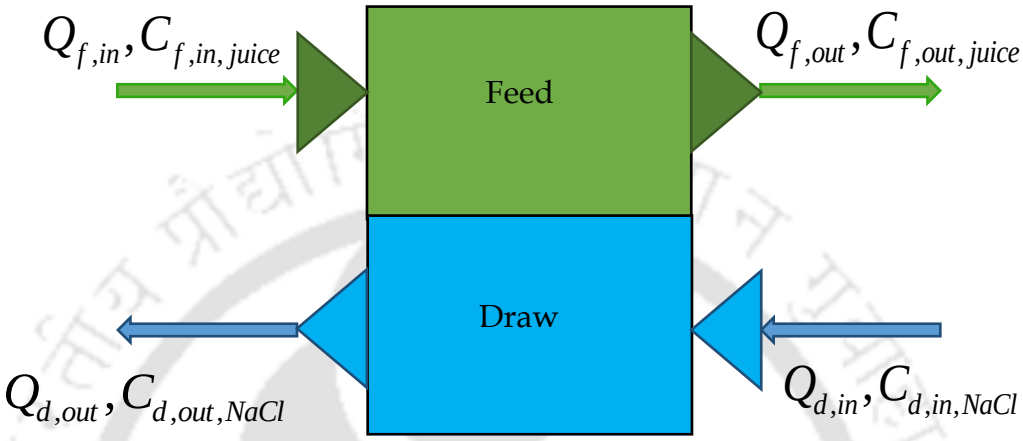


Fig. 5.2 Mass and component balance on membrane module

The species mass balance across the draw side is given as,

$$Q_{d,in} C_{d,in,NaCl} - Q_{d,out} C_{d,out,NaCl} = -J_{s,NaCl} A_m \quad (5.18)$$

Where, C_d A_m and $J_{s,NaCl}$ are draw concentration, active membrane area across feed and draw channel and reverse solute flux respectively.

Similarly, the mass balance across the feed side can be represented as:

$$Q_{f,in} C_{f,in,NaCl} - Q_{f,out} C_{f,out,NaCl} = -J_{s,NaCl} A_m \quad (5.19)$$

$$Q_{f,in} C_{f,in,Sucrose} - Q_{f,out} C_{f,out,Sucrose} = J_{s,Sucrose} A_m \quad (5.20)$$

$$Q_{f,in} C_{f,in,Glucose} - Q_{f,out} C_{f,out,Glucose} = J_{s,Glucose} A_m \quad (5.21)$$

$$Q_{f,in} C_{f,in,Fructose} - Q_{f,out} C_{f,out,Fructose} = J_{s,Fructose} A_m \quad (5.22)$$

5.1.2.4 Tank model equations

In the FO process, the mass along with solute concentration of both FS and DS varies with time. Here, unsteady sate mass balance equations are used for the change in volume and concentration in the feed and draw tank (Fig. 5.3)

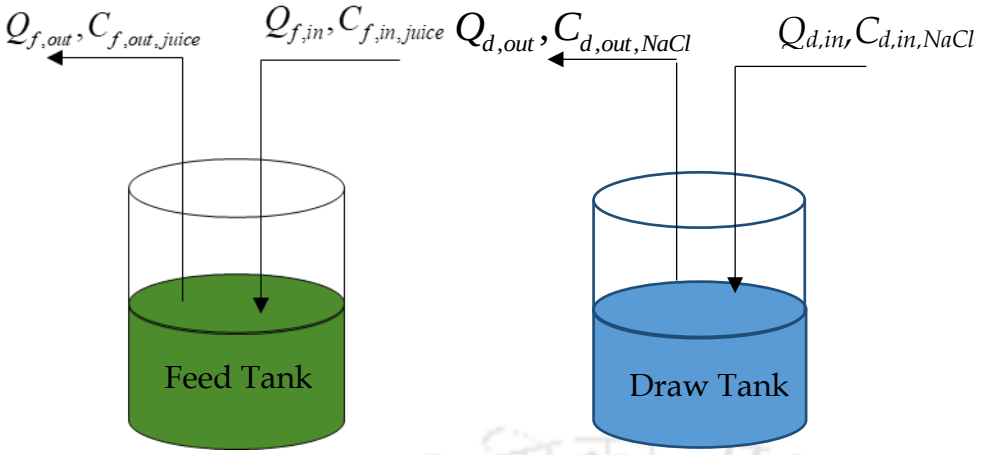


Fig. 5.3 (a) feed tank, (b) draw tank

$$\frac{dV_{FS}}{dt} = Q_{f,in} - Q_{f,out} \tag{5.23}$$

$$\frac{dV_{FS}C_{f,out_{NaCl}}}{dt} = Q_{f,in}C_{f,in_{NaCl}} - Q_{f,out}C_{f,out_{NaCl}} \tag{5.24}$$

$$\frac{dV_{FS}C_{f,out_{Sucrose}}}{dt} = Q_{f,in}C_{f,out_{Sucrose}} - Q_{f,out}C_{f,out_{Sucrose}} \tag{5.25}$$

$$\frac{dV_{FS}C_{f,out_{Glucose}}}{dt} = Q_{f,in}C_{f,out_{Glucose}} - Q_{f,out}C_{f,out_{Glucose}} \tag{5.26}$$

$$\frac{dV_{FS}C_{f,out_{Fructose}}}{dt} = Q_{f,in}C_{f,out_{Fructose}} - Q_{f,out}C_{f,out_{Fructose}} \tag{5.27}$$

Similarly, the mass balance for draw tank can be represented by the following equations:

$$\frac{dV_{DS}}{dt} = Q_{d,in} - Q_{d,out} \tag{5.28}$$

$$\frac{dV_{DS}C_{d,out_{Nacl}}}{dt} = Q_{d,in}C_{d,in_{Nacl}} - Q_{d,out}C_{d,out_{Nacl}} \tag{5.29}$$

Where, V_{DS} and V_{FS} are volumes of DS and FS tank in (L) respectively, $Q_{d,in}$ and $Q_{d,out}$ are inflow and outflow of DS in the module and similarly, $Q_{f,in}$ and $Q_{f,out}$ are inflow and outflow of FS in the module in (L h^{-1}) respectively.

5.1.2.5 Pressure drop equations

Following equation is used to estimate shell side pressure drop for both laminar and turbulent flow [114]

$$\frac{dP_{shell}}{dz} = F_{vis.}u_{shell} + F_{inertial}u^{1.75}{}_{shell} \tag{5.30}$$

Where, $F_{vis.}$, $F_{inertial}$ and u_{shell} are the viscous drag, inertial drag constant and shell side flow velocity in (mh^{-1}) respectively. From literature, it was found that for packing density of 42.5% values of $F_{vis.}$ and $F_{inertial}$ are 0.2 and 1.72. In the above equation, $F_{vis.}u_{shell}$ represents laminar component of pressure drop and $F_{inertial}u^{1.75}{}_{shell}$ is the local turbulent loss.

The Hagen-Poiseuille equation is used to describe the pressure drop in the lumen side (tube side) [115].

$$\frac{dP_{tube}}{dz} = -\left(\frac{32\mu_d u_{tube}}{d^2_{i,fibre}}\right) \tag{5.31}$$

Where, $d^2_{i,fibre}$ is the inner diameter of the HFFO module μ_d and u_{tube} are the viscosity of DS and flow velocity ($m\ h^{-1}$) in tube and z is the axial direction coordinate in (m).

5.1.2.6 Power Consumption

In this study, the power consumption is analysed. Here, the power consumed during the FO process is calculated by equation (5.32) and (5.33).

$$E = P_{DS,inlet}Q_{DS,inlet} + P_{FS,inlet}Q_{FS,inlet} \tag{5.32}$$

$$E = \frac{dPw_{inp}}{dt} \tag{5.33}$$

where, E is the energy consumption $P_{DS,inlet}$, $P_{FS,inlet}$ are the input pressure of DS and FS. $Q_{DS,inlet}$, $Q_{FS,inlet}$ are the input flowrates and Pw_{inp} is the power consumed by the pump.

5.1.3 Method for solving the model equation

In this study, it was found that the model equations are highly nonlinear when ICP and ECP both were taken into consideration. These model equations were solved iteratively and numerically [98]. Here, a one dimensional mathematical model for aquaporin HFFO module was developed by connecting '*n*' number of continuous stirred tank (CST) unit in series which is equivalent to plug flow reactor (PFR). Again, by integrating equation 5.23 to 5.29, a model is developed for a dynamic lumped system for draw and feed tank. Finally, a complete model is developed by integrating all the three models viz FS tank model, the DS tank model and HFFO model for the flowsheet simulation. The model equations are solved by using Dymola software and flowsheets are also developed by using this software. In Fig. 5.4, CST's arrangement in co-current mode for 12 CST is shown.

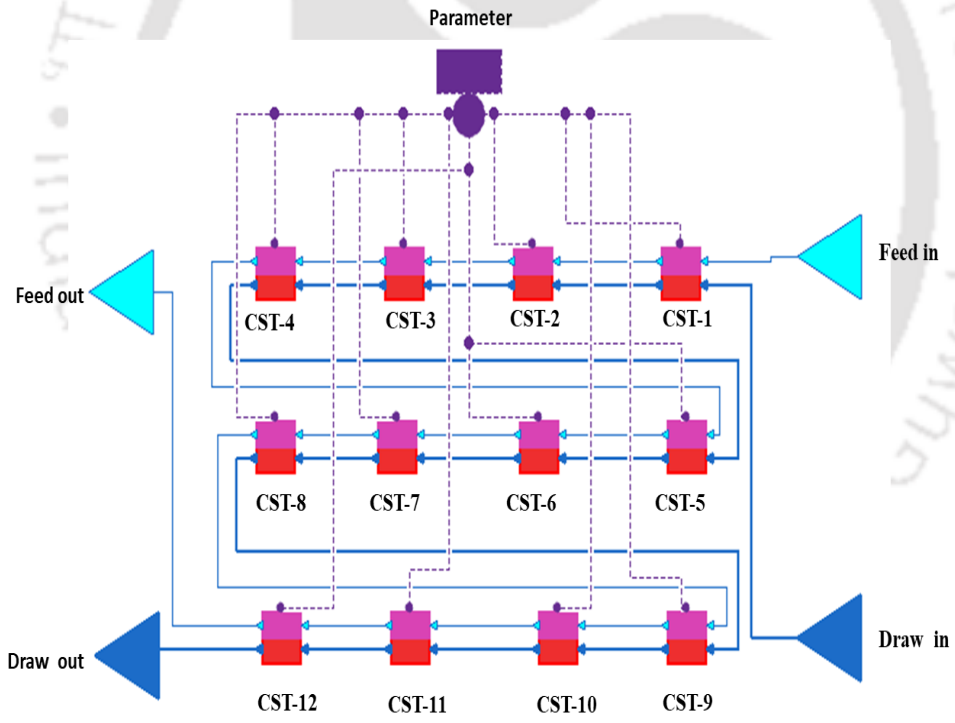


Fig. 5.4 CST's arranged in co-current mode

Using the Dymola design library by minimization of error between experimental and model data, a new model was proposed. The objective functions like the change of concentration of FS and DS tank and the change in volume of feed tank and draw tank are used to estimate the model parameters. One of the critical parameters to minimize

the computational time is the total number of CST in a HFFO module. Here, to optimise the number of CST in the HFFO module, a simulation is done by increasing the number of CST in the HFFO module. Here from 1-18 CST units are simulated one by one and it is found that 12 CST unit is the optimal number of CST unit in a HFFO module for both co-current and counter-current mode of FO process. Again, it is seen that with the increase in DS flow rate, mass transfer co-efficient also increases. In this simulation study, the effect of mass transfer co-efficient is also considered. In Fig. 5.5 Grid independency test (the optimal CST unit for co-counter current) is shown.

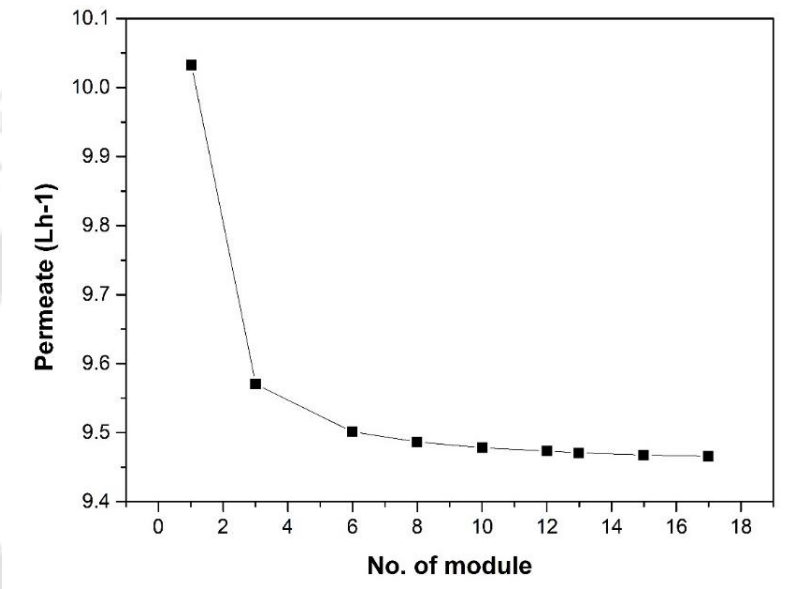


Fig. 5.5 Grid independency test (the optimal CST unit analysis for co-current and counter-current)

5.1.4 Method for membrane parameter estimation

The Dymola software® is used to solve the model equations and estimate the parameters by minimizing the error between the experimental results and model results. Here, for an ideal condition, it is considered that change in feed tank volume is equal to change in draw tank volume with time. In these conditions, the model parameters are approximated by minimizing the error between experimental results and model outputs. The error function for the parameter assessment is given below:

$$Error = \sum_{i=0}^{1} \left[\left(\frac{M_{d,\exp} - M_{d,model}}{M_{d,model}} \right)^2 + \left(\frac{M_{f,\exp} - M_{f,model}}{M_{f,model}} \right)^2 + \left(\frac{C_{d,NaCl,\exp} - C_{d,NaCl,model}}{C_{d,NaCl,model}} \right)^2 + \left(\frac{C_{f,NaCl,\exp} - C_{f,NaCl,model}}{C_{f,NaCl,model}} \right)^2 + \sum_{i=1}^{3} \left(\frac{C_{f,juice_i,\exp} - C_{f,juice_i,model}}{C_{f,juice_i,model}} \right)^2 \right] \quad (5.34)$$

For the estimation of the model parameters and to get an effective process design flowsheet is used as shown in Fig. 5.6.

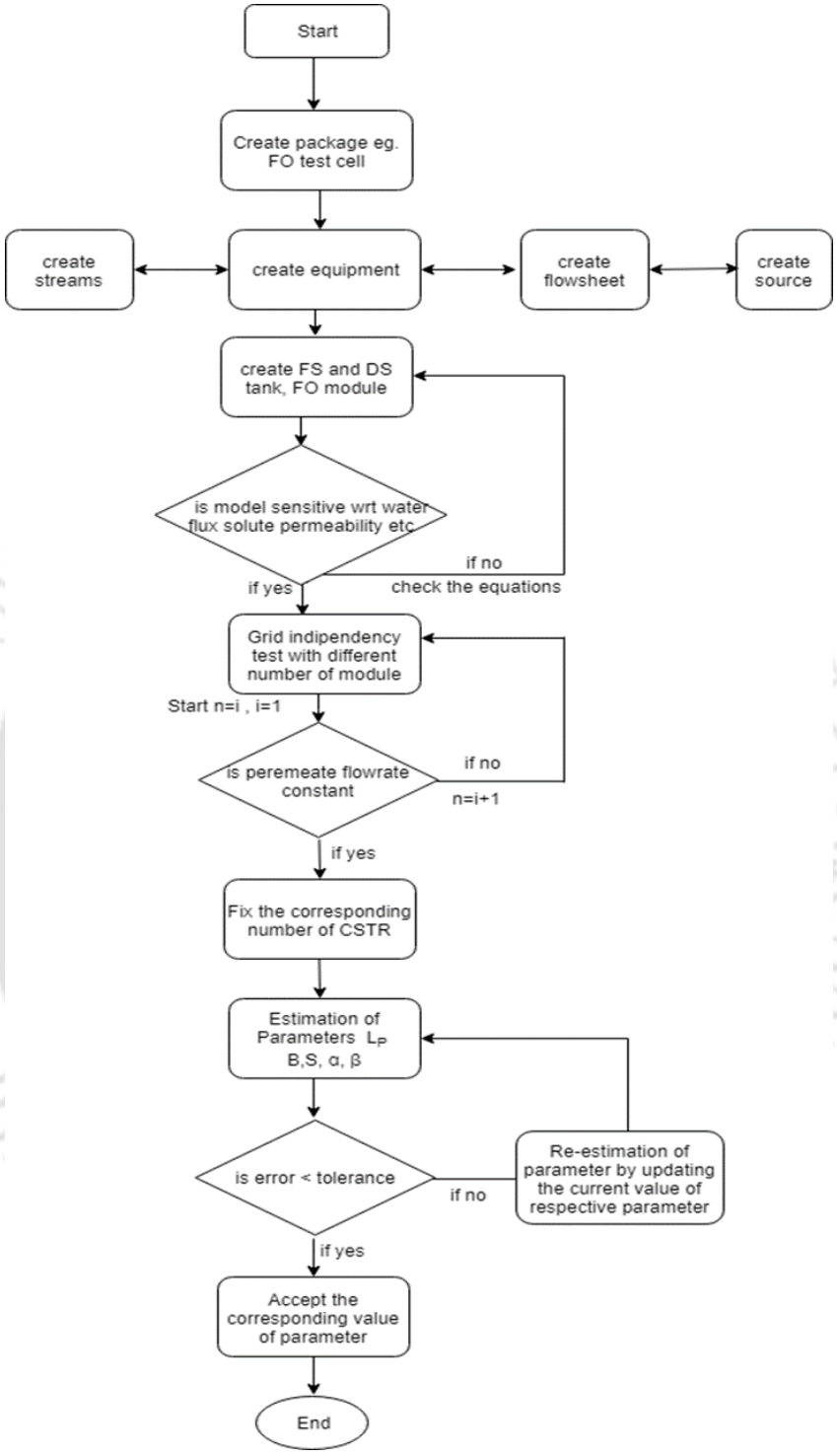


Fig. 5.6 Flowchart for solving the hollow fiber forward osmosis model

The bounds that are used in the model are 0.1 < L_p < 3, 0.01 < B < 2, 50 µm < S < 500 µm, 1e^{-3}< α_f < 2, 1e^{-3}< α_d < 2. In this study, Dymola design calibration is done by using quadratic programming technique for the error minimization. The solver used in this model is DASSL, which is designed for the numerical solution of an implicit system of differential/algebraic equations. The membrane transport parameters were estimated concerning changes in $Q_{DS,inlet}$, $Q_{FS,inlet}$, $P_{DS,inlet}$ and $P_{FS,inlet}$. The estimated water permeability using unsteady state FO data is 0.83 L h^{-1} m^{-2} bar^{-1} which is closer to that of the water permeability estimated from the RO mode (0.91 L h^{-1} m^{-2} bar^{-1}) as shown in Fig. 5.7.

$$J_w = L_p \Delta P \tag{5.35}$$

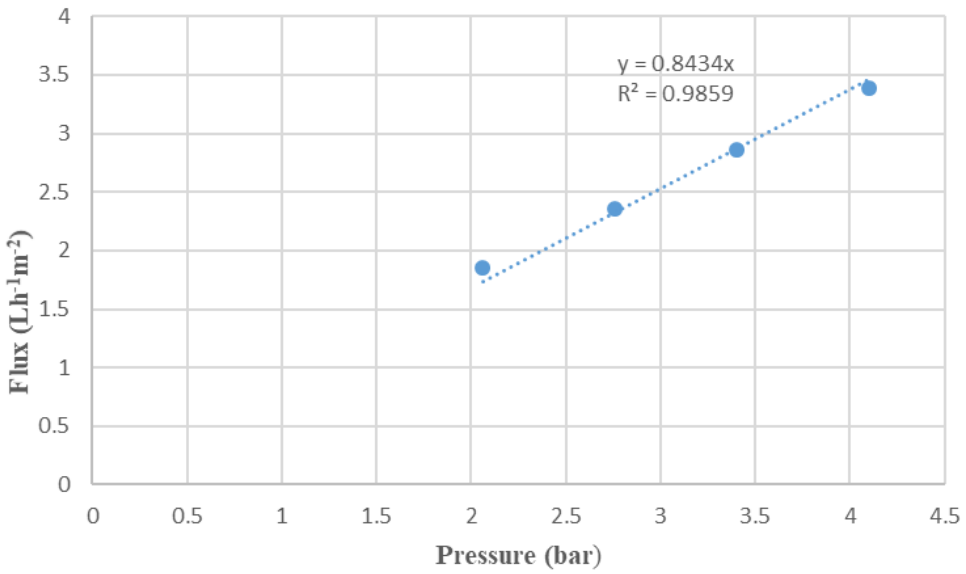


Fig. 5.7 Estimation of water permeability of membrane by RO mode

5.2 Process flow sheet simulation

A simulation study of the different flowsheet was done to estimate the optimal process design in terms of juice concentration, energy consumption, reverse solute flux and processed volume. In the experimental result, it was observed that at FS flow rate of 25 L h^{-1} and DS flowrate 45 L h^{-1} for counter-current mode showed more efficient results than the other DS flow rates (25, 35 L h^{-1}). By considering this, all flowsheets simulations are done at DS flow rate 45 L h^{-1} and feed flow rate 25 L h^{-1}. Here, three cases are evaluated for simulation.

5.2.1 Case 1:Feed and draw solution in recycle mode

Case 1, in Fig. 5.8 presents the schematic module of two FO modules connected in series such that both feed and draw stream in recalculation mode. The feed and draw flow rates were maintained at 25 L h^{-1} and 45 L h^{-1} respectively.

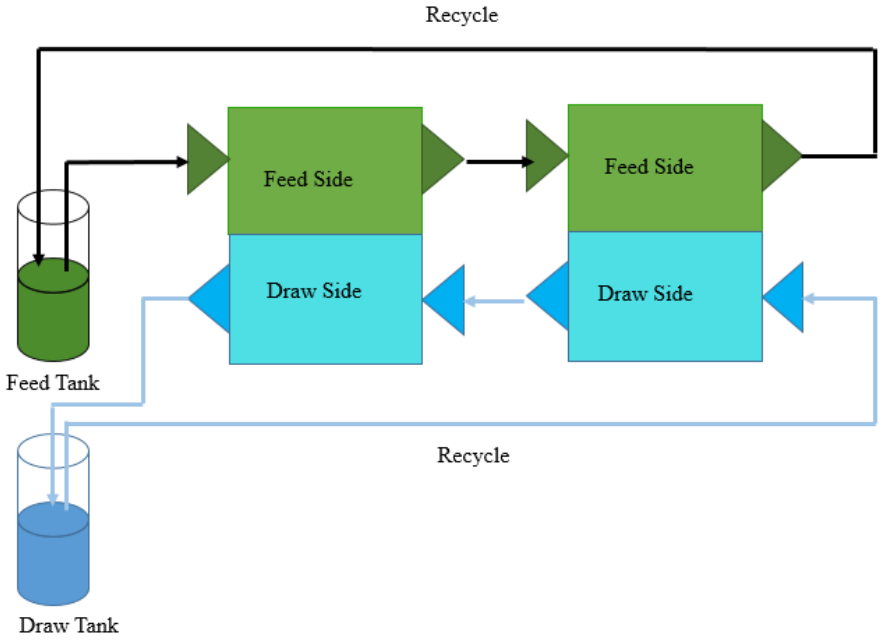


Fig. 5.8 Process flowsheet for feed and draw recycle

5.2.2 Case 2: Feed solution in recycle mode and draw solution in continuous mode

Another, case study was done where feed stream is recycled back and DS is in continuous mode. Here, for the case 2a single membrane module system is used and for case 2b double-membrane module configuration is used which has been shown in Fig. 5.9 and Fig. 5.10 respectively. This type of configuration has the disadvantage of low production rate with higher energy consumption.

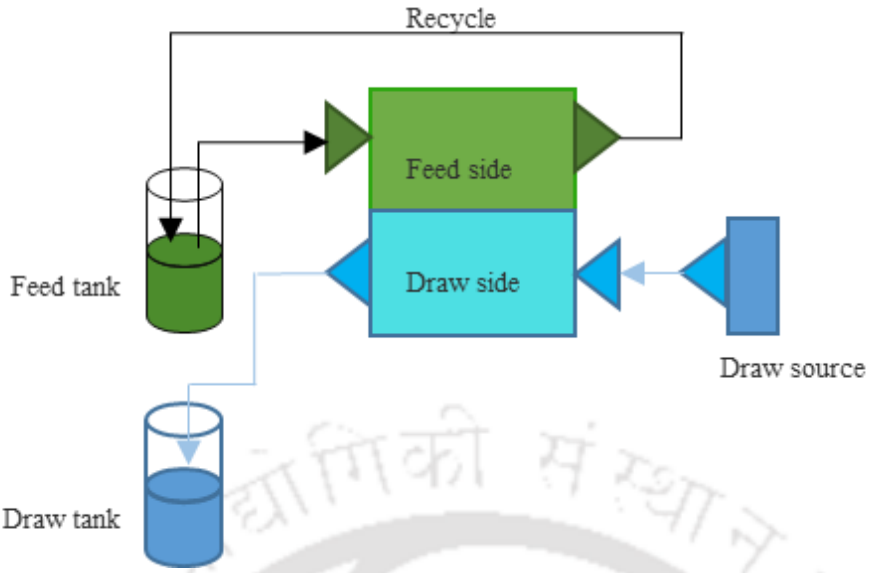


Fig. 5.9 Process flowsheet for feed recycle and draw continuous with single-stage FO system

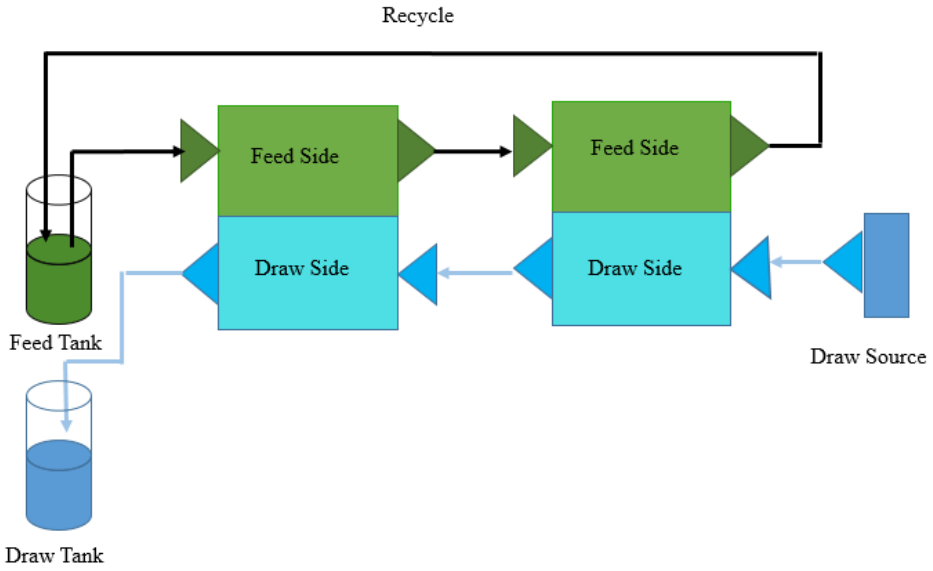


Fig. 5.10 Process flowsheet for feed recycle and draw continuous with two-stage FO system

5.2.3 Case 3: Feed and draw solution in continuous mode

In Fig. 5.11, the flow sheet for the case 3 whereboth FS and DS were in continuous mode with two membrane module configuration system. In this simulation study FS and DS flow rates were maintained at 25 L h^{-1} and 45 L h^{-1} respectively. This case can be applied for large scale production.

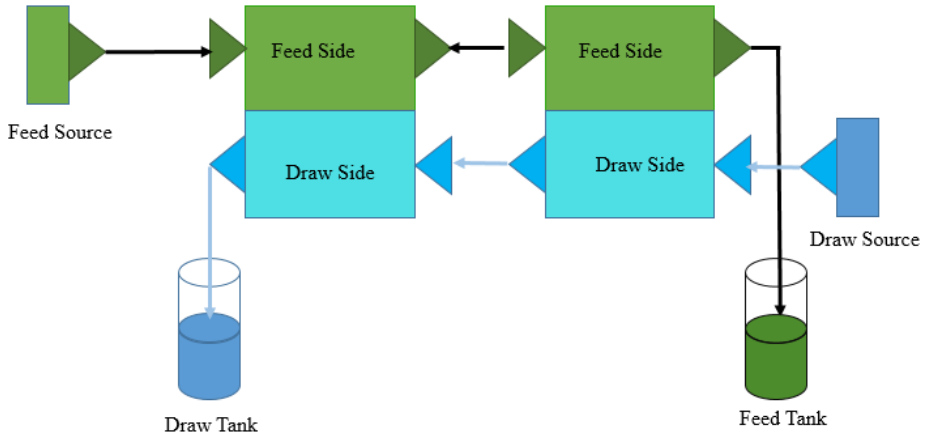


Fig. 5.11 Process flowsheet for both feed and draw continuous

5.2.4 Effect of different flow rate configuration with feed and draw solution in continuous mode

In Fig. 5.12, a schematic of different flow rate configuration is shown with DS and FS both in continuous mode for the two-module system where NaCl concentration was 100 g L^{-1}. Here, the FS flow rate was fixed at 25 L h^{-1}. Different configuration of DS flow rate was simulated to study the effect of it in the concentration process of sugarcane juice. The draw flow rate 45 L h^{-1} was divided into different ratios to observe the performance. In the first case of simulation, the first membrane module used 60 % of total DS flow rate (45 L h^{-1}) and the second membrane module used 40% of total DS flow rate. Again, in the second simulation case, 45 Lh^{-1} DS flow rate was divided equally to both first and second membrane module. In the third simulation case, the first module used 40% of DS flow rate (45 L h^{-1}) and in the second module used 60% of DS flow rate (45 L h^{-1}).

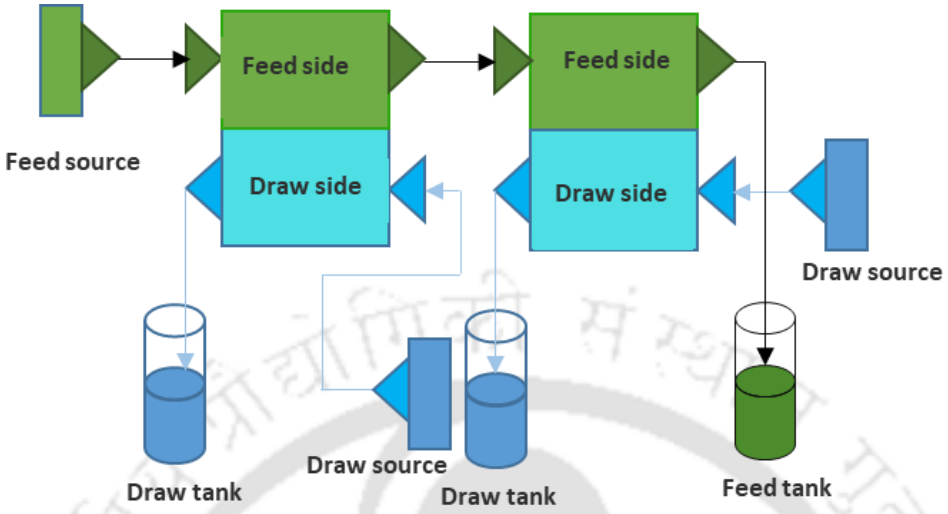


Fig. 5.12 Process flowsheet with different DS flowrate configuration

5.3 Material and method

In this work the performance of aquaporin HFFO membrane is studied by developing a 1D mathematical model as well as by flowsheet simulations. All the experimental details are discussed here.

5.3.1 Sugarcane juice

Raw sugarcane juice was collected from the local vendor near the campus of Indian Institute of Technology Guwahati (IITG), India. This Juice was filtered through 100 mesh size sieve and further clarification of sugarcane juice was done by 19 channel ceramic membrane to remove the suspended solids.

5.3.2 Aquaporin HFFO membrane

The HFFO membrane was purchased from Aquaporin A/S, Denmark. It was a biomimetic HFFO membrane (Aquaporin Inside HFFO06 Hollow Fibre FO Membrane Module) composed of polyamide thin film composite with integrated aquaporin proteins. The active area of the membrane was 2.3 m^2. These aquaporin membranes were characterized for high water flux and negligible reverse salt flux.

5.3.3 Draw solution

One of the foremost elements for an effective FO process is the selection of DS. The DS should have the properties of high water flux, high osmotic pressure, low reverse solute flux and economically viable. In this work, NaCl (M/s Merck Life SciencePvt.Ltd) was used to prepare the DS by dissolving it in deionized water (DI). A concentration of 100 g L^{-1} NaCl DS was prepared.

5.3.4 Experimental setup and procedure

The experiments for the FO model validation were done by using a HFFO aquaporin membrane module on a laboratory scale. The pure water permeability (L_p) was also determined in RO mode at different pressures of 1 to 3 bar. All the experiments were carried out for both co-current and counter-current mode. Two plunger pumps were used to circulate the feed and DS in the shell side and lumen side of the Aquaporin HFFO membrane module. The flow rates of FS and DS were measured by using flow-meter (Intelligent flow totalizer, Ascord). TDS of both the solutions were measured by using digital conductivity meter (HANNA edge®, M/S HANNA Instrument) with data collecting system at an interval of every 5 s. For the sample collection at an interval of every minute, a micro-pipette (M/S Tarson Ltd.) was used. In both feed and draw tank, magnetic stirrers were used to maintain uniform concentration during the FO process. The feed and DS containers were placed on digital weighing balance and every 5 s interval, data was recorded.

A schematic diagram of the lab-scale experimental set up of the FO process is shown in Fig. 5.13. Here, prior to the experiment, the membrane was stabilized with DI water in both shell side and lumen side. After stabilization, tube side DI water was removed by passing DS through tube side, by keeping the feed side of the membrane module in close condition and similarly, shell side water also removed by passing the sugarcane juice through shell side, at tube side closing condition. In the feed side with the help of plunger pump, the pre-treated sugarcane juice at constant flow rate 25 L h^{-1} and in the draw side NaCl of concentration 100 g L^{-1} at a different flow rate 25, 35, 45 L $h^{-1}$are circulatedin co-current and counter-current mode of operation. The experiments were done at atmospheric pressure with draw volume 6.4 L and FS

volume 6.1 L. During the experiment, the sugarcane juice was recirculated back to the feed tank after passing through the membrane module and similarly, NaCl solution was also recirculated back to the DS tank after passing through the FO membrane module. Pure water permeability was taken in RO mode after the experiments. The parameters such as flow rate, pressure, DS concentration (NaCl solution), sugarcane juice concentration, the temperature at inlet and outlet of the membrane and weight of draw and feed tank were measured during the FO process. The change in weight of the DS tank was used to measure the water flux of the aquaporin HFFO membrane. For the validation of the model, different sets of experiments were carried out by varying the draw flow rate and varying the DS concentration. In Fig. 5.14, the experimental setup of the laboratory scale for the concentration of sugarcane juice is shown.

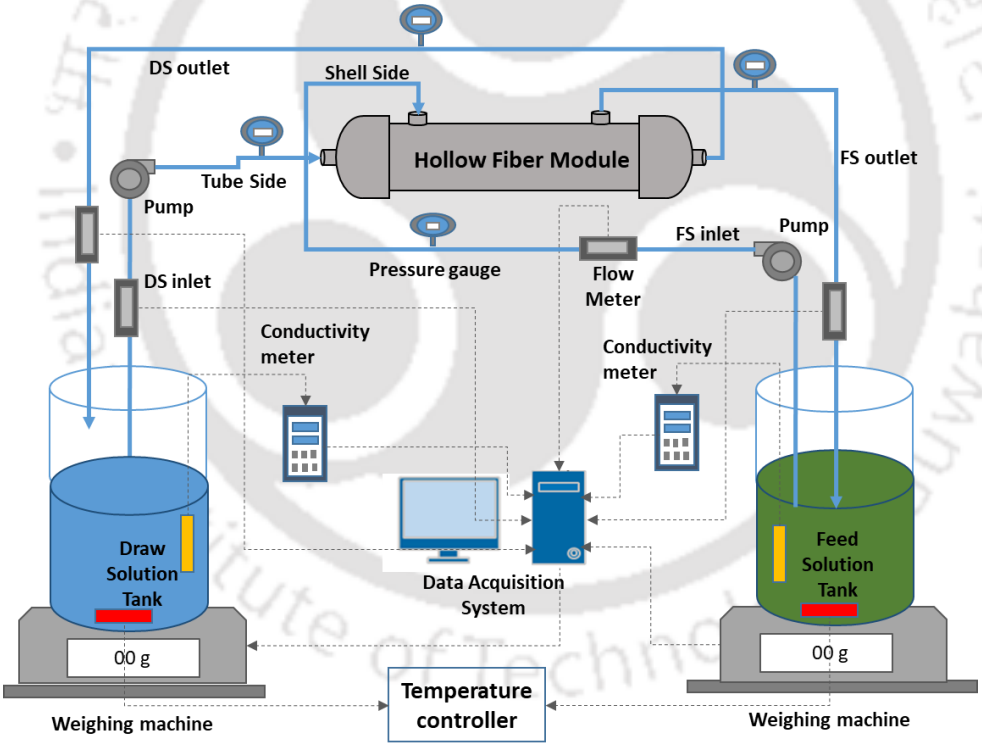


Fig. 5.13 A schematic diagram of the lab-scale experimental setup

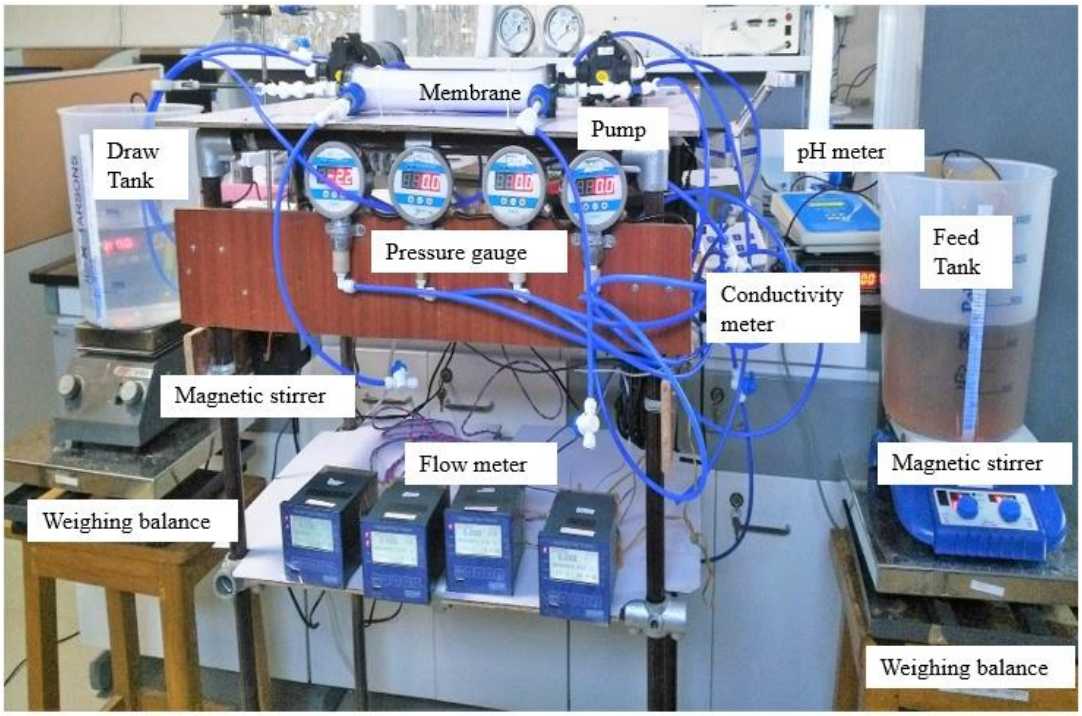


Fig. 5.14 Experimental setup of the laboratory scale for the concentration of sugarcane juice

5.4 Result and discussion

5.4.1 Model validation

The model equation mentioned in the theoretical section was validated with the experimental results by using Modelica language in Dymola tool. The parameters were approximated by reducing the error between the experimental data and model output as we consider the ideal case, that the volume change in feed tank should be equal to the volume change in draw tank. The approximate pure water permeability (A), solute permeability (B), structural parameter (S), α_f and α_d for counter-current and co-current were shown in Table 5.2 and Table 5.3. The estimated values are found to match withthe literature reported values.

Table 5.2 Estimated parameters for counter-current mode

Parameters	25 Lh^{-1}	35 Lh^{-1}	45 Lh^{-1}
L_P ($L\ h^{-1}\ m^{-2}\ bar^{-1}$)	0.83162	0.83317	0.833218
B ($L\ h^{-1}\ m^{-2}$)	0.07	0.07	0.07
S (µm)	387	387	387
α_f	0.2949	0.29497	0.294988
α_d	0.006	0.006	0.006

Table 5.3 Estimated parameters for co-current mode

Parameters	25L h^{-1}	35L h^{-1}	45L h^{-1}
L_P ($L\ h^{-1}\ m^{-2}\ bar^{-1}$)	0.83	0.8336	0.7339
B ($L\ h^{-1}\ m^{-2}$)	0.07036	0.07	0.07
S (µm)	387	387	387
α_f	0.29502	0.295059	0.294619
α_d	0.006	0.006	0.006

5.4.1.1 Counter-current mode model validation

In the counter-current mode of operation, NaCl (DS) and sugarcane juice (FS) were moving in opposite directions as result DS gets diluted and sugarcane juice became concentrated. Fig. 5.15, Fig. 5.16, Fig. 5.17 shows the comparison of experimental results and model outputs such as sugarcane juice concentration (FS), NaCl (DS)

concentration, change in feed and draw tank volume at various draw flow rate condition of 25 L h^{-1},

35 L h^{-1} and 45 L h^{-1} by keeping same feed flowrate i.e. 25 L h^{-1} for batch mode experiment. The concentrations of DS and sucrose were 100 g L^{-1} and 114 g L^{-1} during the experiment. From the simulation study, the parameters like water permeability (L_p), solute permeability (B), structural parameter (S), α_f and α_d for model validation in counter-current mode were reported in Table 5.2. The experimental results of concentration of sugarcane juice were found to be 154.4, 170.07, 173.891 g L^{-1} for 25, 35 and 45 L h^{-1} DS flowrates respectively which was close to the model outputs with less than 5% errors. At the higher flow rate, a higher concentration was observed. From the experimental and model results, it was seen that at a draw flow rate of 45 L gives a high concentration of the sugarcane juice. The increase in cross-flow velocity or cross-flow shear is due to the increase in flowrate, which ultimately augments the mass transfer coefficient as well as water flux. Higher DS flowrate results in higher bulk DS concentration along the membrane surface [101].

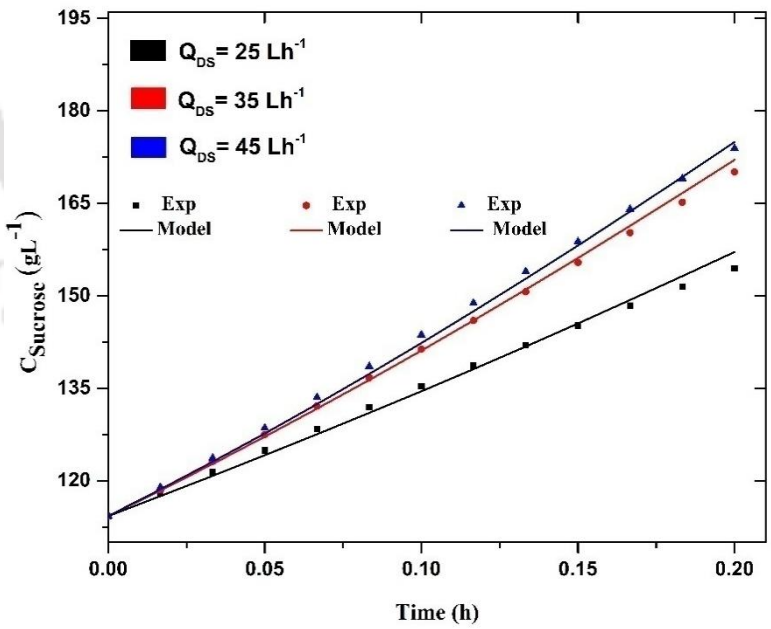


Fig. 5.15 Experimental results and model outputs comparison of sucrose concentration for counter-current mode at $Q_{DS,in}$ = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h-1, $C_{DS,int}$=100 g L^{-1}, $C_{Sucrose,int}$= 114.252 g L_{-1}, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

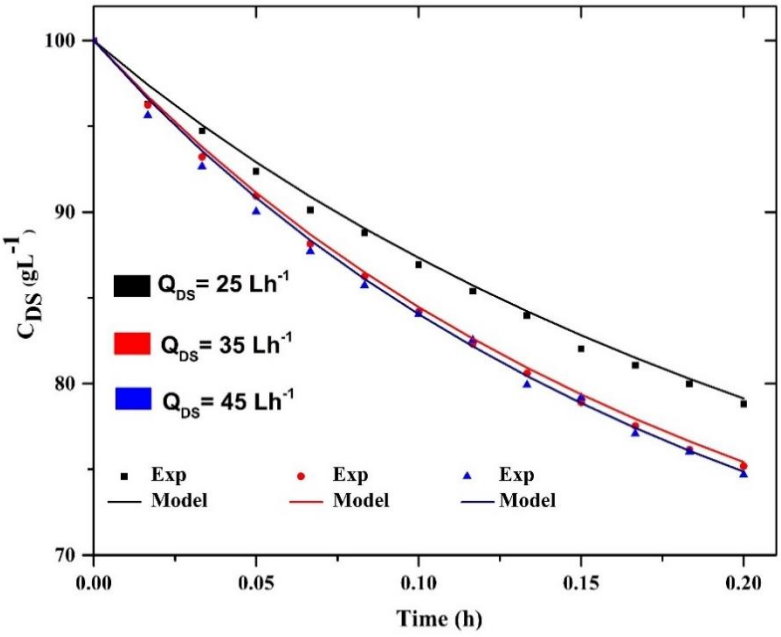


Fig. 5.16 Experimental results and model outputs comparison of DS concentration for counter-current mode at $Q_{DS,in}$ = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h-1, $C_{DS,int}$=100 g L^{-1}, $C_{Sucrose,int}$= 114.252 g L$_{-1}$, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

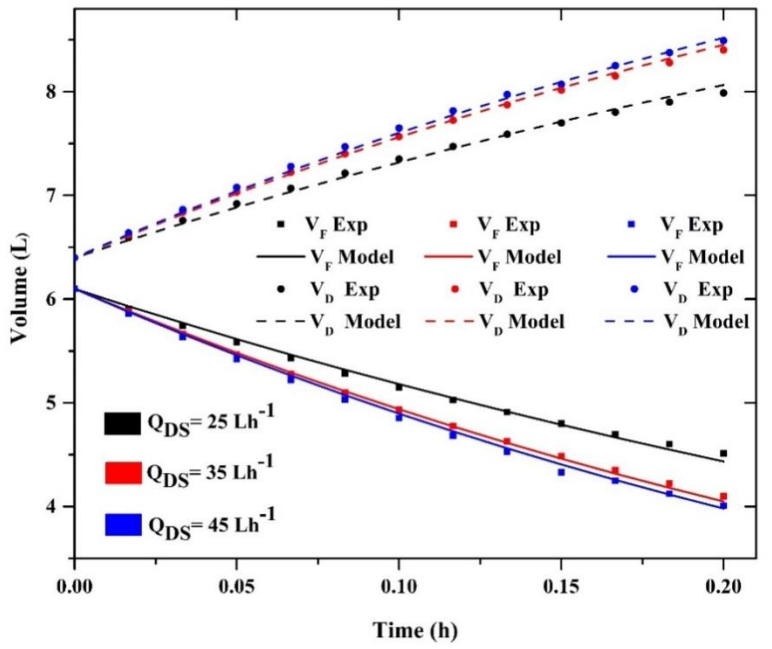


Fig. 5.17 Experimental results and model outputs comparison of change in volume in feed and draw tank for counter-current mode at $Q_{DS,in}$ = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h-1, $C_{DS,int}$=100 g L^{-1}, $C_{Sucrose,int}$= 114.252 g L$_{-1}$, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

5.4.1.2 Co-current mode model validation

All the experiments that were performed in counter-current mode of the FO process were also performed in co-current mode. The co-current mode of the FO process also suggested that, at a draw flow rate of 45 L h^{-1}, sugarcane juice gets more concentrated as shown in Fig.5.18. The change in DS concentration and the change in feed tank volume and draw tank volume are shown in Fig. 5.19 and Fig. 5.20 respectively. Here, also the experimental results of the concentration of sugarcane juice were close to the model outputs with less than 5% errors. The initial DS concentration is 100 g L^{-1} and initial sucrose concentration was 110.252 g L^{-1} during the experiment. From the simulation study, the parameters such as water permeability (L_p), solute permeability (B), structural parameter (S), α_f and α_d for model validation in co-current mode were reported in Table 5.3. The estimated values for co-current and counter-current were similar to the literature reported values. The reported values of parameters for aquaporin HF membrane are, L_p = 0.43 L h^{-1} m^{-2} bar^{-1}, B = 0.05 L h^{-1} $m^{-2}$and S = 210µm [116]. A summary of experimental results of co-current and counter-current mode is reported in Table 5.4.

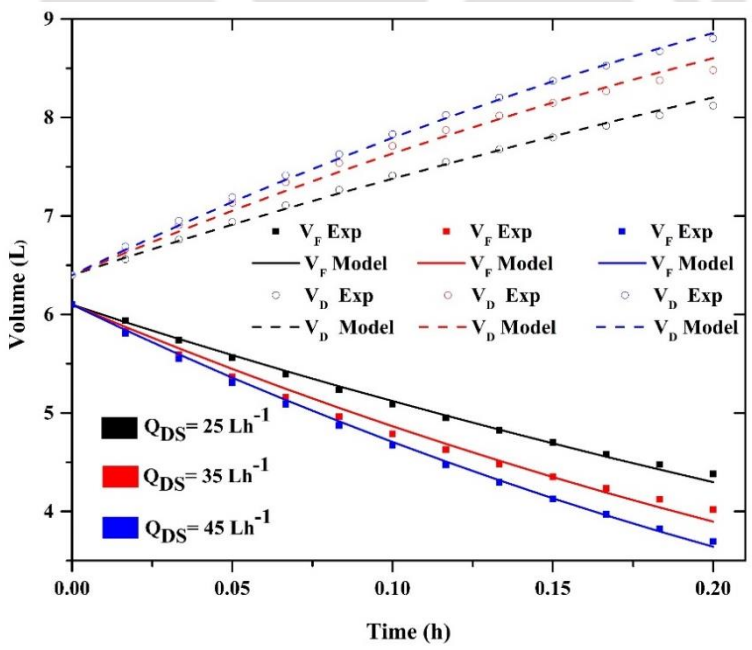


Fig. 5.18 Experimental and model comparison of sucrose concentrationfor co-current mode at Q_{DSin} = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h^{-1} ,$C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$ = 110.2 g L^{-1}, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

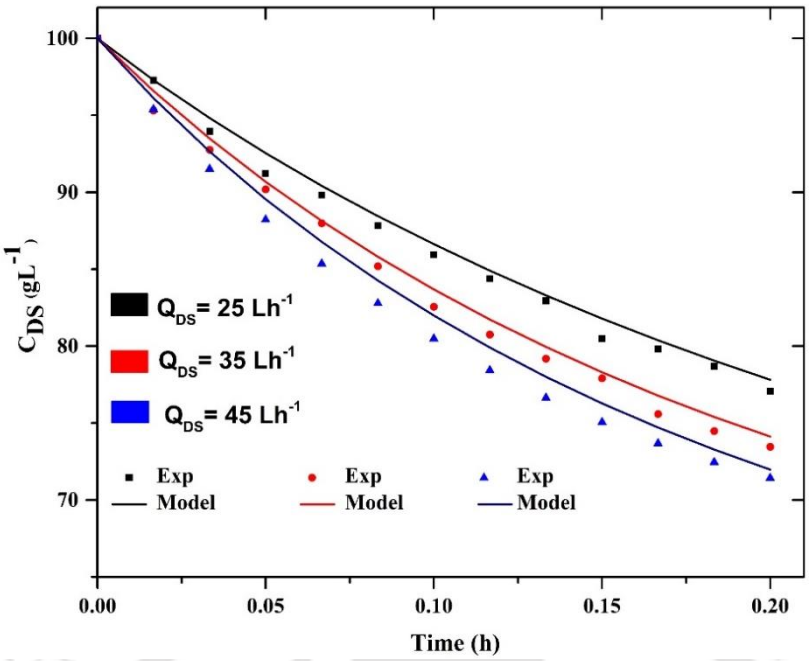


Fig. 5.19 Experimental and model comparison of DS concentration for co-current mode at Q_{DSin} = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h^{-1} ,$C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$ = 110.2 g L^{-1}, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

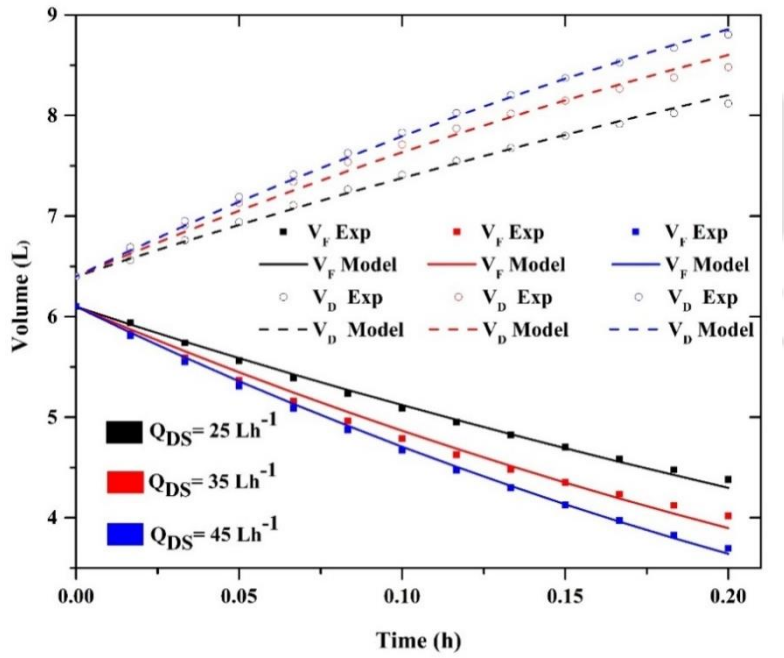


Fig. 5.20 Experimental and model comparison of change in volume in FS and DS tank for co-current mode at Q_{DSin} = 25, 35 and 45 L h^{-1}, $Q_{FS,in}$ = 25 L h^{-1} ,$C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$ = 110.2 g L^{-1}, $V_{DS,int}$ = 6.4 L, $V_{FS,int}$ = 6.1 L

Table 5.4 Experimental results of co-current and counter-current mode

Parameters	Unit	Co-current mode			Counter-current mode		
Flowrate	Lh^{-1}	25	35	45	25	35	45
V_F	L	4.38	4.019	3.696	4.513	4.098	4.008
V_D	L	8.023	8.481	8.804	7.987	8.402	8.492
$C_{Sucrose}$	$G\ L^{-1}$	149.66	163	173	154.43	170.07	177.89
C_{DS}	$G\ L^{-1}$	85.025	84.42	83.2	78.008	72.88	71.287

Note: Initial concentration of DS was 100 gL^{-1} and Sucrose concentration was 110 gL^{-1} for co-current experiments and 114 gL^{-1} for counter-current experiments.

5.4.2 Process flow sheet design and simulation

5.4.2.1 Case 1:Feed and draw solution in recycle mode

For the case, both FS and DS in recycle in batch process, a simulation study was performed with different DS concentration. From the simulation result (Fig. 5.21) of DS concentration of 100 g L^{-1} and 200 g L^{-1} it was clearly seen that processed volume was 19% more for DS concentration of 200 g L^{-1} than 100 g L^{-1}. As a result, a higher concentration of sugarcane juice occurred and with more DS permeation in the FS. The juice concentration for the case of DS concentration 100 g L^{-1} increases from 114 to 339 g L^{-1} and for DS concentration 200 g L^{-1} increases from 114 to 628 g L^{-1}. For higher DS concentration, higher concentration of juice occurred, due to the availability of more driving force (difference in osmotic pressure). It was observed from the simulation results that NaCl concentration was 2.98 g L^{-1} in FS tank for the case of DS concentration 100 g L^{-1} which was 67% less as compared to another case in which DS concentration is 200 g L^{-1}. It could be due to the accumulation of NaCl on the membrane surface was more for higher DS concentration and thus more NaCl permeates to the FS i.e. $C_{DM,\,200} >> C_{DM,\,100}$.

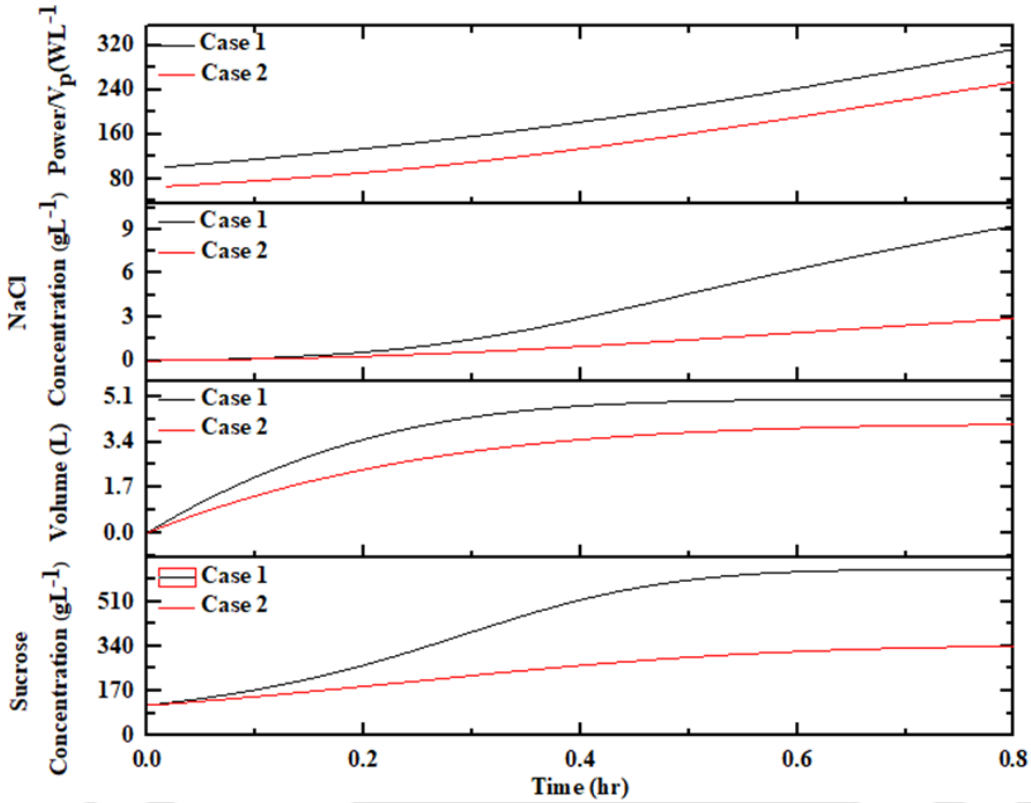


Fig. 5.21 Flowsheet simulation results for batch process with 200 g L^{-1} (case 1) and 100 g L^{-1}(case 2) DS concentration. Note: $Q_{DS,in}$= 45L h^{-1}, $Q_{FS,in}$= 25L h^{-1}, $C_{Sucrose,int}$= 114 g L^{-1}

5.4.2.2 Case 2: Feed solution in recycle mode and draw solution in continuous mode

In Fig. 5.22, Case 2a represents single module FO where, feed was recycled and draw was in continuous mode, Case 2b represents the two modules where FS was recycled and DS was in continuous mode and the case 3 represents both FS and DS in continuous mode with two FO membrane module. Here, the horizontal axis indicates the time taken for the concentration process of FO and the vertical axis indicates different parameters like processed volume (*L*), sucrose concentration (g L^{-1}), SEC (W L^{-1}), NaCl concentration (g L^{-1}). From the simulation results, it was seen that for single module, the juice concentration changes from 114 g L^{-1} to 342 g L^{-1} at 1st optimal point (X at 0.375 h) where the NaCl concentration increases in feed tank to 1.34 g L^{-1} and per unit power consumption was 141.86 W L^{-1}. Again, all the properties were observed for

2 module system at point Y (after 0.616 h). It was observed that, initially, the rate of sugarcane juice concentration increases in the direction of time used in FO process and it was also observed from the Fig. 5.22 that sugarcane juice concentration is more for the two-module system than the single module system at the initial stage. But at point Y (after 0.616 h) for both the system, the sugarcane juice concentration become same 540 g L^{-1} wherethe NaCl concentration for singe module system is 0.58 g L^{-1} and that for the two module system higher than the single module system at X.

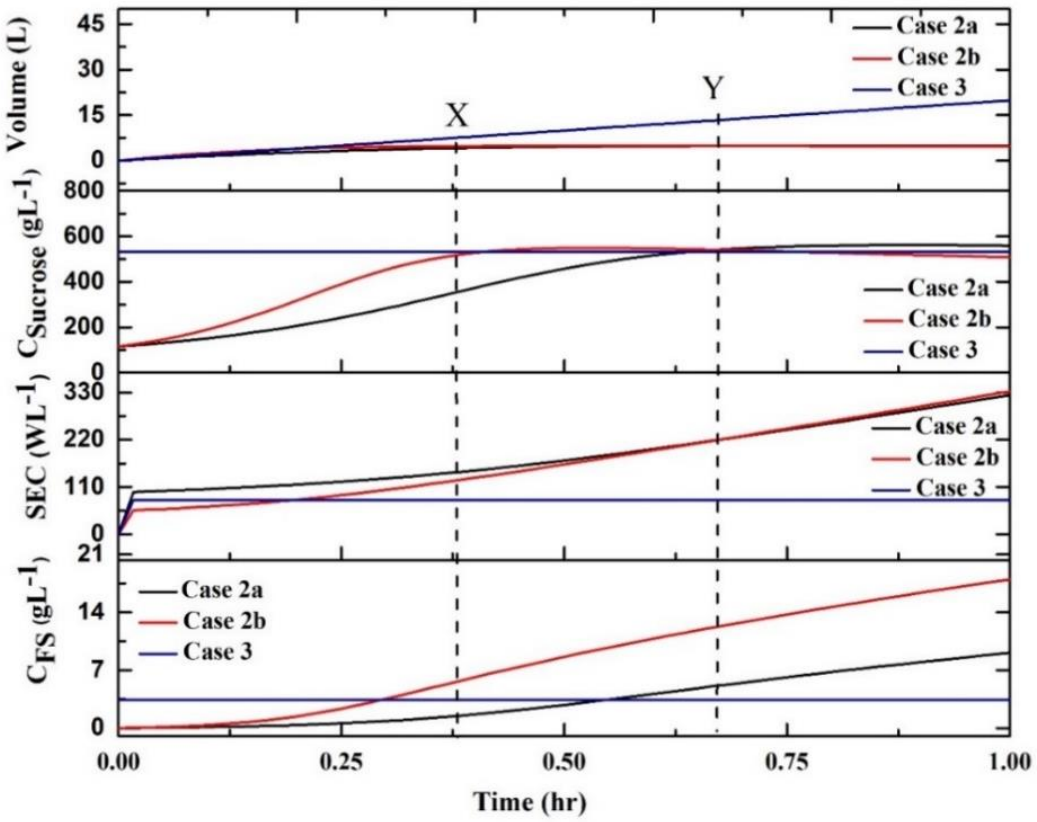


Fig. 5.22 Flowsheet simulation results for case 2a: FS recycle DS continuous mode with single, Case 2b: two-stage FO system and case 3: FS and DS both in continuous mode at $Q_{DS,in}$ = 45 L h^{-1}, $Q_{FS,in}$ = 25 L h^{-1}, $C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$ = 114.2 g L^{-1}

5.4.2.3 Case 3: Feed and draw solution in continuous mode

The results shown in Fig. 5.22 (case 3) is the simulation result for the condition where both FS and DS are in continuous mode with two FO module system at a flow rate of 25 L h^{-1} and DS flow rate of 45 L h^{-1}. Here, point X and Y are considered as optimum conditions for the simulation results. Base on the simulation result, it is clearly seen

that at point X (at time 0.375 h) the processed volume of water is 16.50 L from the sugarcane juice of the feed tank to the draw tank and with a constant product (sucrose) concentration of 531.40 g L^{-1}. During the concentration process, the amount of NaCl concentration in the FS is observed to be 4.02 g L^{-1}. It is clearly visible from the simulation results at point Y (at time 0.616 h), the processed water volume from the sugarcane juice to the draw tank containing NaCl solution is 27 L which is 38.89% more in comparison to the result at point X. The SEC in both X and Y point is 78.85 W L^{-1} which is comparatively less than the other two conditions (FS in recycling mode and DS in continuous mode for single module system and FS in recycling mode and DS in continuous mode for two FO module system). The overall performance of FO for all the three cases (case 2a: FS in recycle with DS in continuous mode for single module system, case 2b: FS in recycle with DS in continuous mode for two modules system and case 3: both FS and DS are in continuous mode with two module system) are mentioned in the Table 5.5. From the simulation results, it can be stated that for large production, two-module system of the continuous mode of operation is a better solution with less consumption of specific energy than the other two cases. Again, for a small scale production capacity plant the single module system with FS in recycle and DS in continuous mode configuration is better solution because in this case less solute diffusion take place with similar juice concentration as in continuous mode at time 0.675 h.

Table 5.5 Overall performance of FO process for different flowsheet simulation conditions

Case	Vp at X	Vp at Y	C_sucrose at X	C_sucrose at Y	C_{FS} at X	C_{FS} at Y	SEC at X	SEC at Y
Case 2a	4.06	4.80	342.17	540	1.34	5.05	141.86	217.94
Case 2b	4.73	4.81	510.45	540	5.27	12.16	121.73	217.74
Case 3	7.27	13.22	531.40	540	3.40	3.40	78.85	78.85

5.4.2.4 Effect of different flow rate configuration with feed and draw solution in continuous mode

The performance of FO for the two module system with different configurations were reported here. The DS flow rate 45 L h^{-1} DS was divided into different ratios to observe the performance of FO with respect to concentration of sucrose, NaCl concentration in FS and SEC. In the Fig. 5.23, the performance results of all the different cases were shown. Table 5.6 shows the results of different cases of change of DS flowrates ratios. Here, DS flow rate ratio 60:40 case shows optimum performance than the other cases of the FO membrane for two membrane module system. At this ratio, sucrose concentration was 341.81g L^{-1} and 1.57 g L^{-1} salt concentration in feed tank due to use of high flow rate in the first module. The SEC for the two module system for the case of 60:40 is 92.14 WL^{-1} and this was the lowest SEC used among all other DS flow rate ratios.

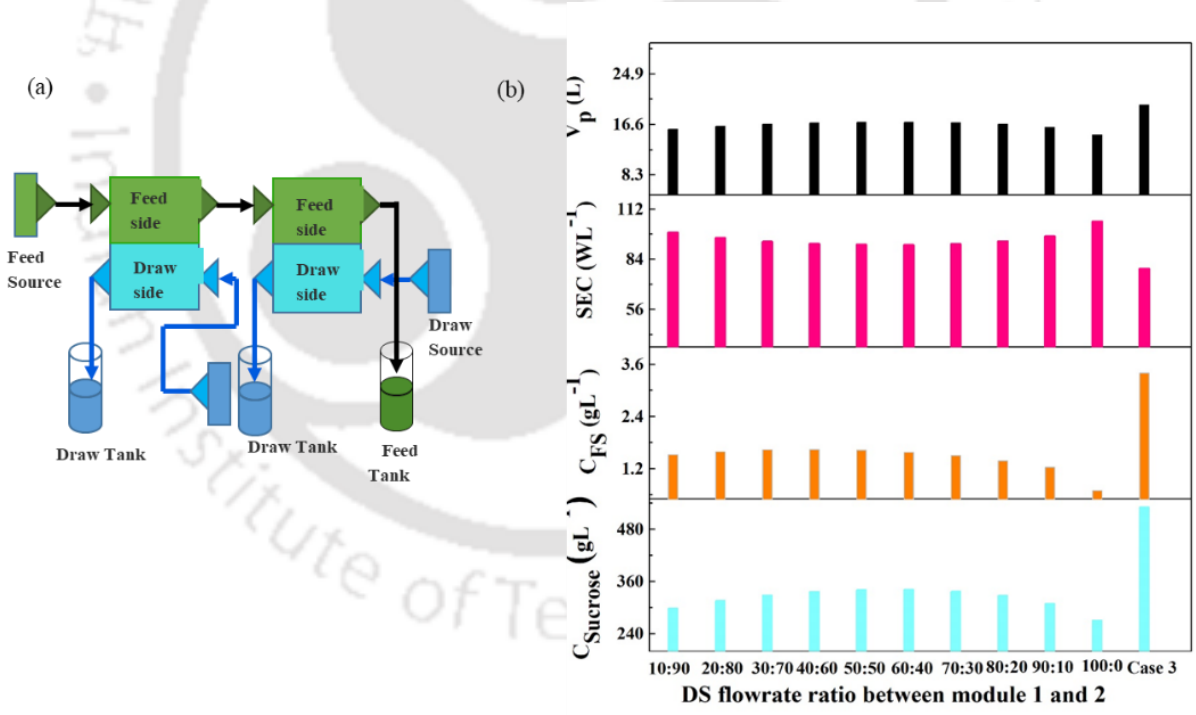


Fig. 5.23 (a) flow sheet diagram of two module FO system (b) flowsheet simulation results for different DS flowrate conditions for analysis of processed volume, SEC, NaCl concentration in feed tank and sucrose concentration at $C_{DS,int}$ =100 g L^{-1}, $C_{Sucrose,int}$ = 114.2 g L^{-1}

Table 5.6 Flowsheet Simulation with respect to different DS flow rate ratio of 45 L h^{-1}

DS flowrate ratio	$C_{Sucrose}$ (gL^{-1})	C_{FS} (gL^{-1})	SEC (WL^{-1})
10:90	297.86	1.52	99.05
20:80	315.54	1.59	95.92
30:70	328.10	1.63	94
40:60	336.59	1.64	92.82
50:50	331.23	1.62	92.22
60:40	341.81	1.57	92.14
70:30	337.73	1.5	92.67
80:20	327.46	1.38	94.05
90:10	309.44	1.23	97.01
100:0	270.85	0.69	105.15

5.5 Summary

The experimental and modelling study results on sugarcane juice concentration using aquaporin HFFO module presented in this study enables future direction and viability of FO process for liquid food concentration applications. This study includes the significance of various FO operating parameters and mathematical model and its importance while designing the FO process. A simplified mathematical model has been developed by considering the effect of ICP and ECP in the membrane for HFFO membrane under co-current and counter-current mode. The summary of the key finding of both experimental and simulation study is given below

The following conclusions is drawn from this study:

- ✓ The complete rejection of sugarcane juice components is achieved by aquaporin HFFO membrane module with specific RSF of 1.57 g L^{-1} at optimised experimental condition
- ✓ A simplified mathematical model proposed in this study is able to predict the Aquaporin HFFO module performance with error limit of 5% for water flux and RSF. The estimated model parameters such as pure water permeability (A), solute permeability (B), structural parameter (S), α_f *and* a_d are found to be similar with the literature reported values and can be used for design and optimization industrial FO process.
- ✓ From the experimental results, it can be concluded that optimization of FO process parameter such as DS flowrate, concentration, flow configuration between DS and FS is very important aspect to achieve maximum water flux and minimum RSF for a given DS.
- ✓ From all the three cases of simulation studies, the continuous FO process is found to consume minimum energy consumption than the batch process.

However, for all simulation cases membrane fouling is not taken in to consideration. Hence in future work this has to be incorporated in the simulation study for the FO processes. In addition, recovery of DS needs to be developed for reusability of the water in further concentration process.

Chapter: 6

Conclusion and Scope of Future Work

This chapter summarizes the inferences drawn from various works presented in this thesis. It includes some suggestions towards the scope for future research.

6 Conclusion

The main aim of this research work was to investigate the application of novel low-cost Lanthanum phosphate ($LaPO_4$) coated tubular ceramic membrane for the clarification of sugarcane juice without the application of lime by measuring polyphenol oxidase enzyme, bacteria removal efficiency and permeate flux decline profile. Another aim is to investigate the performance of a commercially available aquaporin HFFO membrane for concentration of sugarcane juice by adopting appropriate UF pre-treatment technique and targets the modelling, validation and process simulation of forward osmosis membrane for the concentration of sugarcane juice. The mathematical model was developed based on the tank mass balance and concentration polarization by minimizing the error between experimental and model data, using Dymola software. The model equation mentioned in the theoretical section was validated with the experimental results with Modelica language in Dymola tool. A simulation study was performed for different flowsheets to estimate the optimal process design in terms of juice concentration, energy consumption, and processed volume.

The most important findings from this study are summarized below.

6.1 Sugarcane juice clarification by ultrafiltration membrane with fouling and cleaning study:

- The clarification of sugarcane juice was successfully performed using $LaPO_4$ coated and uncoated ceramic membrane. The $LaPO_4$ coated ceramic membrane offered best physico-chemical characteristics of permeate in terms of turbidity reduction 99.3%, colour reduction 99.58%, TDS reduction 49.76% and increase in clarity by 99.84% compared to feed (raw sugarcane juice). The pH of permeate has undergone less change.
- A separate study was performed with uncoatedmembrane offered and the physico-chemical characteristics of permeate in terms of turbidity reduction

92.54%, colour reduction 83.29% and increase in 89.77% clarity compared to feed (raw sugarcane juice).

- Polyphenol oxidase (PPO) enzyme present in the sugarcane juice is responsible for the colour change of the juice from green to yellow and the activity of the PPO enzyme decreased by 70% in permeate of $LaPO_4$ coated membrane due to the removal of the PPO enzyme
- The long term storage study of sugarcane indicated that the $LaPO_4$ coated ceramic membrane clarified juice can be stored in refrigerator up to 7 weeks without significant change in sugarcane juice quality.
- A hybrid cleaning strategy involving an innovative brushing action on the membrane surface for physical cleaning combined with chemical cleaning was implemented for $LaPO_4$ coated ceramic membrane.
- Comparative analysis of permeate flux decline profile among innovative brushing action on the membrane surface for physical cleaning and without physical cleaning was observed.
- In the present study, membrane flux improvement up to 50 times was obtained when physical cleaning was introduced during the juice clarification process.

6.2 Concentration of sugarcane juice using forward osmosis membrane with fouling and cleaning study

- An Aquaporin commercial HFFO module was used for concentration of sugarcane juice.
- Optimal DS concentration, the effect of draw, FS flowrate and its direction of flow such as co- or counter-current on water reverse solute flux in batch mode were evaluated.
- Counter-current flow configuration between FS and DS was able to provide 7% high water flux than co-current flow configuration.
- At optimal DS flow rate and flow configuration, the aquaporin HFFO module was able to concentrate UF pre-treated sugarcane juice up to 60%

of initial concentration in 12 mins of batch FO operation with the initial DS concentration 100 gL^{-1}.

- The average water flux and SRSF were increasing nonlinearly with DS concentration, i.e., water flux increased by 155%, and average SRSF increased by 1257% while increasing DS concentration by 200%.
- The investigation of fouling was evaluated for UF pre-treated sugar cane juice and unclarified sugarcane juice. The pure water permeability of membrane fouled by unclarifiedjuice was reduced by 53.3% and that for UF clarified juice 11.2%.
- The fouled membrane was regenerated with only DI water wash for 30 min for UF clarified juice, however in case of untreated juice, the FO membrane was not able to regenerate with DI water wash and osmotic backwash, and it required 0.1 M NaOH wash.

6.3 Modelling, validation and process simulation of forward osmosis membrane for the concentration of sugarcane juice

- A mathematical model is developed and parameters such as pure water permeability (A), solute permeability (B), structural parameter (S), α_f and α_d for counter-current and co-current were estimated.
- The experimental results of concentration of sugarcane juice in counter-current mode are found to be 154.4, 170.07, 173.891 g L^{-1} for DS flowrates 25, 35 and 45 L h^{-1} respectively and which is close to the model outputs with less than 5% errors.
- From the three cases of simulation study, it is observed that case 3 where both FS and DS are in continuous mode was more effective in terms of concentration, reverse solute flux and specific power consumption. The SEC is 78.85 W L^{-1} for the case of both feed and DS in continuous mode while, SEC is 217.74 W L^{-1} in case 2 (FS in recycle mode and DS in continuous mode) with two-module system.
- Again, for two module system, to find the optimal DS flow rate ratio, simulation study was carried out. From the simulation results, it is

confirmed that in two-module system, 60:40 ratio was the optimum DS flowrate ratio since at this ratio sugarcane juice concentration was 341.81 g L^{-1} and salt concentration in feed tank is 1.57 g L^{-1} and SEC is 92.14 W L^{-1}, which was found to be the lowest among all the other DS flowrate ratio.

6.4 Scope of future work

Research finding of this work provide some of the new areas of research, that can be carried out to further the applicability of membranes in juice processing. Some of the important research areas or future work as an extension of the present study are presented as follows:

- Investigation of $LaPO_4$ coated UF ceramic membrane application for other type of juice such as orange, pineapple, watermelon has to be explored.
- Pilot plant study for sugarcane juice clarification using $LaPO_4$ coated UF ceramic membrane has to be explored.
- The phenomenological models of fouling have not been studied for $LaPO_4$ membrane, to illustrate the dependency of total hydraulic resistance of membrane ΔP, time for clarification of sugarcane juice.
- However, for all simulation case studies membrane fouling is not taken in to consideration. Hence in future work this has to be incorporated in the simulation study for the FO processes.
- In addition, recovery of DS needs to be developed for reusability of the water in further concentration process.Development of smart DS suitable for food processing.

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Appendix

Water and solute transport derivation by considering the effect of ICP and ECP

a) At DECP on Active layer (AL) side

The salt flux (Js) across the ECP can be expressed as a combination of convective and diffusive terms:

$$-J_S = J_W C + D\frac{dC}{dx} \tag{A.1}$$

Here,Js = Reverse solute flux.

Jw = Water flux.

Boundary conditions:

$x=0 \qquad C=C_{Dm}$

$x=-\delta_D \qquad C=C_{Db}$

After using above conditions we get,

$$\frac{J_S + J_W C_{Dm}}{J_S + J_W C_{Db}} = \exp\left(-\frac{J_W}{k}\right)_D \tag{A.2}$$

b) At inside AL, convective flux term is zero only we have to consider molecular diffusion term. Therefore,

$$-J_S = -D\frac{dC}{dx} \tag{A.3}$$

At inside AL, convective flux term is zero only we have to consider molecular diffusion term, Therefore we have ;

Now, applying boundary conditions Inside AL:

$x=0 \qquad C=C_{Dm}$

$x=t_a \qquad C=C_{im}$

$$J_S = -B_{NaCl}\left(C_{di} - C_{dm}\right) \tag{A.4}$$

c) At inside the support layer.

$$-J_S = J_W C + D\frac{dC}{dz} \tag{A.5}$$

Boundary conditions,

$z = 0 \qquad C = C_{im}$

$z = t_s \qquad C = C_{sm}$

On solving Equation (A.5) and applying boundary conditions we get,

$$\frac{J_S + J_W C_{im}}{J_S + J_W C_{sm}} = \exp(J_W K) \tag{A.6}$$

d) At CECP on support layer surface:

$$-J_S = J_W C + D\frac{dC}{dk} \tag{A.7}$$

Boundary conditions,

$k = 0 \qquad C = C_{sm}$

$k = \delta_f \qquad C = C_{Fb}$

Similarly, after applying boundary condition we get,

$$\frac{J_S + J_W C_{sm}}{J_S + J_W C_{Fb}} = \exp\left(\frac{J_W}{k}\right)_f \tag{A.8}$$

On solving Equation. (A.2) and (A.4),

$$C_{Dm} = \frac{B_{NaCl}}{J_W}(C_{Dm} - C_{um})\left[\exp\left(-\frac{J_W}{k}\right)_D - 1\right] + C_{Db}\exp\left(-\frac{J_W}{k}\right)_D \tag{A.9}$$

Similarly, on Equation. (A.4) and (A.6),

$$C_{im} = \frac{B_{NaCl}}{J_W}(C_{Dm} - C_{im})\left[\exp\left(\frac{J_W}{k}\right)_f \exp(J_W K) - 1\right] + C_{Fb}\exp\left(\frac{J_W}{k}\right)_f \exp(J_W K) \tag{A.10}$$

On subtracting Equation. (A.9) and (A.10)

$$\left(C_{DS,m}-C_{im}\right)_{NaCl}=\frac{C_{Db}\exp\left(-\frac{J_W}{k_d}\right)-C_{FS,b}\exp\left[J_W\left(\frac{1}{k_f}+K\right)\right]}{1+\frac{B}{J_W}\left[\exp\left[J_W\left(\frac{1}{k_f}+K\right)\right]-\exp\left(-\frac{J_W}{k_D}\right)\right]} \quad \text{(A.11)}$$

Where, K is the solute resistivity and is given by,

$$K=\frac{S}{D_{diff}}=\frac{t\tau}{\varepsilon D_{diff}} \quad \text{(A.12)}$$

Where, S, D_{diff}, t, τ and ε are structural parameter (μm), diffusion coefficient ($m^2\ h^{-1}$), thickness (m), tortuosity and porosity of the support layer.

Water permeability estimated by RO mode

The Pure water permeability is estimated by using the Equation. (A13) by calculating the flux at different pressure for a pre-conditioned membrane. It is well known that the permeate flux is directly proportional to the applied hydraulic pressure. The pure water permeability can be estimated from the slop.

$$J_w=L_p\Delta P \quad \text{(A.13)}$$

The estimated pure water permeability of the membrane in RO mode is 0.8438 L $h^{-1}m^{-2}$ Bar^{-1}.

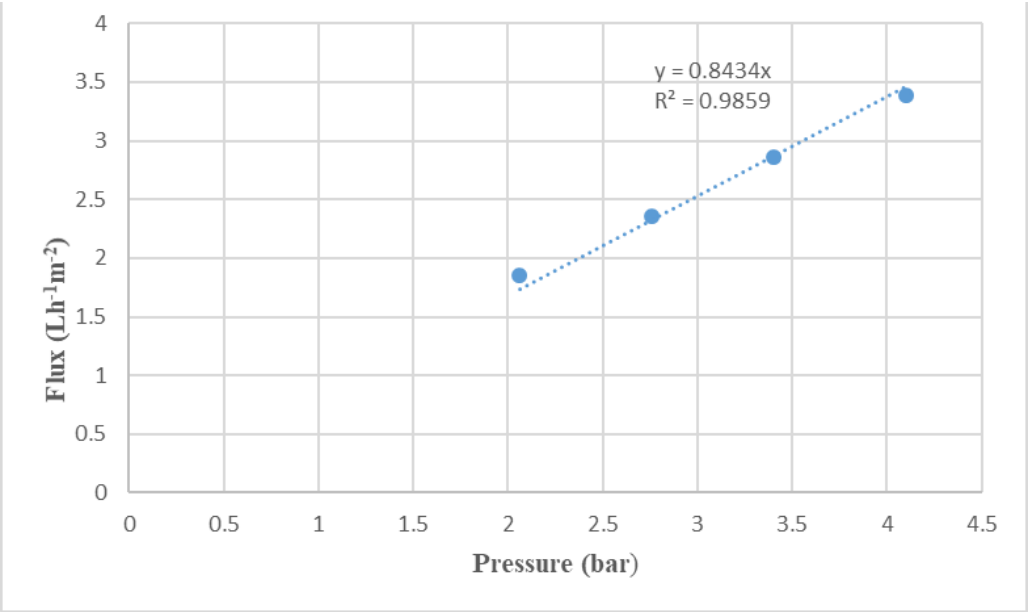

Fig. A.1. Estimation of water permeability of membrane by RO mode.

Error Analysis

In experimental investigation the uncertainty in the calculated quantities arise due to the differences exist between the sets of values at various time. Therefore, based on several experimental runs average values are used for reporting as error. This error analysis is done to determine the accuracy of calculation as well as reliability of the experimental data (reported). Errors arises due to variation in precision of measured parameters i.e. the errors occurred due to the minor variation in the successive measurement under the same experimental conditions. In this work various instruments are used for measuring such as weighing balance, Turbidity meter, UV spectrophotometer, High performance liquid chromatography (HPLC), Ion Chromatography (IC) etc. For concentration measurement calibration curves were prepared by measuring known concentration of solution. From the calibration curve standard deviation was calculated and it was observed that the standard deviation between calculated values and actual values is more than 0.9901 for three different cases. Again for the case of permeate flux measurements standard deviation is generally used to estimate the uncertainty. For example, u_1, u_2, u_3, ……. u_n are n

numbers of experimental results of permeate flux. And u_{av} is the mean vale and is given by equation (A14)

$$\bar{u} = \frac{u_1 + u_2 + u_3 + \ldots\ldots\ldots + u_N}{N} = \frac{1}{N}\sum_{i=1}^{N} u_i \qquad \text{(A 14)}$$

Again uncertainty in the results are expressed in root mean squared deviation (Δu) and it can be computed by using equation (A15)

$$\Delta u = \sqrt{\frac{(u_1 - \bar{u})^2 + (u_2 - \bar{u})^2 + (u_3 - \bar{u})^2 + \ldots\ldots\ldots + (u_N - \bar{u})^2}{N-1}} \qquad \text{(A 15)}$$

List of Publications and Conference presentations

International Journals

- **Aanisha Akhtar**, Senthilmurugan Subbiah,Kaustubha Mohanty, R. Sundar, R. Unnikrishnan, U.S. Hareesh, Sugarcane juice clarification by lanthanum phosphate nano-fibril coated ceramic ultrafiltration membrane: PPO removal in absence of lime pre-treatment, fouling and cleaning studies, ***Separation and Purification Technology***, 249, **2020**, 117-157 (doi.org/10.1016/j.seppur.2020.117157)

- **Aanisha Akhtar**, Mandeep Singh, Senthilmurugan Subbiah, Kaustubha Mohanty, Modelling, experimental validation and process design of forward osmosis process for sugarcane juice concentration, ***LWT - Food Science and*** Technology, Volume 141, April 2021, 110852(https://doi.org/10.1016/j.lwt.2021.110852)

- **Aanisha Akhtar**, Mandeep Singh, Senthilmurugan Subbiah, Kaustubha Mohanty: Sugarcane juice concentration using a novel aquaporin hollow fiber forward osmosis membrane, ***FBP-Food and Bioproducts Processing***, Volume 126, March 2021, Pages 195-206 (https://doi.org/10.1016/j.fbp.2021.01.007)

Proceedings of the international / national conferences

- International conference on engineering sciences and technologies for environmental care (estec-2020): **Aanisha Akhtar,** Mandeep Singh, Senthilmurugan Subbiah, and Kaustubha Mohanty "Energy efficient forward osmosis membrane process for the sugarcane juice concentration" page -99

- 3rd International Conference on Materials Science and Research November 28-29, 2019 Kuala Lumpur, Malaysia: **Aanisha Akhtar**, Kaustubha Mohanty and Senthilmurugan Subbiah, "A Solution to Sugar Industry by potential use of UF Ceramic Membrane for Clarification of Sugarcane Juice and Concentration of Juice by FO Membrane", DOI: http://dx.doi.org/10.18689/2638-1559.a3.003

- 4thInternational conference on desalination using membrane technology, PerthAustralia (1-4 December 2019) **Aanisha Akhtar**, Senthilmurugan Subbiah and Kaustubha Mohanty, "Aquaporin Forward Osmosis membrane for concentration of sugarcane juice"

- 6th Bio Processing India conference, IIT Delhi, 2018, **Aanisha Akhtar**, Mandeep Singh, Senthilmurugan Subbiah, and Kaustubha Mohanty "Concentration of sugarcane juice by Hollow Fiber Forward Osmosis (HFFO) Aquaporin membrane and analysis of juice properties post-concentration", BPHN-29, page 100
- 7th Bio Processing India conference, CSIR-CFTRI, Mysuru 2019 **Aanisha Akhtar**, Senthilmurugan Subbiah, and Kaustubha Mohanty "Concentration of sugarcane juice by aquaporin forward osmosis membrane: Experimental results and process design", FP-001, page 57
- **Aanisha Akhtar**, Senthilmurugan Subbiah and Kaustubha Mohanty "A study on Clarification of sugarcane juice by Ultra Filtration and Concentration using Aquaporin membrane" poster presented in Research Conclave March 14-17, 2019 at IIT Guwahati
- **Aanisha Akhtar**, Senthilmurugan Subbiah and Kaustubha Mohanty "A fouling and cleaning study on Clarification of sugarcane juice by Ultra Filtration" poster presented in Research Conclave March, 2018 at IIT Guwahati

Book Chapter

- Ananya Bardhan, Aanish Akhtar, Senthilmurugan Subbiah, 2022,Microfiltration and Ultrafiltration membrane technologies, "Advancement in Polymer based Membrane for Water Remediation, 3-42, Elsevier.

Awards:

- Best Poster Award in the 6th Bioprocessing India Conference,organized by IIT Delhi (16-18 December 2018)
- Best poster Award in Recycle , International conference, IIT-Guwhati, 2016