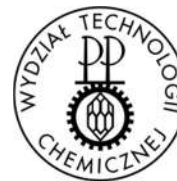




POZNAN UNIVERSITY OF TECHNOLOGY
FACULTY OF CHEMICAL TECHNOLOGY
Institute of Technology and Chemical Engineering
Division of Chemical Technology



MASTER THESIS

Separation of Components of Post-Fermentation Broth in
Membrane Hybrid Systems

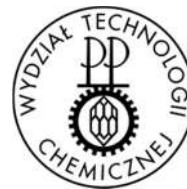
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POLITECHNIKA POZNAŃSKA
WYDZIAŁ TECHNOLOGII CHEMICZNEJ

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PRACA DYPLOMOWA MAGISTERSKA

Separacja składników brzeczek pofermentacyjnych w membranowych układach
hybrydowych

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ABSTRACT

Electrodialysis is a mass separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. It is used for desalination of brackish water, production of portable water.

Succinic acid is widely applicable in the food industry, agriculture and as a precursor of many chemical compounds such as 1,4-butanediol. It can be used to create a large array of chemicals including resins and biodegradable polymers as well as food additives.

In this study, we used available reagent in the laboratory such as succinic acid, glycerol, lactose, ethanol, acetic acid, formic acid, lactic acid, and fumaric acid have been used for preparation of model solutions. Composition of the solution containing 7 components was the most similar to real post-fermentation broth. Equipment unit used including such as ultrafiltration, ionic tower, nanofiltration, electrodialysis with bipolar membrane. Analysis all sample using High Performance Liquid Chromatography (HPLC) which is already available in laboratory analysis. Furthermore, the samples that have been analyzed using HPLC.

All parameter include current density 90 A/m^2 and 120 A/m^2 ; flow rate $50 \text{ dm}^3/\text{h}$ and $100 \text{ dm}^3/\text{h}$; initial concentration of succinic acid in concentrate chamber and diluate chamber (g/dm^3). pH solution was adjusted to 8.5.

The result described with lower current density current density and high flow rate have a good impact to produce 1kg of succinic acid.

ABSTRAKT

Elektrodializa jest procesem separacji membranowej, w którym siłą napędową procesu jest różnica potencjałów elektrycznych, jednocześnie jej głównym zastosowaniem jest separacja jonów od innych składników nie wykazujących budowy jonowej z roztworów wodnych. Głównym obszarem zastosowania procesów elektrodialitycznych w przemyśle jest odsalanie wody słonawej w procesie produkcji woda pitnej.

Kwas bursztynowy jest powszechnie stosowany w przemyśle spożywczym, rolnictwie i jako prekursor wielu związków chemicznych, takich jak: 1,4-butanodiol. Może być również stosowany jako prekursor wielu ważnych chemikaliów, żywic i polimerów ulegających biodegradacji, jak i dodatków do żywności.

W badaniu tym w celu przygotowania roztworów wzorcowych zastosowano takie odczynniki chemiczne jak: kwas bursztynowy, gliceryna, laktoza, etanol, kwas octowy, kwas mrówkowy, kwas mlekowy i kwas fumarowy. Siedmioskładnikowy roztwór modelowy o składzie podobnym do składu rzeczywistej brzezki pofermentacyjnej oraz rzeczywisty płyn pofermentacyjny separowano za pomocą technik separacji tj.: ultrafiltracji, nanofiltracji, wymiany jonowej oraz elektrodializy bipolarnej. Wszystkie próbki analizowano za pomocą wysokosprawnej chromatografii cieczowej (HPLC).

Procesy EDBM prowadzono przy wartości gęstości prądu równej 90 i 120 A/m², objętościowym natężeniu przepływu 50 dm³ i 100 dm³, pH roztworów wyjściowych było równe 8,5.

Stwierdzono, że gęstość prądu i objętościowe natężenie przepływu mają wpływ na wydajność prowadzonych procesów EDBM.

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Glossary

| | |
|--|---|
| <i>UF</i> | Ultrafiltration |
| <i>NF</i> | Nanofiltration |
| <i>EDBM</i> | Electrodialysis bipolar membrane |
| <i>AEM</i> | Anion exchange membrane |
| <i>CEM</i> | Cation exchange membrane |
| <i>BM</i> | Bipolar membrane |
| <i>CE</i> | Current efficiency (%) |
| <i>F</i> | Faraday constant (C/mol) |
| <i>I</i> | Total electric current density passing through the membrane (A/m ²) |
| <i>V_{dil}</i> | Volume of diluate chamber |
| <i>Z, z⁺, v⁺</i> | Ionic valence and number of cations respectively |
| <i>Δt</i> | Time requirement in process |
| <i>C_{SA D}</i> | Concentration succinic acid in diluate chamber |
| <i>C_{SA K}</i> | Concentration succinic acid in concentrate chamber |
| <i>t</i> | Time (s) |
| <i>C</i> | Concentration (g/dm ³) |
| <i>Δt</i> | Different time (s) |
| <i>Q_f</i> | Feed flow (dm ³ /h) |
| <i>TMP</i> | Trans Membrane Pressure (MPa) |
| <i>E</i> | Energy consumption to produce 1kg succinic acid (kWh/kg) |
| <i>η_{des}</i> | Desalination degree of components in diluate chamber (%) |
| <i>R</i> | Retention of the components of solutions (%) |

Chapter I

THEORITICAL PART

1.1. Introduction of membrane technology

Membrane process are a new methods of separation process. Membrane separation is the beginning of the 20th century, 60 years after the separation of the rapid rise of the new technology [1].

Membrane separation technology due to the both separation, concentration, purification and refined features, have high efficiency, energy saving, environmental protection, molecular level filters and filtration process is simple and easy control characteristics, therefore, has been widely used in food, medicine, biology, environmental protection, chemical industry, metallurgy, energy, oil, water, electronics, bionics and other areas, resulting in huge economic and social benefits, has become the separation of science, one of the most important means.

Today membrane process are used in wide range of applications and the number of such application is still growing. From an economic point of view, the present time is intermediate between the development of first generation membrane process such as reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), electrodialysis (ED) and second generation membrane process such as gas separation (GS), pervaporation (PV) [2].

The membrane is the heart of every membrane process and can be considered as a permselective barrier between two phases. Feed phase and permeate is called “feed” and usually is considered as the feed or upstream side phase while phase 2 is considered the permeate or downstream side. The feed stream is divide into two streams in membrane processes, i.e. into the retentate or concentrate stream and the permeate stream, which implies that either the concentrate or permeate stream is the product. It can be shown in Figure 1.1.

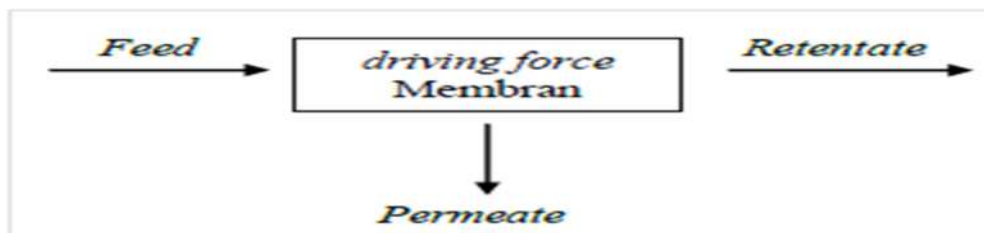


Figure 1.1. Schematic basic principal in membrane technology

The retentate is that part of the feed that does not pass through the membrane, while the permeate is that part of the feed that does pass through the membrane. The optional “sweep” is a gas or liquid that is used to help remove the permeate. The component of interest in membrane separation is known as the solute. The solute can be retained on the membrane and removed in the retentate or passed through the membrane in the permeate.

1.2. Type of Membrane

There are two types of membrane : isotropic and anisotropic membrane (figure 1.2).

1.2.1. Isotropic membrane

- Microporous Membranes

A microporous membrane is very similar in structure and function to a conventional filter. It has a rigid, highly structured network with randomly distributed and interconnected pores. These pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 μm in diameter. All particles larger than the largest pores are completely rejected by the membrane. Particles smaller than the largest pores, but larger than the smallest pores are partially rejected, according to the pore size distribution of the membrane. Thus, separation of solute using a microporous membrane is mainly a function of molecular size and pore size distribution, for example in ultrafiltration and microfiltration [3].

- Nonporous, Dense Membranes

This type consists of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. It can separate permeants of similar size if their concentration in the membrane material differs significantly. Most gas separation, pervaporation and reverse osmosis membranes use dense membranes to perform the separation. Usually these membranes have an anisotropic structure to improve the flux [3].

- Electrically Charged Membranes

Electrically charged membranes should be dense with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is

referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called a cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectivity decrease. Electrically charged membranes are used for processing electrolyte solutions in dialysis and electro dialysis [3].

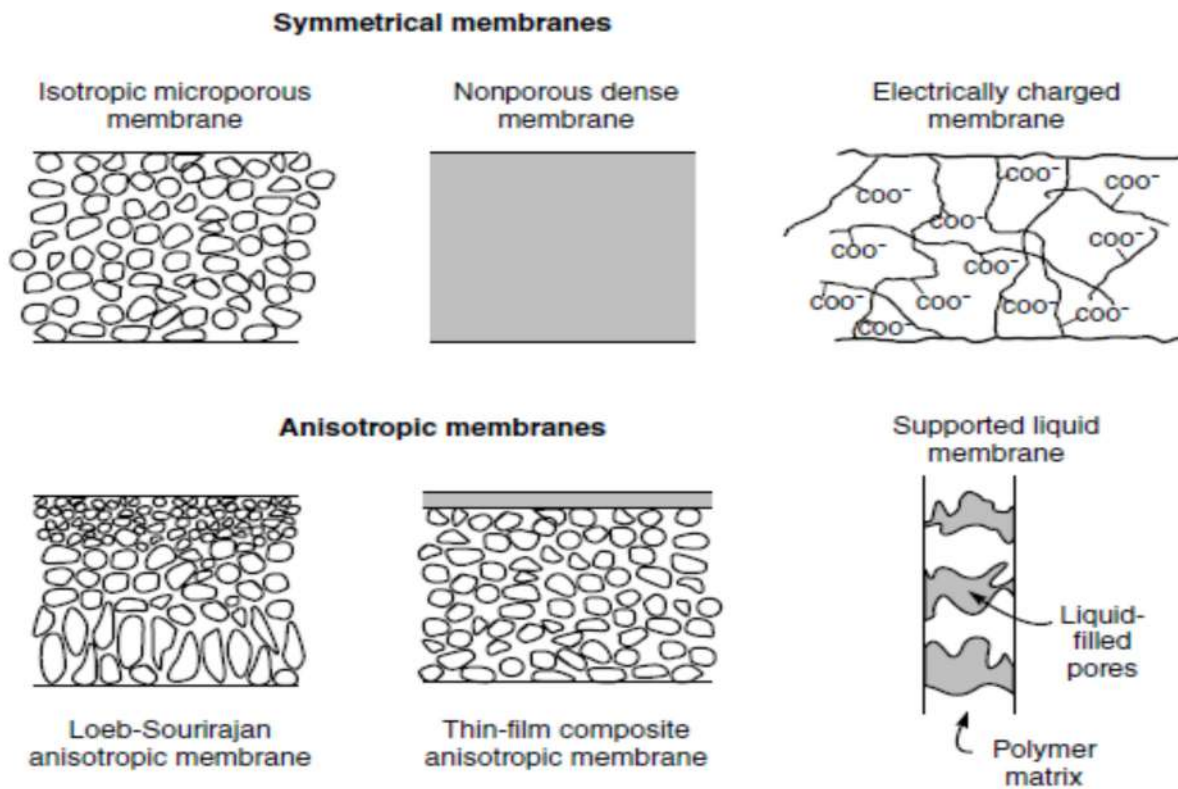


Figure 1.2 Schematic diagrams of the principal type of membranes

1.2.2. Anisotropic Membranes

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons. Therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong, defect free films to about 20

μm thickness. The development of novel membrane fabrication techniques to produce anisotropic membrane structures was one of the major breakthroughs of membrane technology during the past 30 years. Anisotropic membranes consist of an extremely thin active surface layer supported on a much thicker, porous substructure. The surface layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such type of membranes [2].

1.2.3. Ceramic, Metal and Liquid Membranes

Ceramic, metal and liquid membrane are the new membrane material in 1975 - 1980. Before this few years ago, researchers more familiar with organic polymer membrane material. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from gas mixtures, and supported liquid films are being developed for carrier facilitated transport processes [3].

1.3. Classification of membrane technology

In membrane technology, we can divided into 4 classification of it. They are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). On each class, they have specific content, characteristic, application and how they works each other. So, there will be shown all contents one by one.

1.3.1. Microfiltration (MF)

Microfiltration is a type of physical filtration process where a contaminated fluid is passed through a special pore sized membrane to separate microorganism and suspended particles from process liquid.

Microfiltration membranes can generally operate in one of two configurations.

- Cross-flow filtration. This process operate where the fluid is passed through tangentially with respect to the membrane [4]. Part of the feed stream containing the treated liquid is

collected below the filter while parts of the solvent are passed through the membrane untreated. It will be illustrated in Figure 1.3 b.

- Dead-end filtration. This process operate when all of the process fluid flows and all particles larger than the pore sizes of the membrane are stopped at its surface. All of the feed solvent is treated at once subject to cake formation [4]. This process is mostly used for batch or semicontinuous filtration of low concentrated solutions [5] and shown in Figure 1.3 a.

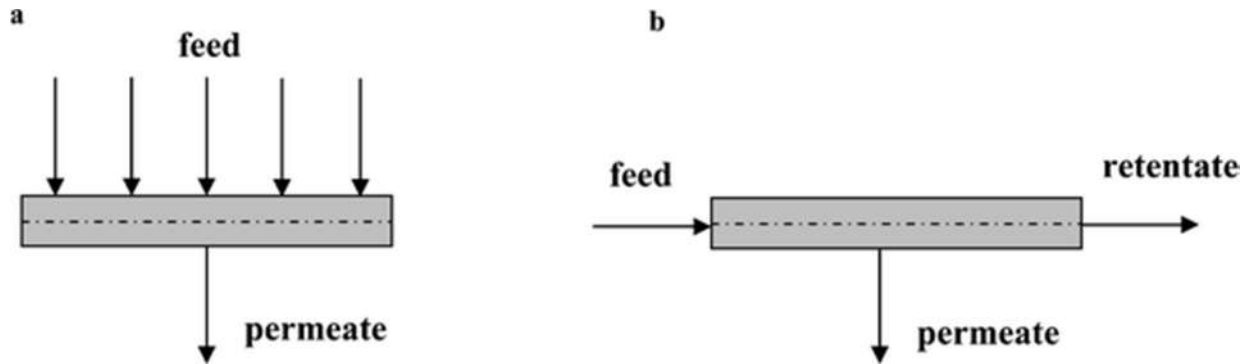


Fig. 1.3 Schematic representation of (a) dead-end filtration and (b) Cross flow filtration.

In mikrofiltration (MF) process for the retention of suspended material particle size of 0.1 to 10 μm [6]. Microfiltration membrane (MF) can be remove of larger bacteria, yeast and particles. Typical operating pressure this membrane is 0.1 - 0.3 MPa. Molecular mass of MF is > 5000 kDa.

In industry process, microfiltration (MF) membrane can be use as an water treatment, sterilization, petroleum refining [6] and dairy processing. Other application are clarification and purification of cell broths where macromolecules are to be separated from other large molecules, proteins or cell debris [6] and also production of paints and adhesives [7].

1.3.2. Ultrafiltration (UF)

Ultrafiltration is a variety of membrane filtration in which forces like pressure or concentration gradients lead to a separation through a semipermeable membrane. Suspended solids and solutes of high molecular weight are retained in the retentate, but for solvent and low molecular weight pass through into permeate. Ultrafiltration is not fundamentally different from microfiltration. Both of them based on the size exclusion or particle capture.

The best known method for UF membranes is molecular weight cut-off (MWCO).

- Molecular Weight Cut off.

The concept of a molecular weight cut off was conceived and introduced into commerce by Amicon Corporation in the middle 1960. Some of the complications arising from the name were foreseen, others were not. To persons totally unfamiliar with ultrafiltration, MWCO communicated a new concept. The convention set by Amicon in the 1960s, now generally but not universally followed, is to define MWCO as the molecular weight of the globular protein which is 90% retained by the membrane [8].

This definition is not however standardized and MWCO can also be defined the molecular weight at which 80% of the solutes are prohibited from membrane diffusion. In microdialysis process probes typically have MWCO with range from 1000 to 300000 Da and larger thresholds filtration are measured in μm .

Ultrafiltration membrane have pore sizes ranging from 20 - 1000 Angstrom (0.1 micron) [1, 9] and are able to remove of proteins, endotoxins, larger viruses, bacteria and macromolecules [1, 9]. Ultrafiltration has diverse applications which span from waste water treatment to pharmaceutical applications.

A medium pressure process offering retention of proteins, colloids and biological material including particles 0.005 microns or larger (molecular weight greater than 1000 Dalton). Typically operating pressure range from 0.1 – 1MPa. Molecular mass separated by UF is 5-5000 kDa [1, 9]. Application UF in industry such as the dairy industry (milk, cheese), food industry (proteins), metal industry (oil/water emulsions separation and paint treatment) [1].

1.3.3. Nanofiltration (NF)

Nanofiltration is relatively recent membrane filtration process used most often with low total dissolved water such as surface water and fresh groundwater, with the purpose of softening and removal of disinfection by product precursors such as natural organic matter and synthetic organic matter [10, 11].

Nanofiltration membrane have pore size from 2-1 nm. Molecular mass separated by NF is 0.1-5 kDa and for pressure operation will be range from 0.3 – 2MPa [1]. In this membrane Nanofiltration can remove such as viruses, and also 2 valent ions [1].

Water and monovalent ions, as well as low molecular weight substances (less than 250 Dalton) pass through nanofiltration membranes. Divalent or multivalent ions, such as divalent salts, are retained. Operating pressure between 0.8 – 4.1 MPa are typical [1].

1.3.4. Reverse Osmosis (RO)

A high pressure process that retains almost all particles and ionic species, while water and some small organic molecules pass through. Substances with molecular weight above 50 Dalton are retained almost without exception. Operating pressure are typically between 2.1 – 5.9 MPa, but may exceed 7.6 MPa in some applications.

| Cut-offs of different liquid filtration techniques | | | | | | | | | |
|--|-----------------|------|------------------|-----------------|------------------|-----------------|-----------------|---------------------|--|
| Micrometer logarithmic scaled | 0,001 | 0,01 | 0,1 | 1 | 10 | 100 | 1000 | | |
| Angstroms logarithmic scaled | 1 | 10 | 100 | 1000 | 10 ⁴ | 10 ⁵ | 10 ⁶ | 10 ⁷ | |
| Molecular weight (Dextran in kD) | 0,5 | 50 | 7.000 | | | | | | |
| Size ratio of substances to be separated | Solved salts | | Viruses | | Bacteria | | Yeast | Sand | |
| | Sugar | | Pyrogens | Albumin (66 kD) | Red blood cells | | Pollen | Human hair | |
| | Atomic radius | | | | | | | | |
| Separating process | Reverse osmosis | | Ultra filtration | | Micro filtration | | | Particle filtration | |
| | Nano filtration | | | | | | | | |

Figure 1.4. Range membrane based on separations

1.4. Advantages and disadvantages

Membrane technology is an emerging technology and because of its multidisciplinary character it can be used in a large number of separation processes. The benefits of membrane technology [1]:

- Energy consumption is low
- Up-scaling is easy
- Membrane processes can easily be combined with other separation processes
- No additives are required
- Low maintenance

The following drawback should be mentioned [1]:

- Low membrane lifetime
- Generally low selectivity
- Concentration polarization/membrane fouling

1.5. Electrodialysis

1.5.1. Introduction

Electrodialysis is a mass separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. And also electrodialysis is an electrical potential driven process to remove ions from an electrolyte solution or to concentrate this solution. Electrodialysis is used widely today for desalination of brackish water and in some areas of the world it is the main process for the production of portable water. In Japan, electrodialysis is used on a large scale as a pre-concentration step for the production of table salt. Stimulated by the development of new ion-exchange membranes with better selectivities, lower electrical resistance and also improved thermal, chemical and mechanical properties. The other application of electrodialysis in food, drug, wastewater treatment and also chemical process industry as well as in biotechnology. In addition to conventional electrodialysis there are other closely related processes, such as diffusion dialysis, Donan dialysis, electro dialytic water dissociation, etc. Most of these processes that are utilizing standard or special property ion-exchange membranes as a key-elements are still in an early stage of development but they are also rapidly gaining commercial

and technical relevance [12-14]. Ion-exchange membrane are used on a large scale in energy storage such as batteries and fuel cells and in electrochemical production processes.

Although the large scale industrial utilization of electro dialysis began about 20 years ago, the principle of the process has been known for about 100 years. First development began in 1890 from Ostwald who studied the properties of semipermeable membranes and discovered that a membrane is impermeable for any electrolyte if it is impermeable either for its cation or its anion. In 1911, Donnan [15] confirmed this postulate for the boundary of an ion-exchange membrane and its surrounding solution. He also developed a mathematical equation describing the concentration equilibrium and it called “Donan exclusion potential”

The first basic studies related to ion-selective membranes were carried out in 1925 by Michaelis with the homogeneous, weak acid collodium membranes. Around 1940, interest in industrial applications led to the development of synthetic ion-exchanged membranes on the basis of phenol formaldehyde polycondensation resins [16]. In 1940 Meyer and Strauss proposed and electro dialysis process in which anion-selective and cation selective membranes were arranged in alternating series to form many parallel solution compartments between two electrodes [17]. After the importance of the multicell stack arrangement for the economy of the electro dialysis was recognized, and with the development of stable, highly selective ion membrane of low electric resistance in the late 40s by Juda and McRae of Ionic Inc. [18] and Winger et al. at Rohm and Haas [19].

A completely different use of electro dialysis was envisaged in Japan. Here electro dialysis was used for concentrating sodium chloride from seawater to produce table salt [20]. In this application the electrical resistance of the membrane was of prime importance for the economics of the process. The requirement have led to the development of homogeneous membranes with very low electrical resistance but less mechanical strength.

For drugs and food industry and especially into the treatment of certain industrial effluents, further improvements of both the cell system design and the membrane properties, especially their chemical and thermal stability, became necessary. In the early 80s a completely new area of application of electro dialysis had been opened up. At this time Liu et al [21], introduced bipolar membranes for the recovery of acids and bases from the corresponding salts by electrical potential induced water dissociation on an industrial cake.

Electrodialysis can be used to reduce inorganics like radium, perchlorate, bromide, fluoride, iron and manganese and nitrate in drinking water. In addition the technology can be used to recycle municipal and industrial wastewater, recovering reverse osmosis reject, desalting wells, surface waters, final effluent treatment for reuse in cooling towers, whey and soy purification and many other industrial uses. For this kind of applications, this technology has shown best hydraulic recovery and cost effective in front of other membrane technologies, specially compared with Reverse Osmosis (RO). In these sense, the lower residues produced during ED process, is another important advantages of this technique. Moreover, electrodialysis is not always a cost effective option for seawater desalination and does not have a barrier effect against microbiological contamination.

1.5.2. Theory

The schematic diagram described in Fig. 1.5. Electrodialysis is an electrochemical separation process in which ions are transferred through ion exchange membranes by means of a direct current voltage. The process uses a driving force to transfer ionic species from the source water through cathode and anode to concentrate wastewater stream, creating a more dilute stream. Generally, two independent hydraulic circuitries are considered: dilute stream (D) and concentrate stream (C).

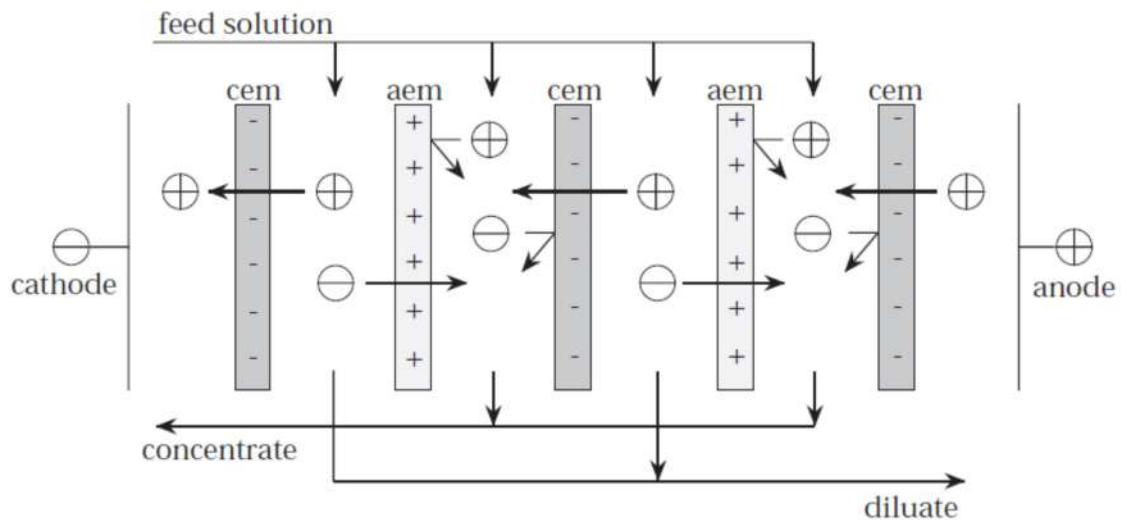


Figure 1.5. Schematic diagram illustrating the principle of electrodialysis

Electrodialysis selectively removes dissolved solids, based on their electrical charge, by transferring the brackish water ions through a semi permeable ion exchange membrane charged with an electrical potential. It points out that the feed water becomes separated into the following three types of water [22]

- Product water, which has an acceptably low conductivity and TDS level
- Brine, or concentrate, which is the water that receives the brackish water ions
- Electrode feed water, which is the water that passes directly over the electrodes that create the electrical potential

1.5.3. Membrane stacks

All electro dialysis systems are designed specifically for a particular application. The amount of ions to be removed is determined by the configuration of the membrane stack. A membrane stack may be oriented in either a horizontal or vertical position. Cell pairs form the basic building blocks of an electro dialysis membrane stack (Figure 1.5). Each stack assembled has the two electrodes and groups of cell pairs. The number of cell pairs necessary to achieve a given product water quality is primarily determined by source water quality, and can design stacks with more than 600 cell pairs for industrial applications [23] A cell pair consists of the following :

- Anion permeable membrane
- Concentrate spacer
- Cation permeable membrane
- Dilute stream spacer

In each stack, we can observe different flows (Figure 1.6):

- Source water (feed) flows parallel only through demineralizing compartments, whereas the concentrate streams flows parallel only through concentrating compartments.
- As feed water flows along the membranes, ions are electrically transferred through membranes from the demineralized stream to the concentrate stream.
- Flows from the two electrode compartments do not mix with other streams. A degasifier vents reaction gases from the electrode waste stream.
- Top and bottom plates are steel blocks that compress the membranes and spacers to prevent leakage inside the stack.

Effluent from these compartments may contain oxygen, hydrogen, and chlorine gas. Concentrate from the electrode stream is sent to a degasifier to remove and safely dispose of any reaction gases.

The first type of commercial electro dialysis system was the batch system. In this type of electro dialysis system, source water is recirculated from a holding tank through the demineralizing spacers of a single membrane stack and back to the holding tank until the final purity is obtained. The production rate is dependent on the dissolved minerals concentration in the source water and on the degree of demineralization required. The concentrate stream is also recirculated to reduce wastewater volume, and continuous addition of acid is required to prevent membrane stack scaling.

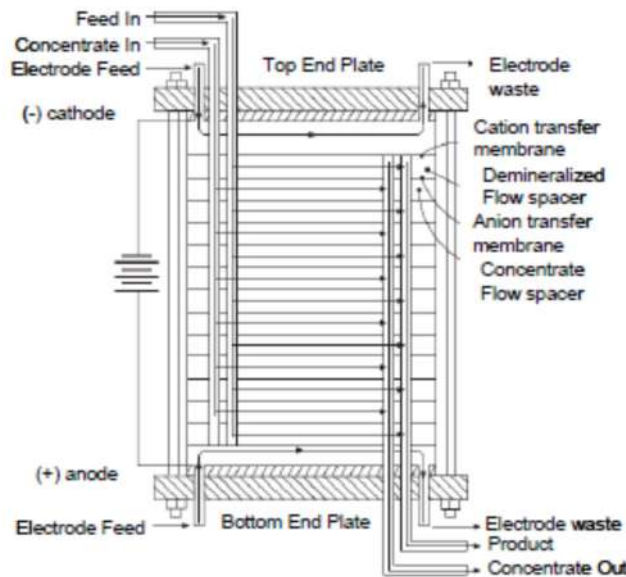


Figure 1.6. Stack description of electro dialysis [24]

The second type of commercially available system was the unidirectional continuous type electro dialysis. In this type of system, the membrane stack contains two stages in series; each stage helps demineralize the water. The demineralized stream makes a single pass through the stack and exits as product water. The concentrate stream is partially recycled to reduce wastewater volume and is injected with acid to prevent scaling.

1.6 Ion exchanged membrane

Ion exchange membranes transport dissolved ions across a conductive polymeric membrane [25]. The membranes are often used in desalination and chemical recovery applications, moving ions from one solution to another while preventing the passage of water [26].

When placed in an electrolyte solution, the affinity of an ion exchange membrane for the ions in the solution is different. The cations, which had the positively charged ions in the solution, are able to penetrate a cation exchange membrane due to the negatively charged fixed groups in the membranes. But the fact, the anions are more or less excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed groups. Ion distribution in a cation exchange membrane and the adjacent solution will be shown in figure 1.7. The mobile ions with opposite charge of the fixed groups are called counter ions, and the mobile ions with the same charge are called co-ions. The exclusion of co-ions is called Donnan exclusion, in honour of his pioneering work [25].

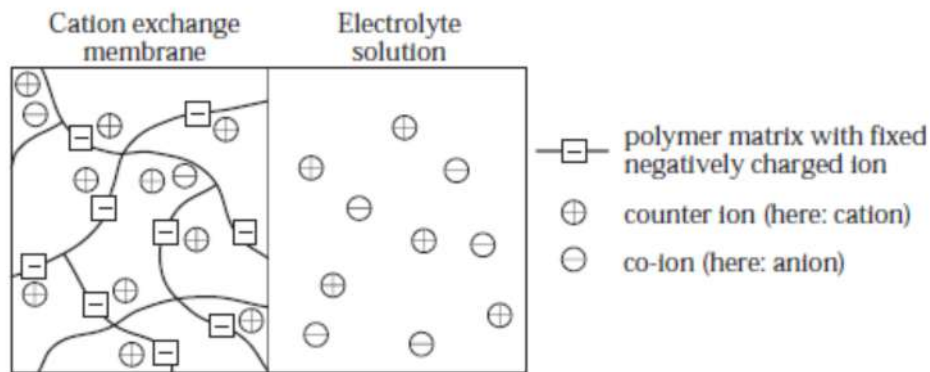


Figure 1.7. Principles of separation achieved by ion exchange membranes

There are two primary classes of membranes:

- (1). *Heterogeneous membranes*. These membranes are low cost, have a thicker composition with higher resistance and rough surface that can be subject to fouling.
- (2). *Homogeneous membranes*. These membranes are more expensive but they have a thinner composition with lower resistance and a smooth surface less susceptible to fouling. Homogeneous membrane surface can be modified to alter the membrane permselectivity to protons, monovalent ions and divalent ions [26].

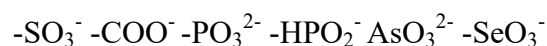
The most desired properties for ion-exchange membranes are :

- *High permselectivity.* An ion exchange membrane should be highly permeable to counter ions but should be impermeable to co-ions.
- *Low electrical resistance.* The permeability of an ion exchange membrane for the counter ions under the driving force of an electrical potential gradient should be as high as possible.
- *Good mechanical and form stability.* The membrane should be mechanically strong and have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions.
- *High chemical stability.* The membrane should be stable over a pH range from 0 to 14 and in the presence of oxidizing agents.

It is difficult to optimize the properties of ion exchange membranes because opposing effects occur. For instance, a good mechanical strength can be achieved by a high degree of crosslinking in the membrane, but this also causes an undesired increase in the electrical resistance. A high concentration of fixed charges in the membrane matrix leads to a low electrical resistance but, in general, causes a high degree of swelling combined with poor mechanical stability.

The properties of ion exchange membranes are determined by the basic polymer matrix and the type and concentration of the fixed ionic moiety. The basic polymer matrix determines to a large extent the mechanical, chemical and thermal stability of the membrane. Often the matrices of ion exchange membranes consist of hydrophobic polymers such as polystyrene, polyethylene or polysulfone. Although these polymers are insoluble in water and show a low, degree of swelling, they may become water soluble by the introduction of ionic groups. Therefore, the polymer matrices are often crosslinked. The degree of crosslinking determines to a large extent the swelling and the chemical and thermal stability, but it also has a large effect on the electrical resistance and the permselectivity.

The type and concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane, but, as mentioned before, they also have a significant effect on the welling and the mechanical properties of the membrane. The most usefull and commercially in cation exchange membrane:



In anion exchange membranes fixed charges may be :



These different ionic groups have significant effects on the selectivity and electrical resistance of the ion exchange membrane. For example, the sulfonic acid group ($-\text{SO}_3^-$), is completely dissociated over nearly the entire pH range, while the carboxylic group $-\text{COO}^-$ is virtually undissociated in pH range < 3 . The quaternary ammonium group $-\text{R}_3\text{N}^+$, again, is completely dissociated over the entire pH range, while the primary ammonium group $-\text{NH}_3^+$ is only weakly dissociated. Ion exchange membranes are referred to as being weakly or strongly acidic or basic in character. Most commercially available ion exchange membranes have $-\text{SO}_3^-$ or $-\text{COO}^-$ groups, and most anion exchange membranes contain $-\text{R}_3\text{N}^+$ groups [27].

1.7 Bipolar membranes

1.7.1 Introduction

A bipolar membrane, a special type of polymeric layered ion-exchange membrane and its consist of an cation and anion-exchange layer which joined together. Bipolar membranes allow the electro dissociation of water into hydroxide ions and protons without generating gases. This membrane water splitting technology is a typical example for process intensification. Electrodialysis with bipolar membrane combines reaction and separation in one unit and allows the design of unique processes like the production and recovery of acids and bases, the variation of the pH of a process stream and the separation of proteins.

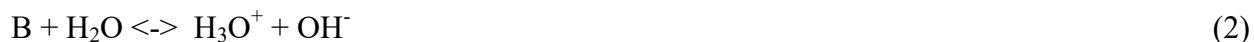
1.7.2 Principle of an Bipolar Membrane

If a CEM (Cation Exchange Membrane) and an AEM (Anion Exchange Membrane) are placed in an electric field and salt solution is fed in between the two membranes, the salt ions are removed from the enclosed compartment (Figure 1.8a). This desalination proceeds until all ions are depleted from the compartment. As a result, a significant increase of the electrical resistance due to the decreased ion conductivity is observed. After the salt ion depletion, current can be only transported by hydroxyl ions and protons generated by water dissociation (Figure 1.8b). To minimize the electrical resistance, the AEM and CEM have to be placed closely together. Laminating both on top of each other results in minimum resistance and a BPM (Bipolar Membrane) is formed. Water diffuses into the BPM from the surrounding solutions and

dissociates under the electric field, at the interface between the anion and the cation exchange membrane, to generate protons and hydroxyl ions (Figure 1.8c).



The layer H^+ and OH^- ions further migrate out of the junction layer through the anion and cation-exchange layers of the BPM. The thickness of the transition region, where the water dissociation take place, is less than 10 nm [28]. Strathmann et al. [29] reported that the water dissociation in BPM is accelerated up to 50 million times compared to the rate of water dissociation in aqueous solutions. This acceleration is influenced by the strong electric field across the transition region. The main driving force for the enhanced water dissociation seems to be the reversible protonation and de-protonation of the functional groups of the ion-exchange membranes, mainly of the tertiary amino groups B of the anion-exchange layer (see Eqs. (2) and (3)) [30].



The BPM can be used not only for the dissociation of water, but also for the splitting of other self-dissociating liquids, like methanol [31].

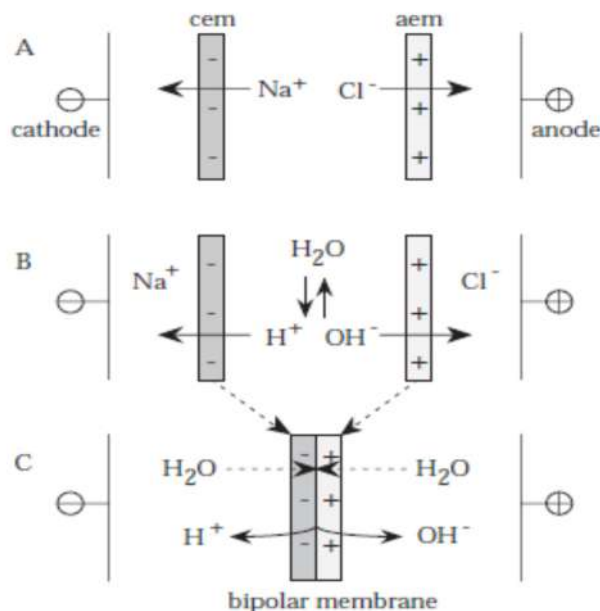


Figure 1.8. The principles of a bipolar membrane (cem is cation exchange membrane, aem is anion exchange membrane)

In combination with anion and cation exchange membranes the water dissociation feature of bipolar membrane can be used to produce acids and bases from the corresponding salt solution. This process is shown in figure 1.9.

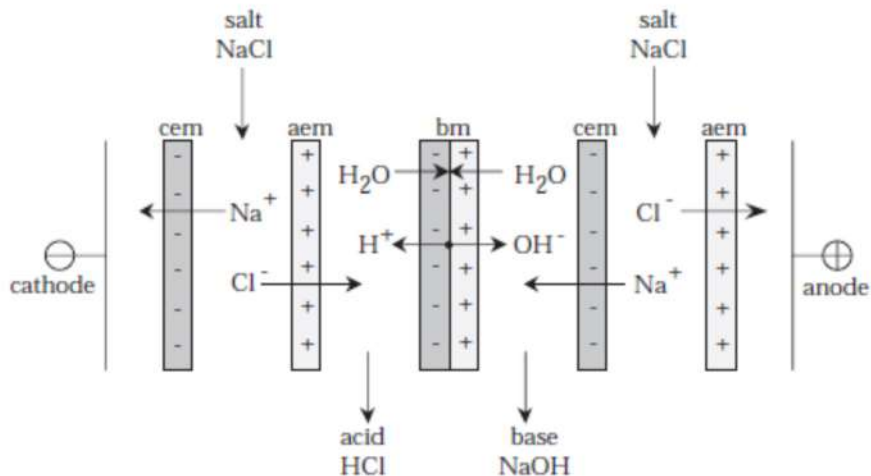


Figure 1.9. Production of acid and base with bipolar membranes (cem refers to a cation exchange membrane, aem refers to an anion exchange membrane and bm to a bipolar membranes).

Bipolar membranes are of considerable interest because their water dissociation capability is an energy efficient process to produce acids and bases. The theoretical potential difference across a 100% permselective bipolar membrane for the generation of a one molar acid and base solution at 25°C can be calculated to be 0.83 Volt. The actual potential bipolar membrane would be higher than this theoretical value because of irreversible effects due to the electrical resistance of the cation and anion exchange layers and the interphase region of the membrane.

An alternative method to produce acids and bases is electrolysis in which water is split by electrode reactions for obtaining the desired H⁺ and OH⁻. Compared to electrolysis the electrochemical production of acids and bases with bipolar membranes has several advantages. A large number of membranes are assembled between one set of electrodes. In contrast, electrolysis needs a set of electrodes for each cell unit, resulting in much higher costs of electrodes and electrical connections. And, electrolysis requires considerably more energy, because of the co-production of oxygen and hydrogen gas at the electrodes. The theoretical energy requirement for production of acid and base depending on the salt being used: to produce one molar acid and

base between 2.1 and 2.2 Volts at 25°C. The advantages of electrolysis is that usually higher concentrations and higher purities of the acid and base can be obtained.

The production of acid and base solution with bipolar membranes offers a broad spectrum of possible applications. Aqueous salt streams are generated as waste streams in many diverse chemical processing operations. With bipolar membranes these streams can be regenerated into acids and bases, in which usually are the precursor chemicals for such waste streams. Other example of bipolar membrane applications are the regeneration of ion exchange resins, the removal of sulfur dioxide from flue gases, the recovery of acid from pickle liquor in the steel production industry and based on the decreasing demand for chlorine, the production of sodium hydroxide as an alternative to the chlor-alkali process.

1.7.3. Limitations of EDBPM

One of the main limiting phenomena of EDBPM (Electrodialysis Bipolar Membrane) is the water splitting performance [32, 33]. Water, which is consumed by the dissociation into protons and hydroxide ions, has to be replenished by diffusion of water from the outer solution of the two monopolar layers into the Bipolar Membrane (BPM) interphase. When the rate of the water dissociation is faster than the water transport into the Bipolar Membrane (BPM) transition region, water transport is the limiting step and results in drying out of the BPM, which cause a drastic increase in the resistance [28, 34]. This performance is controlled by the permselectivities transport. An additional loss of process permselectivity is obtained by the leakage through the monopolar ion exchange membranes (Fig. 1.9). Due to these leakages, the current efficiency of the process is reduced and the purity of the products is limited [35].

Another major limitation is the concentration range in which the EDBPM processes can be used. At very low concentrations, the electric resistance of the electrolyte solution in the compartments between the membranes is very high, whereas at high concentrations the selectivity of the BPM and the ion exchange membranes is very low [36]. Additionally, the chemical stability of the BPM, especially against a concentrated base on the anion permeable side is not always sufficient [37].

1.8 Succinic Acid

Succinic acid also known as butanoic acid, is widely applicate in the food industry, pharmaceuticals, agriculture and as a precursor of many chemical compounds including: adipic acid, 1,4-butanediol tetrahydrofuran N-methyl pyrrodidinone, 2-pyrrolidinone, succinate salts and gamma butyrolactone. Succinic acid is a chemical compound became of significant in recent years, and was identified as one of the top 12 value added chemicals to be produced from biomass in a report released by the US Department of Energy [38]. The properties of succinic acid are listened in the table 1.1. Chemical structure of succinic acid can be shown in Figure 1.10.

Table 1.1: Physical properties of succinic acid

| | |
|-------------------|--|
| CAS Number | 110-15-6 |
| Molecular Formula | $(\text{CH}_2\text{COOH})_2$ |
| Molecular Weight | 118.09 g/mol |
| Melting Point | 188°C |
| Boiling Point | Decomposes at 235°C |
| Specific Gravity | 1.56 |
| Solubility | 100g/100ml at 100°C 7.69g/100ml at 25°C |
| pK _{A1} | 4.21 |
| pK _{A2} | 5.64 |

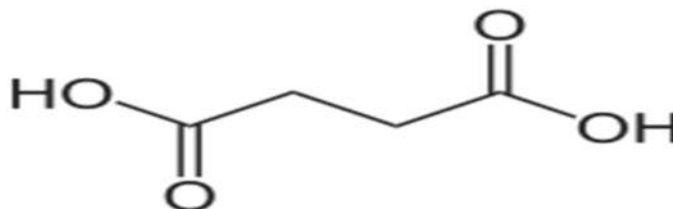


Figure 1.10. Chemical structure of succinic acid

Succinic acid can be used to create a large array of chemicals including resins and biodegradable polymers, as well as surfactants, detergents, pharmaceuticals and food additives [39, 40]. It can also be used as an ingredient in animal feeds and used to stimulate growth in plants [41]. Another major area in which succinic acid can serve as an intermediate chemical is in the creation of 1,4-butanediol, a chemical that was expected to have a demand of 479,000 tons per year by 2008 and 1.5 million tons per year by 2011 [42]. In addition to succinic acid itself, succinate salts were being consumed at a rate of 92,000 tons per year as of 2003, showing a very large demand for succinic acid and its derivatives [42]. Chemical derivatives of succinic acid is shown in figure 1.11.

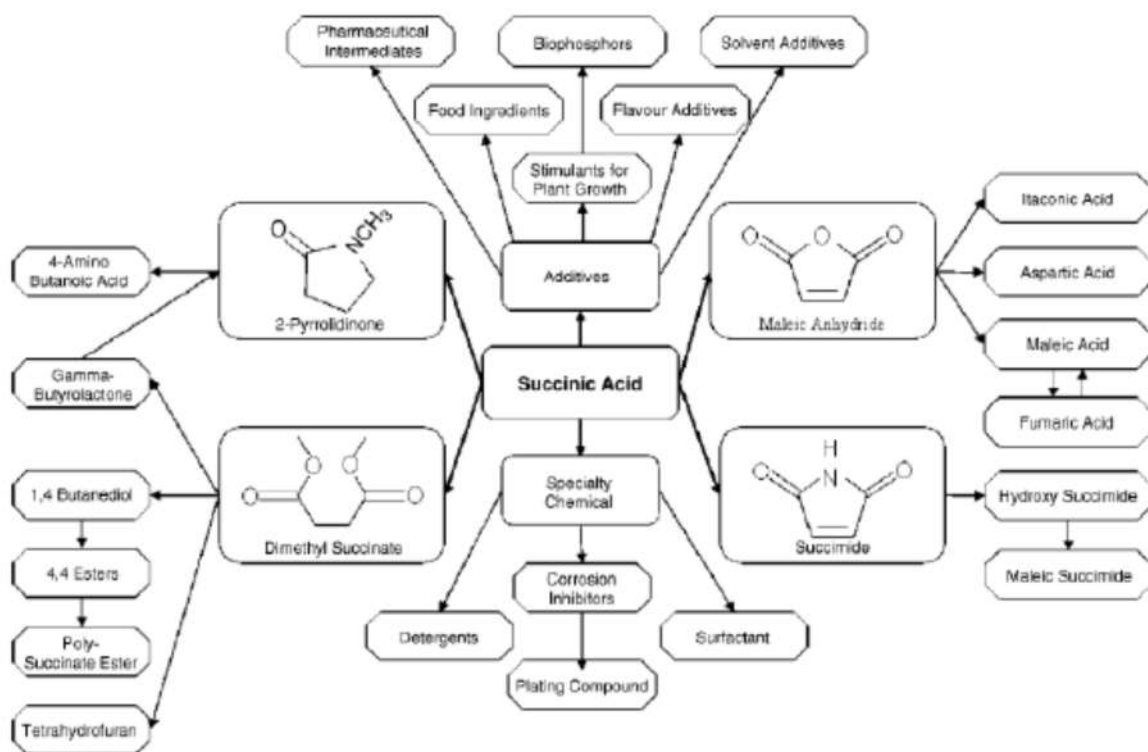


Figure 1.11. Succinic acid and chemical derivatives

Succinic acid can be produced anaerobically through fermentation by bacteria isolated from ruminant animals and is an intermediate of the reductive TCA cycle [39]. Through biochemical production, succinic acid exists in its dissociated form since the pH of fermentation is above its pK_A values of 4.20 and 5.61 [43]. When succinic acid is synthesized from petrochemical sources, it is labelled as chemically produced whereas succinic acid from

bioproduction is considered naturally produced as it is sourced from biomass [44]. This distinction of chemical versus natural production can change the areas in which succinic acid can be used as well as affect the selling price. Industries such as foods and pharmaceuticals will prefer to use succinic acid produced from resources to avoid potential health hazards from production residues even though the product is identical through both production methods [45]. As of early 2008, succinic acid was sold between \$6 and \$9 per kilogram with annual demand of 15,000 tons with growth at six to ten percent per year [46]. As fermentation becomes a more cost efficient method and the number of chemical synthesized from succinic acid increases, demand will rise [47]. Current succinic acid production through petrochemical processing has raw material input cost of \$1.03 per kilogram whereas fermentation has higher costs, although the bioproduction cost estimate varies based on the scale of production [47]. Currently there is no process for bioproduction on an industrial scale and all succinic acid produced today is done so through chemical synthesis.

1.9 Succinic acid production through fermentation

The process of fermentation is receiving increasing attention which is can use renewable feedstocks as substrates and is more green technology compared to chemical production because of its renewable resource consumption and its limited impact on the environment [42]. When succinic acid produced through fermentation, converts glucose to succinic acid along a portion of the reductive cycle of the tricarboxylic acid (TCA) cycle [39]. Figure 1.12 depicts the reaction and enzymes in a typical fermentation process that transforms glucose to succinic acid.

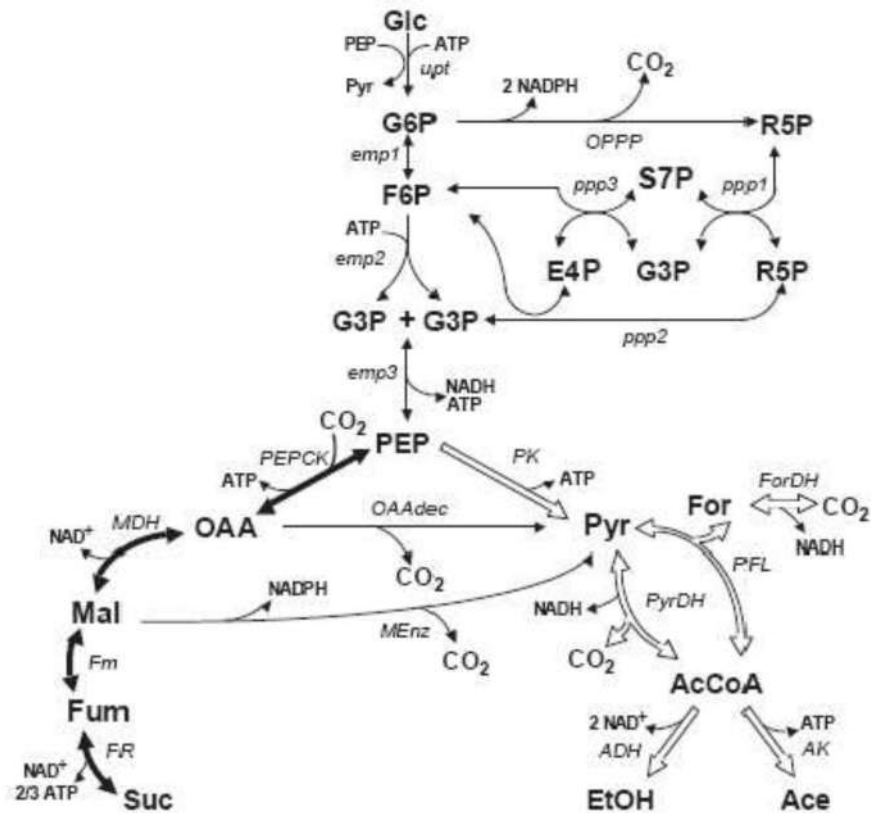


Figure 1.12. Metabolic pathway of a typical succinic acid producing microorganism

First, glucose is converted to glucose 6 phosphate by *hexokinase*, which also adds phosphate to the molecule [48]. Next, three separate enzymes that are part of the *Embden Meyerhoff Pamas* glycolytic pathway lead to the production of phosphor enol pyruvate (PEP) [48]. From PEP, the metabolic pathway can take one of two paths depending on the level of carbon dioxide available to the system [42]. If there is not enough CO₂ present in the system, the preferred metabolic pathway creates end products of formate, ethanol and acetate, as shown the right side of figure 1.12. With ample supply of carbon dioxide to the system, the microorganism favours the production of succinic acid, the left half of figure 1.12 [42]. Through this pathway, PEP is converted to oxaloacetate by PEP carboxykinase with the addition of CO₂. This creates a 4-carbon chain, giving this series of reactions the name “C4 pathway” [43]. The presence of high levels of carbon dioxide in the system strongly regulates the activity of PEP carboxykinase [44]. The next reaction add hydrogen to oxaloacetate to produce malate, which is converted to fumarate by fumarase with the removal of a water molecule. Finally, with the addition of hydrogen, succinate is formed in its ionic state, which is common as the pH range of production

is above the pK_A values for succinic acid [44, 48]. Succinic acid can be created by protonating the succinate ion and producing the undissociated acid, which can be done in a number of different processes. The theoretical yield of succinic acid from glucose plus carbon dioxide should be 1.17 moles of glucose based on stoichiometry [48].

The production method is not without unwanted by products, however. In a study on the fermentation of wheat., acetic acid and formic acid were moderate by products produced in concentration of 9.2g/L and 6.1g/L, respectively. These values are lower than the final concentration of succinic acid at 27.2g/L, but still make the separation process more time consuming and costly. Another major problem, shown on the metabolic pathway in figure 1.12, is that the conversion of glucose to glucose 6 phosphate takes place with the side reaction of converting PEP to pyruvate, an irreversible step.

Succinic acid is also a highly reduced product, so throughout the fermentation process from glucose, four electrons are required. Therefore, in addition to carbon dioxide gas, hydrogen has been suggested as an addition to act as a reducing agent since reductant levels can limit the reaction rate. The addition of hydrogen often decreased fermentation time, making the process more efficient. However other studies make no mention of the addition of hydrogen gas and obtain comparable concentrations of succinic acid. Additionally, other reducing agents, including formate and natural red dye have been used with encouraging results [48].

For bioproduction of succinic acid to be economical, major areas of biological process improvement need to be addressed, including limiting the use of low cost amino acids, achieving high yield and concentration and using inexpensive carbon sources [50]. Fermentation requires both substrate and media which contain the energy sources, nutrients and minerals needed to ensure optimal productivity rates [39]. Depending on the microorganism chosen for the fermentation process, there are many carbon source available. In the case of succinic acid production, most of the major sugars present in biomass can be used effectively, including glucose, fructose, arabinose and xylose [48]. While the cost of these sugars is relatively low, other carbon sources have been examined, in attempts to lower the cost of fermentation. These other sugars range from glycerol and wood hydrolysate to waste whey from milk and cheese production [41, 46].

Chapter II

AIM of STUDY

The aim of presented study was to conduct research on the possibility of separation and concentration of succinic acid from solutions of model and real post-fermentation broth with using current membrane separation techniques. An additional objective of the study was the selection of appropriate operating parameters of electro dialysis with bipolar membranes (current density, volumetric flow rate) and the parameters of the test solutions (the initial concentration of salts of succinic acid in the diluate and concentrate chambers, the composition of separated solutions) and a method of carrying out the process (continuous, batch).

The scope of the performed research included:

- Preparation of model solutions with a composition similar to the composition of real post-fermentation broth,
- Preparation of the starting solutions for diluate and concentrate chambers,
- Conducting the processes of bipolar electro dialysis (EDBM) (sampling chamber diluate and concentrate during the process),
- Analysis of changes in the concentration of components in the solutions undergoing the process of separation,
- Calculation of: the degree of desalination, the unit value of the energy required to produce 1 kg of succinic acid and the current efficiency of carried out processes, the degree of retention of the components separated in the EDBM process.

CHAPTER III

EXPERIMENTAL PART

2.1. Materials

3.1.1. Model solutions

In carried out research succinic acid, glycerol, lactose, ethanol, acetic acid, formic acid, lactic acid and fumaric acid have been used for preparation of model solutions. Model solutions contained from 1 to 7 organic compounds. Composition of the solution containing 7 components was the most similar to real post-fermentation broth. The pH of model solutions was adjusted to 8.5 using sodium hydroxide. All reagents shown in table 2.1, came from Sigma-Aldrich and POCH SA.

Table 3.1. Reagents used in research

| Component | Producer | Purity |
|------------------|---------------|---------|
| Succinic acid | Sigma-Aldrich | 99% |
| Formic acid | POCH SA | 80% |
| Lactic acid | Sigma-Aldrich | 80% |
| Acetic acid | POCH SA | 80% |
| Glycerol | POCH SA | CZ. D.A |
| Ethanol | POCH SA | 96% |
| Lactose | POCH SA | CZ. D.A |
| Sulphuric acid | POCH SA | 95% |
| Sodium hydroxide | POCH SA | 99% |

3.1.2. Post-fermentation broth

Post-fermentation broth applied into multistage process of separation and concentration of succinic acid from solution after bioconversion of glycerol had following composition: succinic acid 14.3 g/dm³, glycerol 34.1 g/dm³, lactose 16.1 g/dm³, ethanol 7.1 g/dm³, acetic acid

7.1 g/dm³, formic acid 4.7 g/dm³, lactic acid 4.1 g/dm³, fumaric acid 0.8 g/dm³ and magnesium salts 12.4 g/dm³. pH of solution was 8.5.

3.2. Research equipment

3.2.1. Electrodialysis with bipolar membrane unit

Bipolar electrodialysis unit was equipped with 10-chamber membrane module containing three kinds of ion-exchange membranes produced by PC Cell GmbH:

- Bipolar membrane PC 200bip (10 pieces)
- Anion exchange membrane PC 200D (10 pieces)
- Cation exchange membrane PC SK 250 (1 piece)

The active area of each membrane was equal to 207 cm². Thickness of the spacers between membranes was equal to 0.5 mm. Detailed parameters of the membranes are shown in Table 2.2.

EDBM unit was also connected with a peristaltic pump (Verder), DC power supply (NDN) and multifunction meter CX-505 (Elmetron) to measure pH-value, conductivity and temperature during bipolar electrodialysis processes.

The cathode was made of steel 314 and the anode was made of titanium plated with iridium.

Table 3.2. Properties of the membrane used in the EDBM processes [51].

| Membrane | AEM | CEM | BM |
|--------------------------------------|--------------|-----------|-----------|
| Symbol | PC 200D | PC SK 250 | PC 200bip |
| Manufacturer | PC Cell GmbH | | |
| Thickness (μm) | 99 | 164 | 222 |
| T _{max} (°C) | 50 | - | 40 |
| pH range | 0-12 | 1-14 | 0-12 |
| Area resistance (Ω/cm ²) | 2 | 1.5-2 | 1-2.5 |
| Voltage drop (V) | - | - | 1.2-2.2 |
| Selectivity (%) | 0.91 | 0.95 | - |
| Efficiency (%) | - | - | >98 |



Figure 3.1. Electrodialysis with bipolar membrane unit

3.2.2. Ultrafiltration unit

Ultrafiltration unit applied in these research was equipped with two ceramic membranes with three-channel tubular configuration and MWCO = 15 kDa. Process was carried out under following conditions: TMP = 0.4 MPa, $T = 25 \pm 2$ °C, $t = 16$ h and $Q_f = 300$ dm³/h. Samples of feed, permeate and retentate were collected at intervals of 1 h. Volume of each sample was equal 2 cm³.



Figure 3.2. Ultrafiltration unit

3.2.3. *Ionic tower unit*

Ionic tower unit with volume 1 dm³, was equipped with sodium ion exchange resin. Ion exchange capacity of tower equals 1.5 mol/dm³.



Figure 3.3. Ionic tower unit

3.2.4. *Nanofiltration unit*

Nanofiltration module was equipped with flat polymeric membrane GE Osmonics Thin Film NF DL, PN: YMDL SP 3001 with MWCO 150-300 Da. NF process was carried out under following conditions: TMP = 1.6 MPa, T = 25 ± 2 °C and Q_f = 300 dm³/h. Samples of feed, permeate and retentate were collected at intervals of 1 h. Volume of each sample was equal to 2 cm³.



Figure 3.4. Nanofiltration unit

3.3. Analytical methods

Concentration of organic components of model solutions and all fractions of real post-fermentation broth obtained during research was determined by high performance liquid chromatography using HP Agilent 1100 Series (Germany) equipped with HP 35900 interface autosampler, HP 1047 RI Detector, HP 1050 pump and Phenomenex® Rezex ROA-OrganicAcid H⁺ (8%) column. 2.5 mM H₂SO₄ have been used as eluent. Flow rate of eluent have been 0.5 cm³/min. Temperature of column and inlet detector was 50 °C, P = 56 bar. All samples were acidified before the measurement to pH ≤ 2 by adding 0.1 cm³ 2.5% H₂SO₄ to 1 cm³ of tested solution. Concentration of inorganic salts was determined by titration with EDTA in the presence of Eriochrome black.

3.4. Calculations

3.4.1. Current efficiency

The current efficiency of bipolar electro dialysis was calculated using the equation (1) [51]:

$$CE = \left(\frac{-F \cdot z_+ \cdot v_+ \cdot V_{dil} \cdot \Delta C_{dil}}{n \cdot I \cdot \Delta t} \right) \cdot 100\% \quad (1)$$

where F (C/mol) is the Faraday's constant, z , z^+ , v^+ is the ionic valence and number of cations respectively, V_{dil} (dm^3) is the volume of diluate, ΔC_{dil} (mol/dm^3) is the concentration difference in diluate chamber at the beginning and the end of the process, I (A) is the current and Δt (s) is the time requirement in process, and n is the number of cell pairs.

3.4.2. Energy consumption

The average value of energy consumption necessary to produce 1kg of succinic acid using bipolar electro dialysis process is described in equation (2) [51] :

$$E = \frac{U \cdot I \cdot t}{m} \quad (2)$$

where E (kWh/kg) is energy consumption, I (A) is current, U (V) is the electric potential difference, and m (kg) is mass of succinic acid.

3.4.3. Desalination degree

The desalination degree of components in diluate chamber was calculated using the equation (3) [52]:

$$\eta_{\text{des}} = (1 - (C_{\text{dil}}^t / C_{\text{dil}}^0)) \cdot 100\% \quad (3)$$

where C_{dil}^0 and C_{dil}^t are the concentrations (g/dm^3) of succinic acid in the diluate chamber respectively at the beginning of process and within a time equal to t .

3.4.4. Retention

The retention of the components of solutions in the nanofiltration process was calculated from the equation (4) [52]:

$$R = (1 - C_p / C_f) \cdot 100\% \quad (4)$$

where C_p and C_f (g/dm^3) are the concentrations of each component in the permeate and feed fractions.

Chapter IV

Results and discussion

4.1. Result data of experimental work

All experimental work was performed with my partner B.Eng. Mateusz Marek Szczygięła.

In table 4.1. shows all the data obtained during the study of EDBM processes on model solutions. All parameters include i (A/m^2), flow rate (dm^3/h), CE (%), E (kWh/kg), $C_{SA} D$ and $C_{SA} C$ (g/dm^3).

Table 4.1. Data of all EDBM processes of model solutions

| Process | i , A/m^2 | Flow rate, dm^3/h | $C_{SA} C$, g/dm^3 | $C_{SA} D$, g/dm^3 | $C_{SA} C:C_{SA} D$ | η_{des} , % | CE , % | E , kWh/kg |
|---------|------------------|------------------------|--------------------------|--------------------------|---------------------|---------------------|-------------|-------------------|
| 1 | 90 | 50 | 4 | 4 | 1:1 | 91 | 25.09 | 4.6 |
| 2 | 90 | 50 | 4 | 13 | 1:3.25 | 91 | 15.1 | 5.66 |
| 3 | 90 | 100 | 43 | 43 | 1:1 | 56.3 | 30.5 | 2.8 |
| 4 | 120 | 100 | 43 | 43 | 1:1 | 68 | 26.3 | 3.4 |
| 5 | 90 | 50 | 43 | 43 | 1:1 | 47.7 | 25.84 | 3.3 |
| 6 | 90 | 100 | 6.6 | 43 | 1:6.5 | 58.7 | 31.84 | 2.7 |
| 7 | 120 | 100 | 6.6 | 43 | 1:6.5 | 70.9 | 28.14 | 3.2 |
| 8 | 120 | 100 | 0 | 43 | 0:43 | 76 | 29.7 | 2.9 |
| 9 | 120 | 100 | 0 | 43 | 0:43 | 78.7 | 55.3/30.7 | 1.7/3.21 |
| 10 | 120 | 100 | 0 | 21.9 | 0:21.9 | 71.3 | 14.2 | 6.7 |
| 11 | 120 | 100 | 0 | 33.3 | 0:33.3 | 76.8 | 23.2 | 4.14 |
| 12 | 90 | 100 | 0 | 33.3 | 0:33.3 | 66.8 | 27.99 | 4.5 |
| 13 | 120 | 100 | 0 | 100 | 1:100 | 53.65 | 49 | 2.2 |
| 14 | 120 | 100 | 100 | 100 | 1:1 | 28.4 | 26 | 3.92 |
| 15 | 120 | 100 | 0 | 200 | 1:200 | 41.55 | 75 | 1.3 |
| 16 | - | 100 | 100 | 100 | 1:1 | 0 | - | - |
| 17 | - | 100 | 0 | 100 | 0:100 | 16 | - | - |

4.2. Separation of succinic acid from the model solutions using bipolar electro dialysis

4.2.1. Effect of current density on EDBM processes

To study of the influence of current density on EDBM processes, two values of current density were used 90 and 120 A/m² respectively for process 6 and 7. Processes were performed for 3 hours. pH of solutions was adjusted to 8.5, which means that all succinic acid molecules present in solution were as dissociated form. Initial parameters of EDBM processes number 6 and 7 are shown in table 4.2. Compositions of solutions in diluate and concentrate chambers are shown in table 4.3.

Table 4.2. Initial parameters of EDBM processes 6 and 7

| Process | i , A/m ² | Flow rate, dm ³ /h | $C_{SA} C$, g/dm ³ | $C_{SA} D$, g/dm ³ | $C_{SA}C:C_{SA}D$ |
|---------|---------------------------|----------------------------------|-----------------------------------|-----------------------------------|-------------------|
| 6 | 90 | 100 | 6.6 | 43 | 1:6.5 |
| 7 | 120 | 100 | 6.6 | 43 | 1:6.5 |

Initial composition of working solutions in diluate and concentrate chambers is shown in table 3.3

Table 4.3. Initial composition of working solution

| Component | C_D , g/dm ³ | C_C , g/dm ³ |
|---------------|------------------------------|------------------------------|
| Succinic acid | 43 | 6.6 |
| Glycerol | 42 | - |
| Lactose | 20 | - |

Changes in concentration of succinic acid during EDBM process 6 and 7 shown in Figure 4.1. and Figure 4.2 indicates, that the transport of succinate ions through the anion-exchange membranes is increasing with increasing value of applied current density. Because of ionic form, succinates migrate easily through the anion-exchange membranes from diluate to concentrate chamber under the influence of current. As can be seen on Figure 4.2, the highest transport of succinate ions from diluate to concentrate is observed in first minutes of process (approximately

15 g/dm³ from start to 30 min), because of high initial gradient of succinates in both chambers. During the process, the gradient of succinic acid concentrations is decreasing, which slows down the migration of ions in the next hours of process (less than 5 g/dm³ between 120 and 180 min). Because of neutral nature of glycerol and lactose, they can't migrate under the influence of current and should be rejected by ion-exchange membranes. However, it can be also seen an insignificant transport of glycerol and lactose from diluate to concentrate, which probably occurs under diffusion transport phenomena as a consequence of their high initial concentration in diluate chamber.

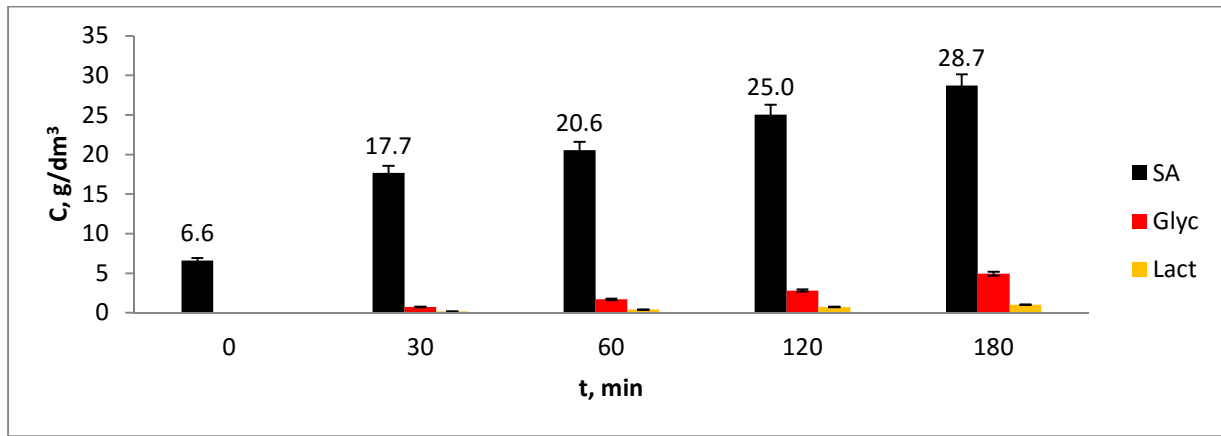


Figure 4.1. Change in concentration of solution components in concentrate chamber during EDBM process 6, $i = 90 \text{ A/m}^2$

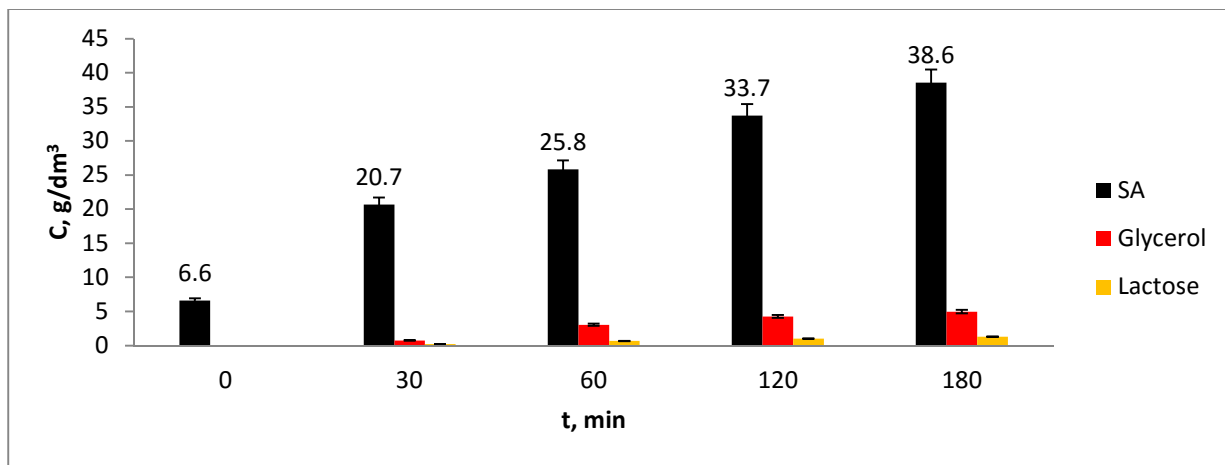


Figure 4.2. Change in concentration of solution components in concentrate chamber during EDBM process 7, $i = 120 \text{ A/m}^2$

Figure 4.3 describe current efficiency during the EDBM process 6 and 7. It can be seen that the higher current efficiency of EDBM is obtained for process which was carried out with lower value of current density (90 A/m^2). In addition, analysis of changing in current efficiency during the process 6 and 7, shown in figure 4.3. indicates, that the current efficiency of EDBM is decreasing with time, independently of applied current density. The current efficiency of process 6, calculated after 30 minutes was equal 98% while after 180 minutes was much lower and equal to 32%. This effect is related with the slowdown in the migration of ions.

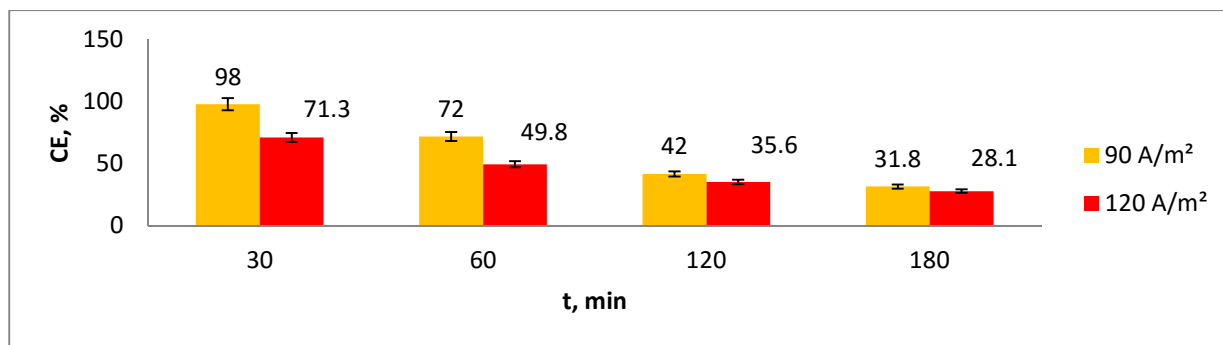


Figure 4.3. Change in current efficiency during EDBM process 6 and 7

The energy consumption necessary to produce 1kg of succinic acid is correlated with the current density applied in EDBM process. As shown in Fig. 4.4, energy consumption was lower for the process conducted with lower current density. After 3 hours of EDBM, the energy consumption in process 6 (90 A/m^2) was equal 2.7 kWh/kg while in process 7 (120 A/m^2) was equal 3.19 kWh/kg.

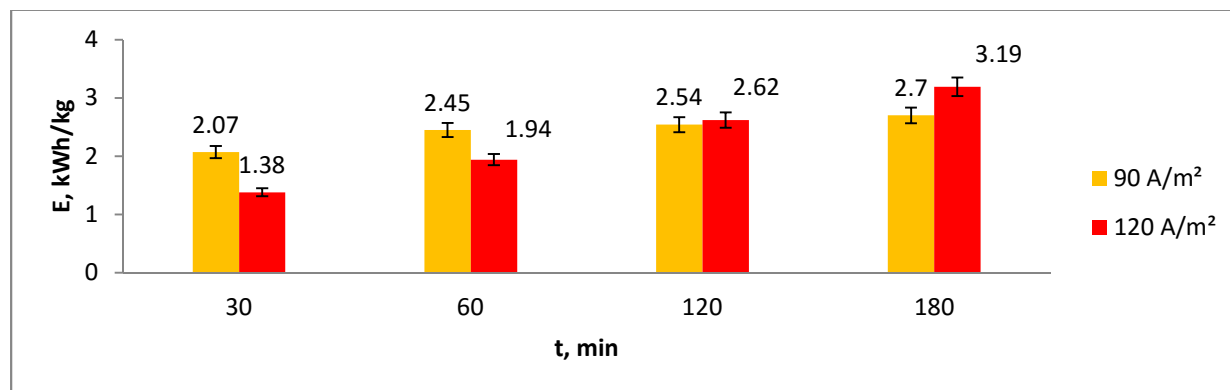


Figure 4.4. Change in energy consumption necessary to produce 1kg of succinic acid during the EDBM process 6 and 7

On the Figure 4.5 is illustrated the summary of energy consumption for producing 1 kg succinic acid (E , kWh/kg), efficiency process (CE , %), percentage desalination (η_{des} , %) process EDBM with applied current density 90 and 120 A/m².

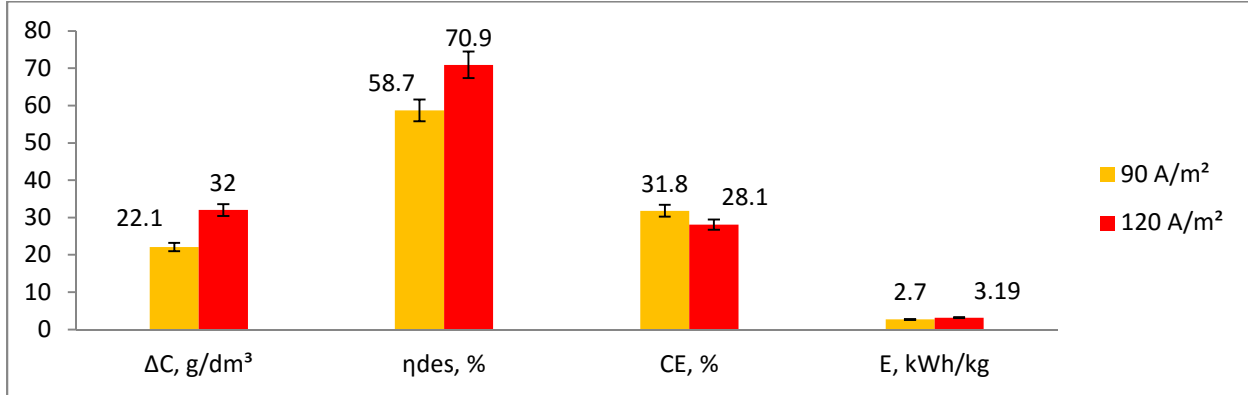


Figure 4.5. Summary in 3 hour in different current density

As shown in Fig. 4.5, with increasing current density, the current efficiency decreased and the energy consumption also slightly increased. The decrease in current efficiency with increasing current density could be explained by hydroxyl anions competition (more hydroxyl anions is generated by bipolar membrane when the current density increases) and the loss of proton after leaking into the diluate chamber through the anion membrane [51]

4.2.2. *Study of the effect flow rate on the bipolar electro dialysis EDBM process*

To study of the influence of flow rate on EDBM processes, two values of flow rate were used 100 dm³/h and 50 dm³/h respectively for process 3 and 5. Processes were performed for 3 hours. pH of solutions was adjusted to 8.5. All parameter of EDBM processes number 3 and 5 are shown in table 4.4.

Table 4.4. Initial parameter of EDBM processes 3 and 5

| Process | i , A/m ² | Flow rate, dm ³ /h | $C_{SA} C$, g/dm ³ | $C_{SA} D$, g/dm ³ | $C_{SA}C:C_{SA}D$ |
|---------|---------------------------|----------------------------------|-----------------------------------|-----------------------------------|-------------------|
| 3 | 90 | 100 | 43 | 43 | 1:1 |
| 5 | 90 | 50 | 43 | 43 | 1:1 |

Initial composition of working solutions in diluate and concentrate chambers is shown in table 4.5

Table 4.5. Initial composition of working solution

| Component | C_D , g/dm ³ | C_C , g/dm ³ |
|---------------|---------------------------|---------------------------|
| Succinic acid | 43 | 43 |
| Glycerol | 42 | - |
| Lactose | 20 | - |

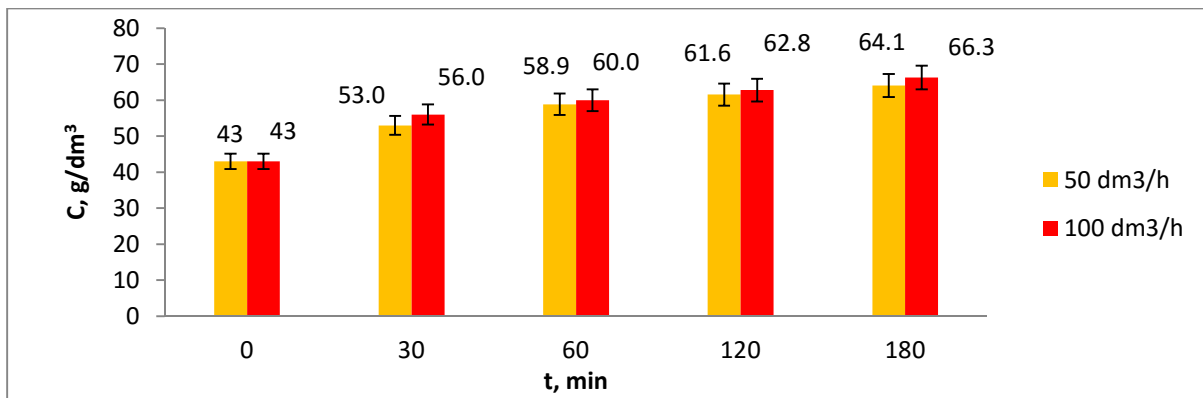


Figure 4.6. Concentration of SA in concentrate chamber with different flow rate

Fig. 4.6. shown on process concentrate chamber, the concentration of succinic acid (SA) was the same when started process (43 g/dm³). After time passes into 30 and 60 minutes, flow rate in process 3 (100 dm³/h) have a high concentration succinic acid (SA) 56 g/dm³ and 60 g/dm³ than process 5 which have concentration of SA 53 g/dm³ and 58.9 g/dm³. But after one

hour left, concentration succinic acid (SA) in process 3 was increased until the end of process (3hour) and also the result was higher than in the case of process 5.

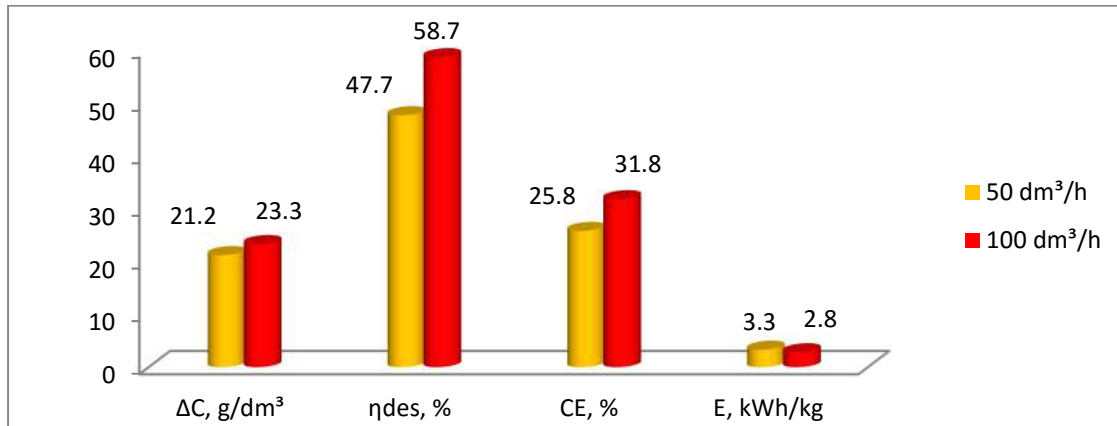


Figure 4.7. The comparison of parameters of EDBM process after 3 hour in different flow rate

The current efficiency (CE), energy consumption (E), desalination degree (η_{des}) and different of concentration of succinic acid (SA) was obtained during EDBM of succinic acid at the flow rate 50 and 100 dm³/h were calculated by Eq. (1) - (3).

As shown in Fig. 3.7, with increasing flow rate, the current efficiency decreased and the energy consumption also slightly increased. So from the graph, we can make conclusion that flow rate 100 dm³/h better than 50 dm³/h to applying into EDBM unit.

4.2.3. Study the effect of amount concentration succinic acid on the chambers (concentrate and diluate) during the EDBM process

In this part of study was analyzed the influence of the amount solution of succinic acid adding into two chambers (concentrate chamber and diluate chamber) on the parameters of EDBM process number 8, 13, 14 and 15. Processes were performed for 3 hour at a constant current density of 120 A/m² and a constant volumetric flow rate of 100 dm³/h. The ratio of the starting salt concentration of succinic acid in the concentrate chamber and diluate chamber will described one by one. Firstly, concentrate chamber: diluate chamber 1:1 which is for process 8, 0:43 for process number 13, 0:100 for process number 14 and 0:200 for process number 15. On the below, table 4.6 shown all parameter of the process, especially for number 8, 13, 14, and 15.

Table 4.6. Initial parameters of EDBM processes 8, 13, 14 and 15

| Proces | i , A/m ² | Flow rate, dm ³ /h | $C_{SA\ C}$, g/dm ³ | $C_{SA\ D}$, g/dm ³ | $C_{SA\ C}:C_{SA\ D}$ |
|--------|------------------------|-------------------------------|---------------------------------|---------------------------------|-----------------------|
| 14 | 120 | 100 | 100 | 100 | 1:1 |
| 8 | 120 | 100 | 0 | 43 | 0:43 |
| 13 | 120 | 100 | 0 | 100 | 0:100 |
| 15 | 120 | 100 | 0 | 200 | 0:200 |

In Figure 4.8, it's about result of different ratio concentration succinic acid depend of the time process in EDBM unit. As seen in figure 3.8., ratio concentration in concentrate chamber and diluate chamber ($C_{SA\ C} : C_{SA\ D}$) 100/100 which yellow color has the lowest ΔC and the highest ΔC was 0/200 which has blue color). ΔC was meaning about the difference gradient of succinic acid between the concentrate and dilute on the process time in EDBM unit.

Look the light blue color (process number 15) which has ratio 0/200 it can be assumed that's ratio has a high different gradient than the other process (number 8, 13, and 14). Because when ΔC high difference on concentrate and diluate chamber, so power for moving or pass through the anion exchange membrane would be easily than the lower ΔC (look process number 8 and 14). This power consists of diffusion transfer and also from applying current density on the system.

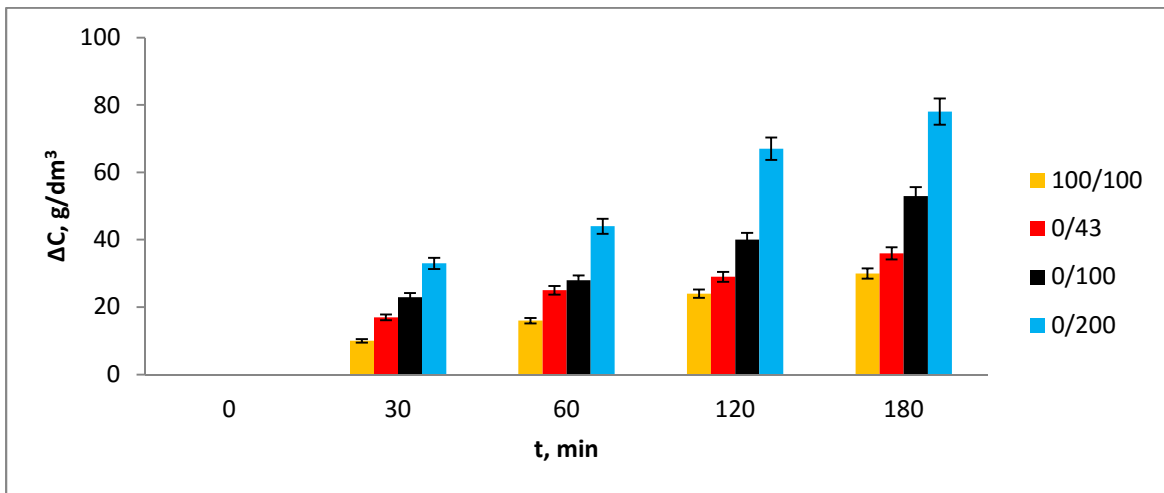


Figure 4.8. Result ΔC of succinic acid in concentrate chamber during the process EDBM

Analysis of changing in different amount succinic acid in concentrate chamber and diluate chamber ($C_{SA} C : C_{SA} D$) on the process 8, 13, 14 and 15, shown in figure 4.9, indicates, that the current efficiency of EDBM is decreasing with the time. Concentration with ratio (0/200) has a greater efficiency process than 100/100. Efficiency process also correlated or connected with energy consumption to produce 1kg of succinic acid. It means that, if the value of efficiency process high, so, energy requirement to production 1 kg of succinic acid will be the better.

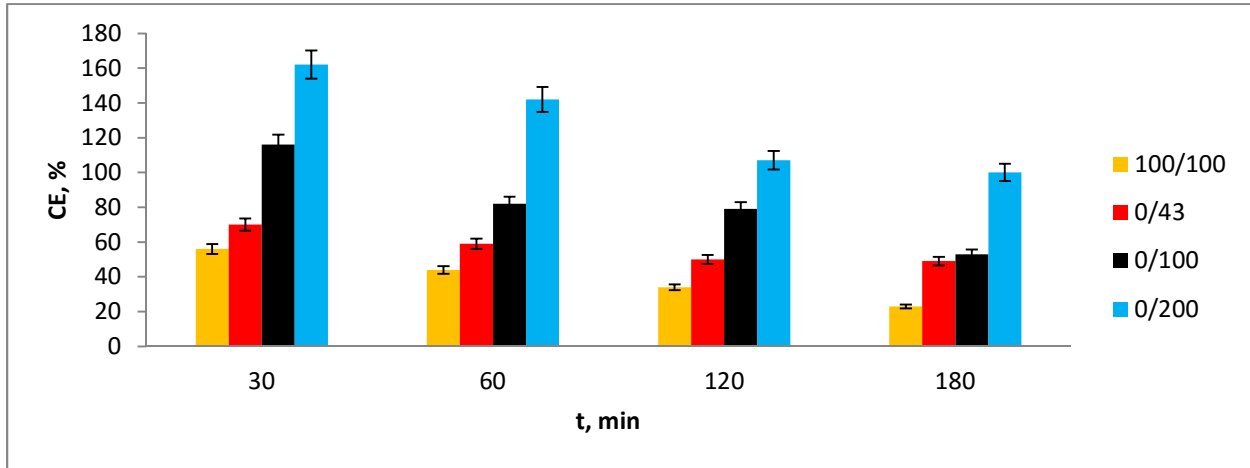


Figure 4.9. Current efficiency with different ratio of succinic acid

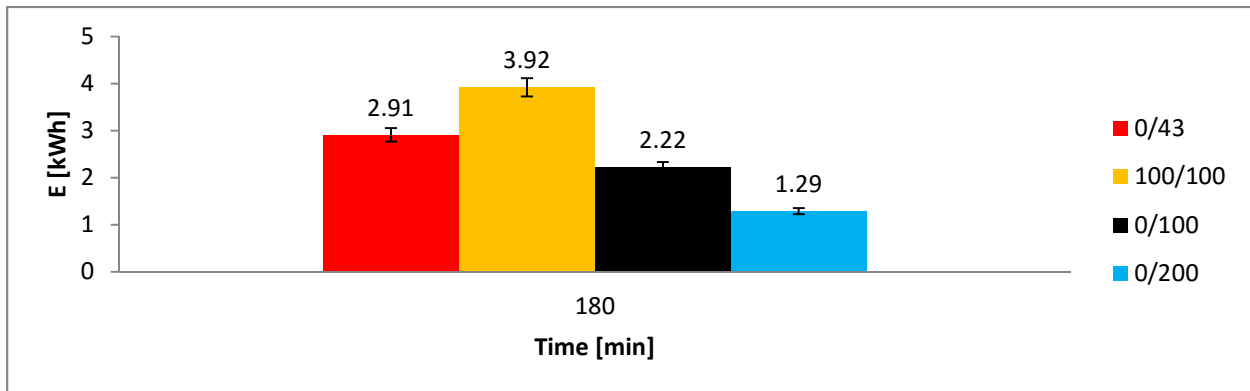


Figure 4.10. Energy consumption for producing 1kg of succinic acid

The energy consumption for producing 1kg of succinic acid are shown in figure 4.10. From figure 4.10, knows that the highest energy to producing 1kg succinic acid with the ratio 100/100 in which E is equal to 3.92 kWh/kg. In other side, the best to produce 1kg of succinic acid was used the ratio 0:200 (process 15). Influence of additional diffusion force has a greatly effect on the transport of succinates ions through the anion exchange membranes in the process

EDBM, an increase in current efficiency of the process and also reducing energy requirements per unit.

4.2.4. Study of the process diffusion dialysis (without current density in EDBM process)

This part explained about the process diffusion dialysis (without applied current density) during the processing. In this work, only two process without applied current density which were performed (process number 16 and number 17). Also these processes using parameter flow rate was 100 dm³/h. The ratio of concentration in concentrate chamber and diluate chamber were different one by one and time operated until 180 minute. Process number 16 was 1:1 (100 g/dm³ : 100 g/dm³) and process number 17 was 0:100 (0 g/dm³ : 100 g/dm³). All parameter for process number 16 and process number 17, shown in table 4.7.

Table 4.7. Initial parameters of EDBM processes 16 and 17

| Proces | <i>i</i> , A/m ² | Flow rate, dm ³ /h | C _{SA} C, g/dm ³ | C _{SA} D, g/dm ³ | C _{SA} C:C _{SA} D |
|--------|-----------------------------|-------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|
| 16 | - | 100 | 100 | 100 | 1:1 |
| 17 | - | 100 | 0 | 100 | 0:100 |

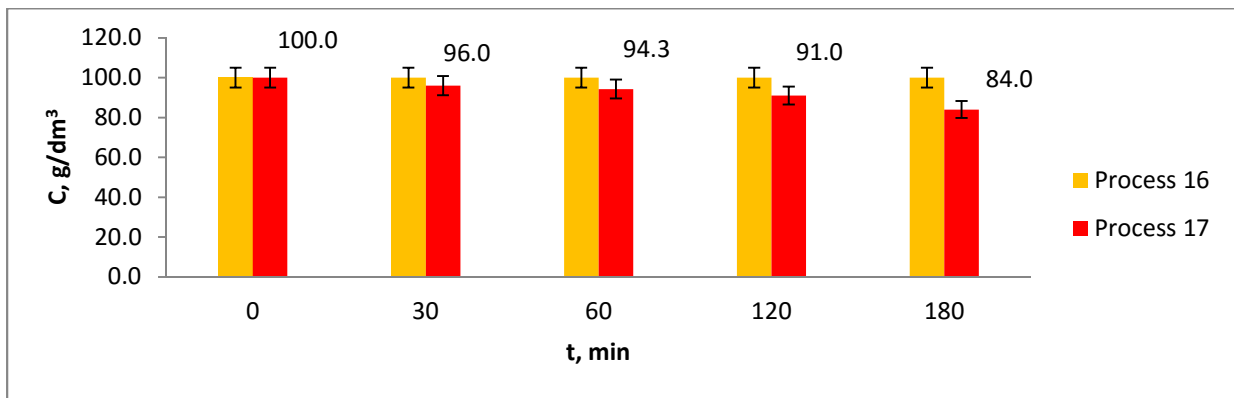


Figure 4.11. Distribution on diffusion dialysis with different concentration amount

In figure 4.11 are show these process of using method of diffusion dialysis, without applied current density on the system. Process number 17 changing and would be decrease concentration of succinic acid in diluate chamber on EDBM unit. It caused by the migration succinate ions from diluate chamber into concentrate chamber. Transport of succinates ions from

diluate to concentrate chamber is not much high in 30 minutes (6 g/dm^3), and also in the next hours of process (less than 6 g/dm^3 between 120 and 180 min).

However, in the process number 16, the concentration succinic acid starting process until the end of processing was the same. This phenomena can be explained by the lack of force and the lack of difference concentration salt (ΔC) in both chamber.

4.2.5. Study of the effect method processing in EDBM unit

Table 4.8. Initial parameters of EDBM processes 8 and 9

| Process | $i, \text{ A/m}^2$ | Flow rate, dm^3/h | $C_{\text{SA}C}, \text{ g/dm}^3$ | $C_{\text{SA}D}, \text{ g/dm}^3$ | $C_{\text{SA}C}:C_{\text{SA}D}$ | Method |
|---------|--------------------|-----------------------------------|----------------------------------|----------------------------------|---------------------------------|------------|
| 8 | 120 | 100 | 0 | 43 | 0:43 | Continuous |
| 9 | 120 | 100 | 0 | 43 | 0:43 | Periodic |

Table 4.9. Initial composition of working solution

| Component | $C_D, \text{ g/dm}^3$ | $CC, \text{ g/dm}^3$ |
|---------------|-----------------------|----------------------|
| Succinic acid | 43 | - |
| Glycerol | 42 | - |
| Lactose | 20 | - |

Method processing in EDBM have been analyzed in process number 8 and 9. Process number 8 used type of continuous system which is circulating process at diluate chamber using closed system and process 9 used type of periodic method which is needed or adding fresh concentrate into the chamber. Time processing of both cases was 3 hour. Current density was setting on 120 A/m^2 , flow rate was $100 \text{ dm}^3/\text{h}$ and the ratio in concentrate chamber and diluate chamber had been $0:43 \text{ g/dm}^3$. Distribution each parameter for process number 8 and 9, shown on the table 4.8. Also distribution components on each chamber before process, shown in table 4.9.

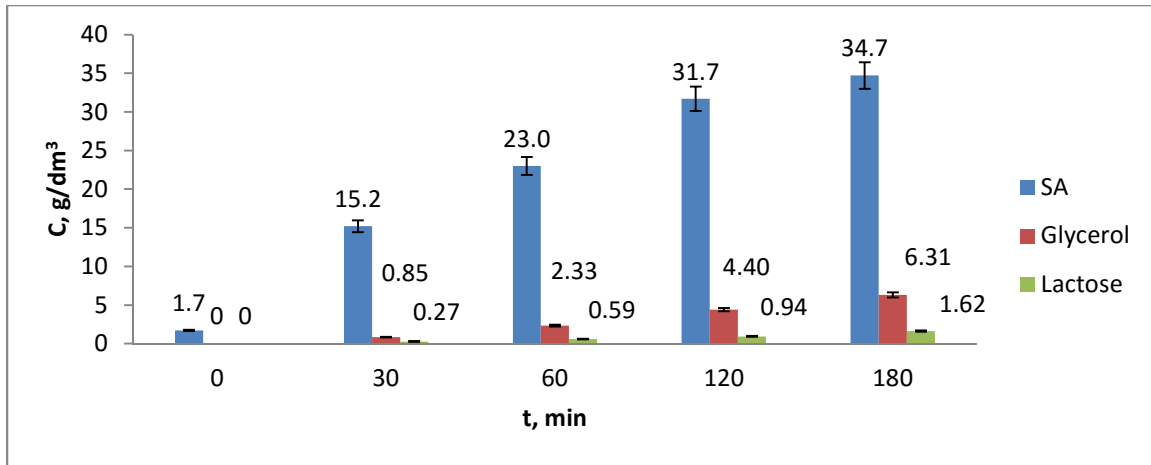


Figure 4.12. Results for all components in concentrate chamber during EDBM process (process number 8)

Figure 4.12. described process number 8 and all result component in concentrate chamber during EDBM processes. As shown in figure 4.12, component succinic acid started with 1.7 g/dm³ when the processes left in 30 minute was 15.2 g/dm³ and after the end of process was 34.7 g/dm³. Based on the result processing at EDBM unit, the huge influence from start into 30 minute left which is 13.5 g/dm³.

This effect is related to the presence of additional diffusion forces to transport succinate ions through anion exchange membrane into the concentrate chamber, caused by the initial concentration gradient between adjacent spaces. However, the growth of succinic acid concentration was decreases during the process. At the same time, it was found that the increase concentration of non-electrolytes in concentrate chamber, in the separate solid solution. And changes linearly during the process EDBM (non-electrolytes are moved through the anion membrane only by transport diffusion).

Based on the results obtained in the process 8, after an hour the passage of EDBM process was found that it is possible to implement a periodic process and simultaneously replenishing the concentrate chamber using 1.5 dm³ clean deionized water to maintain high concentration gradient between adjacent chambers throughout the whole process (180 min.).

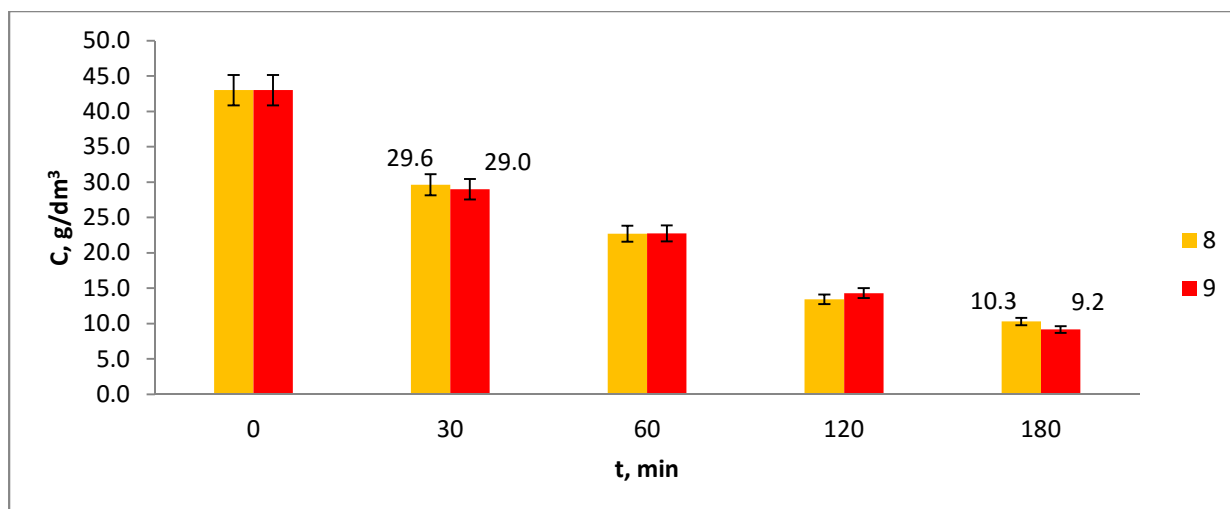


Figure 4.13. Result of concentration succinic acid in diluate chamber

Concentration of succinic acid in diluate chamber (process number 8 and 9) had been no difference each other. From figure 4.13., presented that those data just a little affect for transport/moving ions through into the anion exchange membranes during the EDBM process. Both of method processing way can be applied in EDBM unit because the final amount solution slight similar and no have huge difference with each other.

4.2.6. The study of second step of EDBM process

Table 4.10. Initial parameters of EDBM processes 11 and 12

| Process | i , A/m ² | Flow rate, dm ³ /h | $C_{SA} C$, g/dm ³ | $C_{SA} D$, g/dm ³ | $C_{SA} C:C_{SA} D$ |
|---------|------------------------|-------------------------------|--------------------------------|--------------------------------|---------------------|
| 11 | 120 | 100 | 0 | 33 | 0:33 |
| 12 | 90 | 100 | 0 | 33 | 0:33 |

Process number 11 and 12 using two times separation of succinic acid in EDBM unit. The diluate solution chamber was obtained in the first stage on EDBM processes. Table 4.10, shown that process number 11 and 12 have a same data in with flow rate (100 dm³/h), the ratio between concentrate chamber and diluate chamber were 0:33, time operating being 180 minutes. Then, for current density, process number 11 was operated on 120 A/m² and process number 12 was 90 A/m².

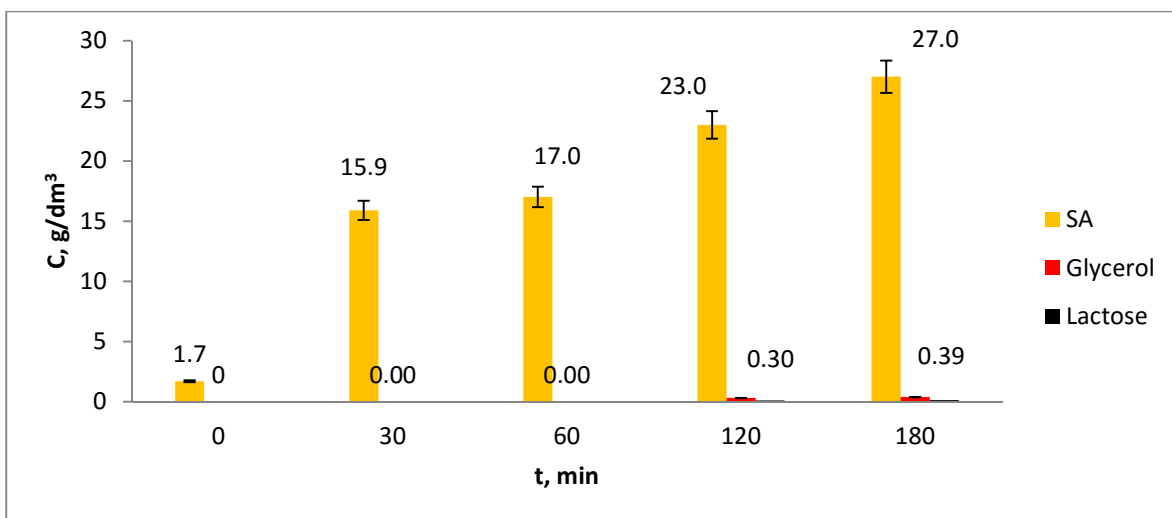


Figure 4.14. Change component during process in concentrate chamber (process 11)

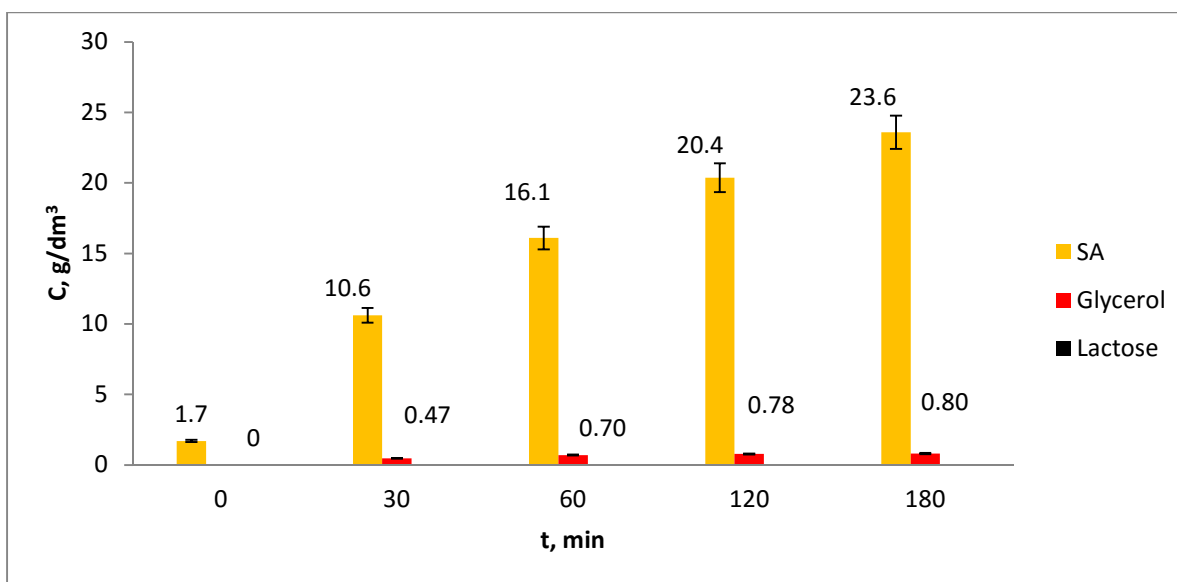


Figure 4.15. Change component during process in concentrate chamber (process 12)

Figure 4.14 and figure 4.15., described about the changing phenomena in concentrate chamber of process number 11 and 12. All component such as succinic acid, lactose and glycerol influence depend of the time passage in this experiment. The highest increase is succinic acid, for glycerol and lactose just minimal development until the end of processes. It means, transport of ions through the anion exchange membranes great affect with succinic acid solution.

Figure 4.14. and figure 4.15., have also correlate with current density which is applied on the EDBM unit. If the current density 120 A/m^2 , there were great achievement and quickly moving transport ions through membrane faster than who has 90 A/m^2 .

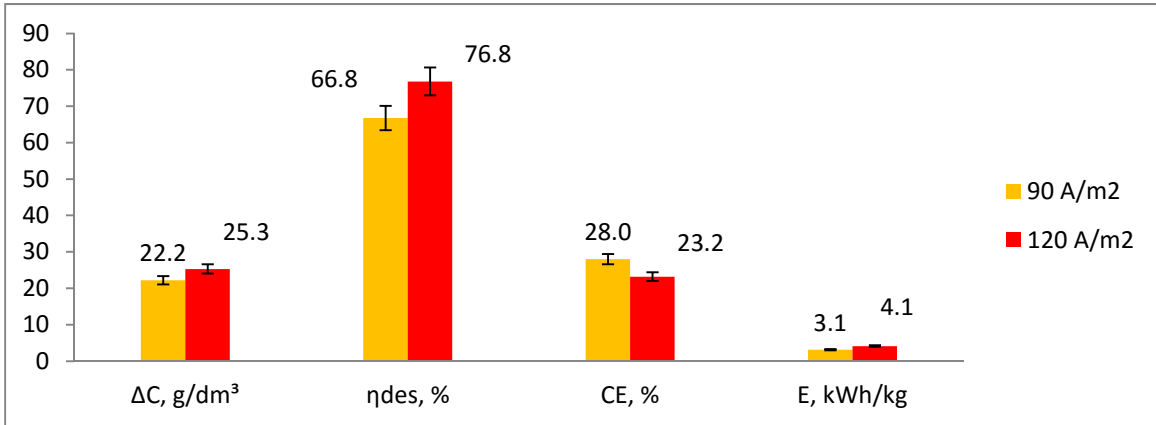


Figure 4.16. Summary all parameter content at 3hour EDBM process

As shown in Fig. 4.16, with increasing current density, the current efficiency decreased and the energy consumption also slightly increased. The decrease in current efficiency with increasing current density could be explained by hydroxyl anions competition (more hydroxyl anions is generated when current density increases) and the loss of proton after leaking into the diluate chamber through the AM (anion membrane) [51]

Chapter V

CONCLUSIONS

Based on the study and the analysis of the results obtained was found that:

1. The composition of separated solution has a significant impact on the performance of bipolar electro dialysis process. The best results are obtained during separation of monocomponent solution of succinic acid. In addition, it was found that the EDBM process yield decreases with increasing amounts of the components present in the separated mixture.
2. The applied value of current density has a significant impact on the performance of the EDBM process. However, the use of higher current density leads to a decrease in current efficiency and an increase in the unit energy required producing 1 kg of succinic acid.
3. It was demonstrated that an increase in the volumetric flow rate in the chamber diluate and concentrate allows a slight improvement in the efficiency of EDBM.
4. The output salt concentration of succinic acid in the concentrate and diluate chamber has a significant impact on process performance EDBM. It has been shown that with the increase in the starting concentration of the salt of succinic acid in the cells a significant increase of the yield of EDBM process (as a result presence of an additional driving force i.e. concentration diffusion) were observed.
5. It was noted a slight increase in the yield of the EDBM processes conducted batchwise with respect to the process conducted continuously (for 3 h).

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