SEPARATION OF HYDROCHLORIC ACID AND GLUCOSE USING ELECTRODIALYSIS

by

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LIST OF SYMBOLS

C_c^t	Electrolyte concentration at time t	[kmole/L]
C_c^0	Electrolyte concentration at initial stage	[kmole/L]
η	Current efficiency	[Dimensionless]
Γ	Recovery percentage	[%]
Δn	Difference in the number of moles of an electrolyte in the product stream at time t (n_c^t) and the initial stage (n_c^o)	[mole]
Δt	Different time	[min]
ΔV	Volume transfer	[L]
ΔX_i	Step change value.	[Dimensionless]
A_m	Overall effective cell pair surface area	[cm^2]
A_{TM}	Total effective membrane area	[cm^2]
D_i	Diffusion coefficient	[Dimensionless]
F	Faraday constant	[C/mole]
I	Current applied to stack	[A]
I_{int}	Current intensity	[A/cm^2]
I_{lim} / S	Limiting current density	[A/cm^2]
J_{Wi}	Water flux	[kmol/m^2.s]
Q_F	Amount of the electrical charges carried by the current	[C]
R_a	Stack resistance	[Ω]
R_{AM}	Resistance of the anion exchange membrane	[Ω]
R_{CM}	Resistance of the cation exchange membrane	[Ω]
R_{cp}	Single-cell-pair resistance	[Ω]
R_F	Resistance of the feed solution	[Ω]
R_P	Resistance of the permeate solution	[Ω]
R_s	Resistance of solution	[Ω]

V	Voltage	[V]
X_i	The natural value of the ith independent variable.	[Dimensionless]
x_i	The coded value of the ith independent variable	[Dimensionless]
X_i^x	The natural value of the ith independent variable at the center point.	[Dimensionless]
Y	The predicted response.	[Dimensionless]
ΔC	Concentration gradient	[mole/L]
ΔE	Electrical potential gradient	[V]
ΔP	Pressure gradient	[N/m^2]
ΔT	Temperature gradient	[K]

LIST OF ABBREVIATIONS

AEM	Anion exchange membrane
CCD	Central composite design
CEM	Cation exchange membrane
CIP	Cleaning-in- place
CV	Constant voltage
DC	Direct current
DoE	Design of experiment
DVB	Divinyl benzene
ED	Electrodialysis
EDI	Electrodialysis ionization
EDR	Electrodialysis reversal
EED	Electro-electrodialysis
EIC	Ion exchange capacity
ES	Electrochemical series
HCl	Hydrochloric acid
PVC	Polyvinyl chloride
RSM	Response surface methodology
UF	Ultrafiltration
$(CH_3)_3N$	Triamine
SO_2Cl	Sulfochlorination
UF	Ultrafiltration
RO	Reverse osmosis
MW	Molecular weight

PEMISAHAN ASID HIDROKLORIK DAN GLUKOSA MENGGUNAKAN ELEKTRODIALISIS

ABSTRAK

Elektrodialisis (ED) merupakan kaedah yang berpotensi untuk pemisahan dan pemekatan asid hidroklorik manakala glukosa yang tidak bertindakbalas diguna semula. Dua bahagian eksperimen dijalankan; bahagian A dan bahagian B. Eksperimen bahagian A dijalankan menggunakan campuran asid hidroklorik dan glukosa dengan kepekatan asid hidroklorik yang berlainan di dalam aliran suapan dan produk; voltan yang dialirkan dan kadar aliran suapan menggunakan membran pertukaran anion (PC Acid 60) dan membran pertukaran kation (PC-SK) dalam mod kelompok. Parameter utama yang menentukan keupayaan proses adalah jangka masa pemisahan lengkap, paras maksimum perolehan semula asid, fluk purata produk, kecekapan arus dan penggunaan tenaga.

Eksperimen bahagian B, dijalankan berdasarkan parameter yang dipilih daripada bahagian A, iaitu kepekatan asid hidroklorik di dalam aliran suapan, voltan yang dialirkan dan kadar aliran suapan, di bawah parameter tetap iaitu kepekatan asid hidroklorik (0.1M) di dalam aliran produk dan kepekatan glukosa (5g/L) di dalam aliran masuk. Ini dilakukan menggunakan rekabentuk ujikaji (DoE). Rekabentuk ujikaji gabungan pusat (CCD) dan metodologi permukaan sambutan (RSM) telah digunakan untuk mendapatkan nilai parameter yang optimum.

Kesimpulannya dibawah nilai optimum (0.1M HCl di dalam aliran suapan dan produk, 1.47 mL/s kadar aliran suapan, voltan yang dialirkan sebanyak 21.21V dan masa pensampelan 100 min), keputusan terbaik bagi penggunaan tenaga, peratusan perolehan semula dan fluk purata produk ialah 37.93 kW.h, 97.4% dan 5.3 $kmol/m^2.s$.

SEPARATION OF HYDROCHLORIC ACID AND GLUCOSE USING ELETRODIALYSIS

ABSTRACT

Electrodialysis (ED) is a method that shows a good potential to separate and concentrate hydrochloric acid while unreacted glucose are partially recycled. Two sections of experiment had been done; section A and section B. Section A of the experiment was carried out using hydrochloric acid and glucose mixture with different concentration of hydrochloric acid in feed and product stream; voltage supplied and feed flow rate using anion-exchange membrane (PC Acid 60) and cation-exchange membrane (PC-SK) in batch mode. The main parameters which quantify the performance of the process are the duration of completing the separation, the maximum recovery level of the acid, the average product flux, the current efficiency and the energy consumption.

Section B of the experiment was done based on chosen effects from section A, which were the concentration of hydrochloric acid in feed stream, the voltage supplied and the feed flow rate, under constant parameters of concentration hydrochloric acid (0.1M) in product stream and glucose concentration (5 g/l) in feed stream. This had been done using design of experiment (DoE). A central composite design (CCD) and response surface methodology (RSM) were used to obtain the optimum values of the parameters.

It can be conclude that under optimum conditions (0.1M HCl in feed and product stream, 1.47 mL/s of feed flow rate,voltage supplied of 21.21V and sampling time of 100 min), the best results of energy consumption, recovery percentage and average flux were 37.93kW.h, 97.4% and 5.3kmol/m^2.s.

CHAPTER ONE

INTRODUCTION

1.1 Research background

1.1.1 Membrane technology

Nowadays "membrane" has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi permeable properties. Membrane exists in solid and liquid. It functions as a separation agent that is very selective based on the difference of diffusivity coefficient, electric current or solubility. The membrane can be defined essentially as a barrier, which separates two phases and restrict transport of various chemicals in a selective manner (Wenten, 2002).

Membrane technology began in 1960. Aided substantially by several key technical breakthroughs, membrane processes had come to compete favorably with more established technologies in such areas such as water desalting, water purification and gas separation. Several new membrane based industries have been established, and membrane research and development (R&D) is now being intensely pursued in the principal industrial countries (Torrey, 1984).

Membrane separations commonly used for water purification or other liquid processing. The driving force of the separation depends on the type of the membrane separation. Pressure-driven membrane filtration, also known as membrane filtration, included microfiltration, ultrafiltration, nanofiltration and reverse osmosis, and used pressure as a driving force, whereas the electrical driving force is used in electrodialysis (ED) and electrodeionization. Historically, membrane separation processes or systems were not considered cost effective for water treatment due to the adverse impacts that membrane scaling, membrane fouling, membrane degradation

and the efficiency of removing solutes from aqueous water streams. Advancements in technology have now made membrane separation a more commercially viable technology for treating aqueous feed streams suitable for use in industrial processes (Zeiher *et al.*, 2005).

ED is an electrochemical membrane separation technique for ionic solutions that has been used in industry for several decades. It can be used in the separation and concentration of salts, acids, and bases from aqueous solutions, the separation of monovalent ions from multivalent ions, and the separation of ionic compounds from uncharged molecules. It can be used for either electrolyte reduction in feed streams or recovery of ions from dilute streams. Industrial applications encompass several industries and include the production of potable water from brackish water, removal of metals from wastewater, demineralization of whey, deacidification of fruit juices, and the removal of organic acids from fermentation broth (Farrell *et al.*, 2003). ED separation using of ion-exchange membranes was different from those involving ultrafiltration (UF) and reverse osmosis (RO) membranes: UF membranes permit electrolyte and low molecular weight (MW) organic solutes to pass through; while RO membranes reject all components apart from pure water (Koide *et al.,* 2004).

1.1.2   Membrane potential and its current status

Probably the leading concern for chemical engineers when evaluating a novel process was the process cost relative to alternative processes performing the same task. While there were a few examples in which the economics of the process have been reported. ED is reported to have superior economics compared to the existing technology, depending on the specific application (Chukwu *et al., 1999;* Lindheimer *et al.,* 1993*;* Onuki *et al.,* 2000).

The ion exchange membrane has been applied in ED. During the last 50 years, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact. Today ion exchange membranes were successfully applied for desalination of sea and brackish water and for treated industrial effluents. They are efficiently used for the concentration or separation of food and pharmaceutical products containing ionic species as well as the manufacture of basic chemical products. The evolvement of an ion exchange membrane does not only make the process cleaner and more energy-efficient but also recovers useful effluents that were now going to wastes (Xu, 2005).

However, the use of electrodialysis in purification and reconcentration of spent acid has been limited by the deficiencies of commercial membranes: they suffered from an important proton leakage through the anion exchange membrane (AEM). This limited the concentration capacity and a poor selectivity of the cation exchange membrane (CEM), which affected the proton/bivalent cation separation. In recent years, new AEM's with lower proton leakage have appeared on the market. These membranes are necessary in order to improve the performance of the electrodialysis process for spent acid recovery (Boucher *et al.*, 1997). Therefore, the choice of membrane type will play an important role in this study.

1.2   Problem statement

From the viewpoints of both environmental protection and economy, the usage of waste can reduce the pollution (Blackburn, 1999). Waste acid solutions are among the most troublesome waste products produced by a manufacturing process and one of the most expensive to dispose of. One of the examples takes place in palm oil industry. In order to produce ethanol from palm solid wastes, the acid hydrolysis process is needed at the first place. However, the glucose produced had to separate from hydrochloric acid because the bacteria used in fermentation process could not life

longer in acidic media. After the separation and recovery of the concentrated hydrochloric acid, the sugars are suitable for further refinement and processing.

Recognized the cost of acid and chemicals for neutralized the acid, the study of separation acid from the hydrolysis mixture have been investigated by many researchers (Forster *et. al*, 1980; Boeteng, 1991). Although the most frequently employed technique for the disposal of spent acid residues was the neutralization-precipitation-discharge sequence, this practice was increasingly being questioned because of the environmental consequences related to the stocking of toxic solid waste (Boeteng, 1991). Other methods used were crystallization, solvent extraction and membrane technology. The disadvantages of crystallization method were due to the low yield; high chemical costs and waste production. While, solvent extraction is energy intensive, leads to problems of toxic waste disposal, and gives a product that requires further purification. Thus, new extraction technologies need to be established for enhancing recovery yields and reducing cost and environmental impact (Yao et al., 1994).

The modularity and profitability of membrane technology in a small scale which offered by the third process is a well suites technique to the treatment of the pollution. The principal advantages of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness (Wenten, 2002). The technology and innovation of membrane separation is rapidly growth. As a result, many different membrane separation processes have been developed and new processes are constantly emerging, which includes, besides other techniques, microfiltration, reverse osmosis and electrodialysis (ED). The use of ED, on the treatment of solutions containing complexes, has shown that this technique is effective not only to ions concentration but also to their separation (Rodrigues *et al.*, 2006).

ED was a feasible method for separation of acid from glucose. Removal (and recycling) of this acid from the products requires a separation process for which a membrane process (electrodialysis) has been proposed. Differ from other membrane separation processes such as ultrafiltration and reverse osmosis; ED process separates ions in aqueous solutions by exploiting the difference in electrical charges between them, instead of particle size. Therefore, ED can separate not only cations from anions, but also ions with the same charge but different valences, which are termed of permselectivity. The permselectivity is closely correlated to the characteristic of the ion exchange membranes and plays a very important role in the ED process, although other parameters, such as ion charge and mobility, solution conductivity, relative concentrations, and applied voltage also influenced the efficiency of the process. Therefore, there was great significance in using high-permselectivity ion exchange membranes in ED processes (Peng *et al.*, 2003).

ED was a technology that is well-suited for pollution prevention exploitation. It had the capability of separated ionic chemicals from nonionic chemicals in process or waste streams to achieve product purity or eliminate wastes, concentrated the separated chemicals relative to concentration in the initial process or waste streams to aid in reuse of the chemicals and being used as a reactor, both electrolytic and otherwise, to convert chemicals at high efficiencies to more desirable products. This technology did not required chemicals and was simple to operate. It adapted to no-continuous feed supplied and different load. Besides, it was not very dependent on temperature (Blackburn, 1999). The product could be concentrated up to a certain amount together with the separation process (Thang *et al.*, 2005). Further, ED had the capability to meet these function simultaneously in a single equipment assembly. It accomplished these tasks with low levels of pollution generation and high energy efficiencies relative to current technologies (Mohammadi *et al.,* 2005).

In spite of the advantages of ED, there were some problems can limit the efficiencies and operation of separation technologies using electrodialysis. The first problem is regarding the fouling which is become the most important limitations in ED processes. The fouling build-up can reduce the performance of the ED process by increasing the resistance and can eventually lead to membrane integrity alteration. Under certain conditions, fouling and integrity alterations are irreversible and membranes must be replaced. Researches on avoiding or preventing fouling are study in order to reduce the cost of cleaning and membrane replacement which is extremely expensive. Fouling is essentially caused by deposition of foulants on the membrane surfaces such as organics, minerals, colloids, biomass and particles causing deterioration in the membrane performance, in terms of flux decline and increase in the electrical resistance. Besides, the fouling sometimes causes a loss in selectivity of the membrane. If the fouling is irreversible, the membranes must be changed frequently, adding to the increased energy cost caused by fouling (Morantes, 2004).

Second problem involved the concentrations of solutions which also affected the membrane resistance. A marked increase in fouling was observed when approaching the saturation concentration (Lindstrand *et al.*, 2000). Membrane fouling easily occurred on the anion exchange membrane more than the cation exchange membrane. It was caused by the precipitation of colloids mostly on the anion selectivity membrane because the colloids are usually charged negatively. Particularly, fouling in the biological process was caused by organic compounds in the fermentation broth. In order to minimize fouling, the selection of suitable membrane (Nikbakht *et.al*, 2007) pre-treatment of foulants and optimization of operating condition, etc is needed (Kim and Moon, 2001).

Another problem ; ideally, the separation of hydrochloric acid from the sugar by electrodialysis should provide a maximum yield of recovered acid at maximum

concentration with minimum power consumption using minimum membrane area. Most of experimental results made it obvious that these conditions cannot be met simultaneously. At the highest current efficiencies and, thus, the minimum membrane area, the final acid concentration in the concentration was too low. At the highest concentration of acid, the percentage of acid transferred decreased, and power consumption and membrane area increased (Goldstein, 1993).

In order to solve these problems, several studies been approached. In the case of electrodialysis which is conducted to a solution containing organic substances as the solution to be treated using an ion-exchange membrane, periodical membrane washing is conducted with an alkaline solution for the purpose of removing fouling substances stuck in the ion-exchange membrane in order to maintain a stable operation for a long period (Aritomi *et al.*, 1996). Many approaches have been examined to minimize fouling during membrane processes. This includes pretreatment of feed solution, turbulence in the compartment, optimization of process conditions and the modification of the membrane properties. However, relevant cleaning-in- place (CIP) is still need in practical processes although all the said methods can reduce fouling to some extent. Consequently, several cleaning methods including hydraulic and chemical cleaning methods have been use effectively. Consider to all the problems; the use of electrodialysis reversal in this study which can avoid membrane fouling is implemented.

Beside that, a suitable membrane for the ED process can reduce the power consumption and achieve a stable long-term operation without membrane fouling. In general, the electrical resistance of ion-exchange membranes is one of the important characteristics that determine the energy requirement and membrane area needed for the ED process. A low electrical resistance membrane is required for the process to be operated at low energy consumption (Kim *et al.*, 2001). For that reason, the membrane used in this study, is based on its low resistance and had been considered the

approach to obtain high efficiencies by electrodialysis in acid medium. Consider the high permeability of acids through standard anion exchange membranes; PC Acid 60 is used together with cation exchange membrane; PC SK, in this separation process.

To improve the ED stack, the electrodialysis reversal (EDR) had been used. It can be enhanced by periodically reversing the polarity of the electrodes that reverse the direction of ion movement within the membrane stack. The dilute stream becomes the concentrate stream and vice versa. The reversal process is useful in breaking up and flushing out scales, slime and other deposits in the cells before they could build up and created a problem. EDR had an advantage with self-cleaning membranes, and the ability to easily disassemble membrane stacks for hand cleaning (Lee *et al.*, 2002).

1.3   Objectives of the research

The goals of this project are:

a) To determine the effects of hydrochloric acid concentration in feed and product stream, the voltage supplied and feed flow rate on separation process performance of acid-glucose solution.

b) To characterize an EDR by means of the determination the optimum working condition with minimum energy consumption.

c) To optimize the separation of hydrochloric acid and glucose using response surface methodology (RSM) followed with central composite (CCD) as statistical design.

1.4   Scopes of the study

The aim of this study was to investigate the most favorable experimental conditions to separate acid and glucose using electrodialysis. The research project was divided into 2 main parts. The first part was deal with experimental to find the characterization of electrodialysis. The second part involves optimization using DoE (Design of Experiment).

The preliminary experiment has been done to evaluate the performance of the ED. Several parameters that affected the electrodialysis performance such as initial concentration of HCl in feed stream, initial concentration of HCl in product stream, voltage supplied and feed flow rate were studied. The influence of the initial concentration of HCl in feed and initial product stream manipulated were 0.1 M, 0.3 M, 0.5, 0.7 and 1.0 M. Different voltage varied from 18 V to 24 V at same initial concentration of HCl feed stream and product was also studied. The pump was calibrated by manual experiment by varied it to respective number (range 0-10). The volume flow out was collected over time taken and the calibration curve is plotted as in Figure A2 (Appendix A). To minimize the range, the feed flow rates were varied from 1.58 mL/s until 2.26 mL/s (respectively number 4-10). For the performances of the ED system, three important indicators were examined, namely energy consumption, product recovery percentage and average flux.

1.5   Organization on the thesis

This thesis has been organized into several chapters.

Chapter One introduces the alternative of membrane separation and their advantage and disadvantages. The problem statement leads to the process study was then discussed in the next section followed by the objective of the research study.

Chapter Two reviews the previous finding and fundamentals related to the previous research. This chapter subdivided into 8 sections. The first section covers the entire topic about membrane such as membrane definition, separation alternatives, type of membrane and history of ion exchange membrane. The second sections cover the whole focus on definition of electrodialysis, development and commercialization and electrodialysis potential as a separator. The third section covers up all the principles, process description, modes and stack of electrodialysis, requirements for electrodialysis membrane and structure of ion membrane. The problem facing by electrodialysis technology and their problem solving has been discussed in section four. The next sections discussed on parameter affecting the electrodialysis performance followed by the key performance indicators. Finally, literature survey on the design of experiment (DoE) which is used to optimize the experiment is discussed.

Chapter Three presents materials and methods will be discussed thoroughly in order to separate the mixture of acid and glucose. The first section show material and chemical used followed by flow chart of the overall experimental works. Specification of material and equipment were listed. Procedure to run the experiment was outlined properly. All stages of experiment were summarized in flow chart.

Chapter Four presents all the result and followed by discussion. In this chapter, all experiments were listed in table form and graph. All figures and graphs were discussed analytically. The detail explanations of the results have been divided into section A and section B. Section A focuses on process in electrodialysis compartment, electrical resistance and characteristic study on electrodialysis system. Section B implements the design of experiment (DoE). The regression models, adequacy and the effects of process variable had been discussed through this section.

Chapter five finally gives the conclusions and recommendations of the thesis.

CHAPTER TWO

LITERATURE REVIEW

This chapter presents a review of the different separation methods; the conventional treatment and possible technologies. Electrodialysis has a great potential of becoming an excellent separation method for hydrochloric acid-glucose mixture, which is chosen to be applied in this study. Finally, the design of experiment (DoE) using response surface methodology (RSM) is presented at the end of this chapter.

2.1   Membrane definition

In the past few decades Membrane based separation has become one of the emerging technologies. The word membrane comes from the Latin word; "membrana" which means skin. Today's word "membrane" has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi permeable properties. Membranes exist in solids and liquids. It functions as a separation agent that is very selective based on the difference of diffusivity coefficient, electric current or solubility (Wenten, 2002). The two phases separated by the membrane, i.e., the feed and permeate; could be present in the liquid or in the gaseous state. The driving force that was necessary for the transport was a transmembrane pressure gradient (ΔP), a concentration gradient (ΔC), an electrical potential gradient (ΔE), or a temperature gradient (ΔT) (Beerlage, 1994). A schematic drawing illustrated a membrane separation process was given in Figure 2.1.
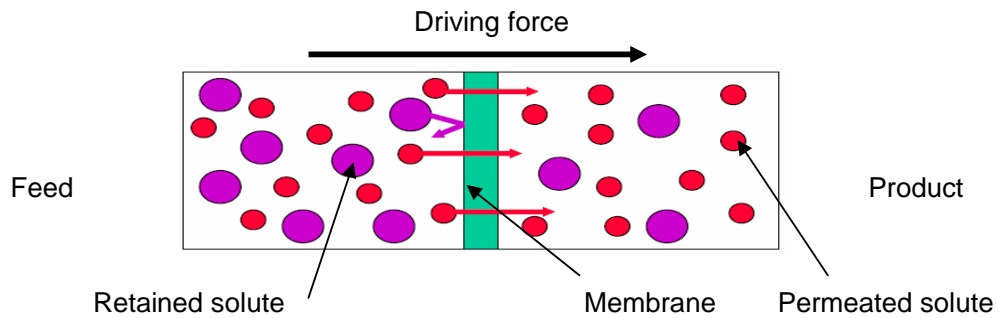
Figure 2.1   Schematic drawing illustrating a membrane separation process
(Beerlage, 1994)

The principal advantageous of membrane processes compared to other separation processes are low energy consumption, simplicity and environmental friendliness. Membrane-based separation is a result of different rates of transfer between each substance in the membrane and not a result of phase equilibrium or mechanically based separation. Therefore, there is no need to add additive materials such as extractors and absorbers to precede the separation. We can then say that membrane technology is "clean technology", in which no additive materials are, needed (Wenten, 2002). Figure 2.2 classifies membranes according to structure, production, essential transport mechanism and areas of application.
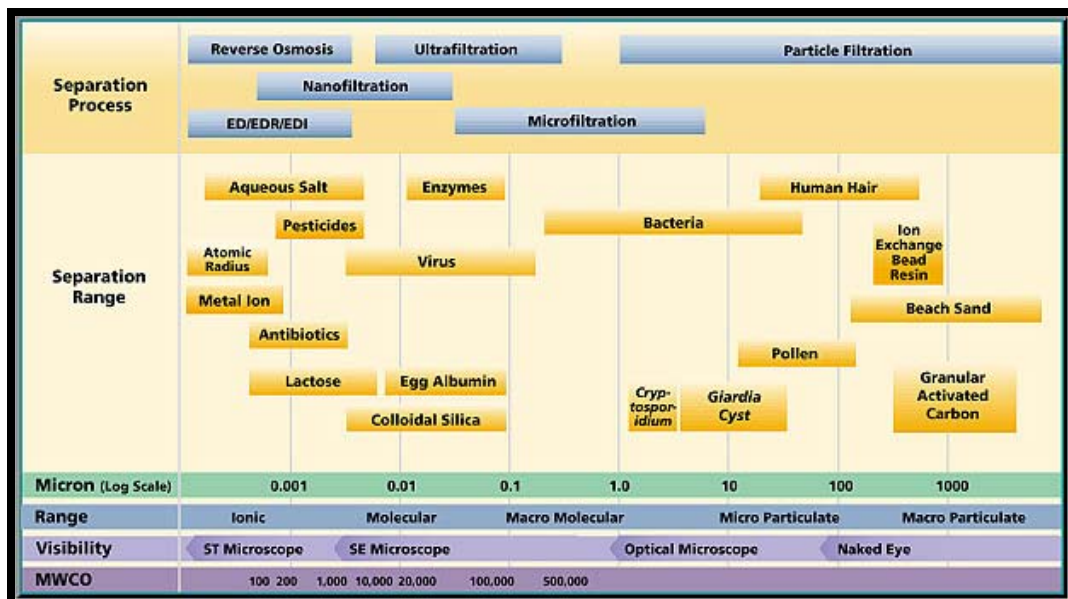
Figure 2.2: Types of separation processes and their applications (Cheryan, 1998)

2.1.1 Types of membranes

Advances in membrane technology, especially in novel materials, can make this technology even more competitive in comparison to traditional, energy intensive, environmentally undesirable and costly processes. There are six major membrane processes that are widely used in industrial application. They are classified based on various driving forces, some use pressure difference (micro filtration, ultra filtration, reverse osmosis, piezodialysis), while others use other driving forces such as concentration difference (gas separation, pervaporation, liquid membrane and dialysis), thermal (membrane distillation, thermo osmosis) and electric (electrodialysis). The key membrane performance variables are selectivity, permeability and durability (Wenten, 2002).

The proper choice of a membrane should be determined by the specific application objective. The types of following membranes were commonly used:

a)   Microporous membranes

b)   Homogenous membranes

c)   Asymmetric membranes

d)   Electrically charged membranes

e)   Liquid membranes

Among these membranes, electrically charged membranes were one of the most advanced separation membranes. These are necessarily ion-exchange membranes which consisting of highly swollen gels that carrying fixed positive or negative charges. These are mainly used in the electrodialysis. The basic applications of the ion exchange membrane process are based on the Donnan membrane equilibrium principle and has been given   attention to solve two important environmental problems, for the recovery and enrichment of valuable ions, and the

removal of undesirable ions from waste water, especially to extract toxic metal ions from effluents (Nagarale, 2006).

Electrically charged membranes are used together with electrodialysis in the separation of hydrochloric acid- glucose. Traditionally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contain negatively charged groups (such as $-SO_3^{3-}$, $-COO^-$, $-PO_3^{2-}$,$-PO_3H^-$, $-C_6H_4O^-$, etc.), fixed to the membrane backbone and allow the passage of cations but reject anions. Anion exchange membranes contains positively charged groups, such as $-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, $-PR_3^+$,$-SR_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations. According to the connection way of charge groups to the matrix or their chemical structure, ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. However, most of the practical ion exchange membranes are rather homogenous and composed of either hydrocarbon or fluorocarbon polymer films hosting the ionic groups (Xu, 2005). Figure 2.3 show the separation principle of the membranes.
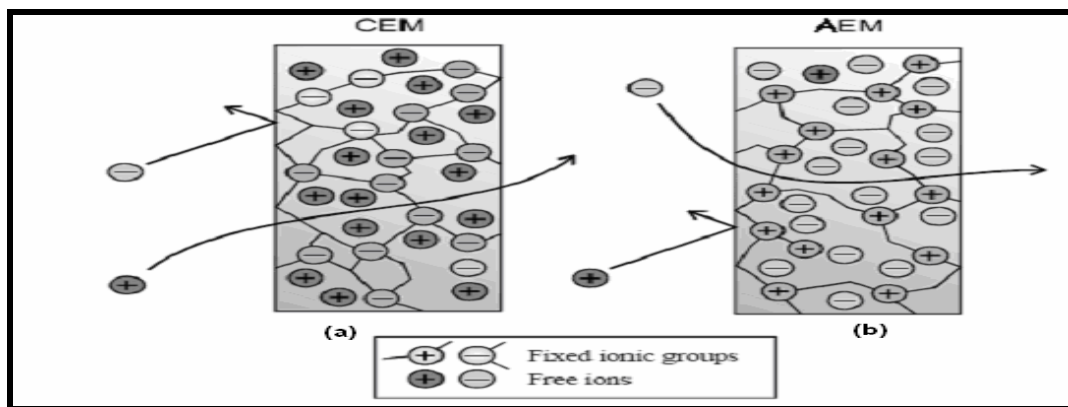
Figure 2.3: The two types of (mono polar) electrodialysis membranes. (a) cation exchange membrane , (b) anion-exchange membrane (Batchelder, 1986)

The development of the ion exchange membrane-based process began in 1890 with the work of Ostwald who studied the properties of semi permeable membranes and discovered that a membrane can be impermeable for any electrolyte if it is impermeable either for its cation or its anion. To illustrate this, the so-called "membrane potential" at the boundary between a membrane and its surrounding solution was postulated as a consequence of the difference in concentration. In 1911, Donnan confirmed the existence of such a boundary and developed a mathematical equation describing the concentration equilibrium, which resulted in the so-called "Donnan exclusion potential". However, the actual basic studies related to ion exchange membranes began in 1925 and was carried out by Michaelis and Fujita with the homogeneous, weak acid collodium membranes. In 1930s, S¨ollner presented the idea of a charge-mosaic membrane or amphoteric membrane containing both negatively and positively charged ion exchange groups and showed distinctive ion transport phenomena. Around 1940, interest in industrial applications led to the development of synthetic ion exchange membrane on the basis of phenol-formaldehyde-polycondensation (Xu, 2005).

With the development of stable, highly selective ion exchange membrane of low electric resistance in 1950 by Juda and McRae of Ionics Inc. and Winger in 1953, electrodialysis based on ion exchange membranes rapidly became an industrial process for demineralizing and concentrating electrolyte solutions. Since then, both ion exchange membranes and electrodialysis have been greatly improved and widely used in many fields (Morantes, 2004). The chronological development of ion exchange membrane and the related processes is shown in Figure 2.4.
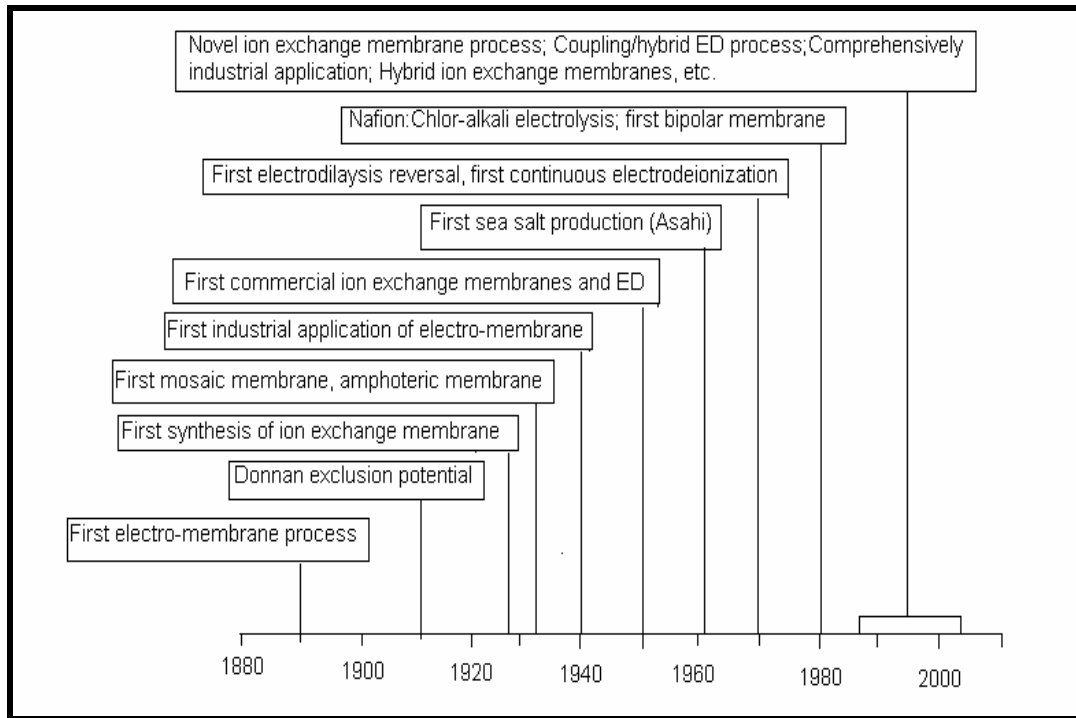
Figure 2.4:Time line of ion exchange membrane development and their related processes (Xu, 2005).

2.1.2 Structure of ion exchange membrane

Commercially available ion exchange membranes are essentially sheets of ion exchange resins made up of (theoretically) a jumble of polymer chains with void spaces between the chains. Ion exchange membranes are selectively permeable to positively charged ions (cations) only or negatively charged ions (anions) only. The structure of an ion exchange membrane is show in Figure 2.5. The most important factor in the electrodialysis (ED) process is the permselectivity of the ion exchange membranes, which permit not only the separation of cations and anions in a solution, but also the separation of ions with the same sign but different valences (Peng *at al.*, 2004).
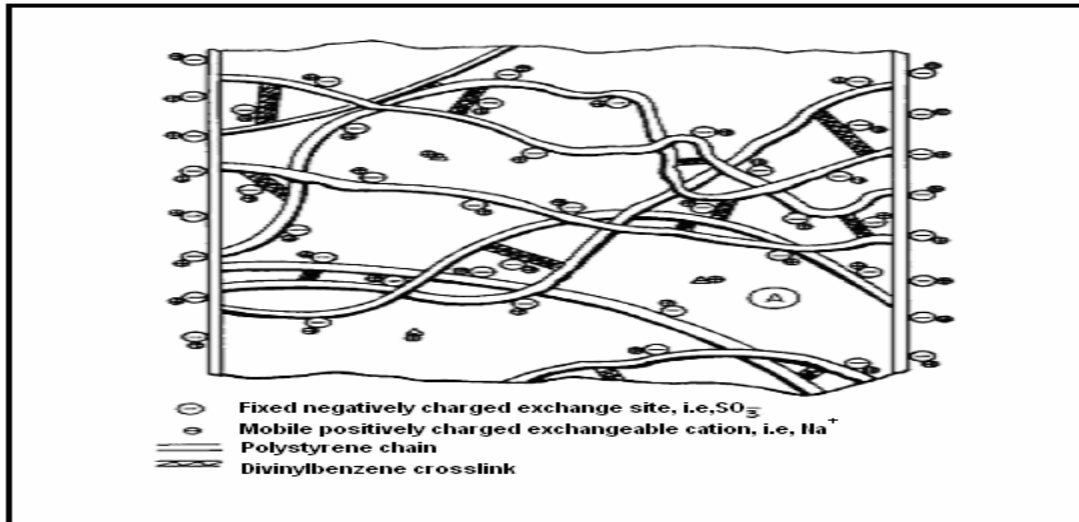
Figure 2.5: Ion exchange membrane structure (Savitri, 2000)

Table 2.1 presents the potential applications of novel ion exchange membrane-based processes, their state of development and possible advantages and experienced problems.

2.1.3 Requirements for electrodialysis membrane

Early commercial ion exchange membranes were limited due to the electrical resistance of membranes itself. It was cause of high energy consumption and high membrane cost. In additions, economical efficiency was low than that of the process. In the 1940's, ion exchange membranes of low resistance were developed by using ion exchange resins. Two types of membranes are available based on the nature of the functional groups attached to the matrix: cation-permeable membranes, called cation-exchange (or cationic) membranes and anion-permeable membranes, called anion-exchange (or anionic) membranes. Both of these membranes are monopolar; this means that they are permeable to only one type of ion (Bazinet *et al.*, 1998).

Table 2.1: Potential applications of novel ion exchange membrane-based processes, their state of development and possible advantages and experienced problems (Xu, 2005)

Applications	State of process development	Potential Advantages	Problem related to application
Electrodialysis with bipolar membranes (BMED)			
-Production of mineral acids and bases from corresponding salts	Pilot plant operation	Lower energy consumption	Contamination of products and low current utilization due to poor membrane
-Recovering/producing of organic acids from fermentation processes	Commercial and pilot plant operation	Simple integrated process, lower costs	Unsatisfactory membrane stability and fouling application experience
-Removal of SO_2 from flue gas	Extensive pilot plant test	Decreased salt production, reduced salt disposal costs	High investment costs, long-term membrane stability
-Recovering and recycling of H_2SO_4 and NaOH from waste waters, such as the rayon production effluent	Laboratory and pilot plant tests, some commercial plants	Purity of the recovered products is not critical, savings in chemicals and sludge disposal costs	No long-term experience, membrane stability under operating conditions, membrane fouling, high investment costs
-Recycling of HF and HNO_3 from steel pickling solutions	Commercial plants	Cost savings due to recovered acids and decreased salt disposal	Relatively complex process, high investment costs
-In food industry	Laboratory and pilot plant tests	Fewer by-products, less chemicals, and salt production and disposal	Application experience, process costs, investment costs
-Energy storage and conversion	Only theoretical considerations	Eventually economical advantages	No experimental verification
-Production of sodium methoxide from methanol	Laboratory tests	More economic than conventional production process	No long-term experience
EDI			
-Ultra-pure water production	Commercial plants	Continuous process without by-products, high efficiency	Higher investment costs, waste disposal, care pretreatment
EED			
-Membrane electrolysis	Commercial plants	Continuous process, high efficiency	High investment costs, membrane stability and selectivity
ED and reactor			
-Denitrification of drinking water,fermentation process	Pilot plant tests, some commercial plants	Continuous process, high efficiency	Membrane stability and selectivity, relatively complex process
-Waste recovery	Commercial plants	Continuous process, more compacted process	Relatively complex process, connection with care for each process

Ion selectivity is the most important of these properties. Perm selectivity is used to describe these membranes and indicates that they are permeable to selected ions. The manufacturers make ion-exchange membranes of various thicknesses and hence, the resistance is tabulated as membrane area resistance of unit's ohms cm^2 (Strathmann, 1992).

Mechanical properties are important in the design of the support structures for the membranes. The membranes must have sufficient mechanical strength to withstand the fluid pressures and mechanical forces to which they are subjected. The method of sealing to prevent leakage is to clamp the edges of the membranes between flat surfaces so it is important for the membranes to be strong to resist fastening forces without deformation. The fluid pressures involved in an electrodialysis cell are those required to cause flow through very narrow passages in the spacers. The membrane must have the ability to maintain its stability under continued exposure to the feed compartment, containing various ions and having pH values from highly acidic to alkaline (Savitri, 2000).

It is difficult to find all of these properties together in the commercially produced membranes. Electrodialysis is characterized by the use of ion-selective membranes and an electric field orthogonal to the membranes. In contrast to other membrane processes, membranes used for electrodialysis can be arranged only in plate and frame modules. The membranes themselves should be as large as possible and the distance between them should be as small as possible, since these conditions are favorable to the economics of the process (Kabay *et al.*, 2003).

Essential requirements for electrodialysis membranes are: (Nagarale *et al.*, 2006):

- High perm selectivity - an ion-exchange membrane should be highly permeable to counter-ion, but should be impermeable to co-ions

- Low electrical resistance - an ion-exchange membranes should have low electrical resistance and thus there will be less potential drop during electro-membrane processes

- Good mechanical stability- the membrane should be mechanically strong and should 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.

- Low degree of water transport - Electroosmosis, the movement of water as a result of current flow, tends to reduce the electrodialytic efficiency of the system, and should be avoided. This can be almost achieved by keeping the porosity low, but cannot be avoided together.

- Inertness - The membrane should not deteriorate in the presence of whatever chemical and biological agents with which it may come in contact. This requirement does not seriously limit the range of suitable membrane materials.

- Low cost - The ion-exchange membranes represent the most important single item of capital investment for electrodialysis. The high cost of membrane replacement, and the limitations inherent in the properties of available membranes represent the most important obstacle to widespread usage of electrodialysis to desalt brackish water.

Higher cross linking improves the selectivity and stability of membranes by reducing swelling, but increases the electrical resistance. However, high charge density reduces resistance and increase selectivity, but promotes swelling and thus constrains higher cross linking (Nagarale *et al.*, 2006). All these factors lead to the conclusion that ED has reached a level where it deserves to be considered as a separator. To obtain high efficiencies by electrodialysis in acid medium, there is the need of special ion exchange membranes because of the high permeability of acids through standard anion exchange membranes. Therefore, ion exchange membrane Acid 60 and PC-SK were chose regarding to the properties listed in Table 2.2.

Table 2.2: Properties of ion-exchange membranes

	Anion- Exchange Membrane	Cation-Exchange Membrane
Commercial name	PC Acid 60	PC-SK
Thickness, µm	110	110
Ion-Exchange capacity, equiv/g-dry.membrane	ca.0.35	ca 0.95
Transport number, N	0.55	0.96
Water per g dry membrane	ca 0.15	ca 0.3

The physical properties of some commercially available membranes are listed in Table 2.3. These properties include manufacturer, type, thickness and area resistance of the membranes. The exchange capacity of the membranes is very important and is represented by the exchanged sites within the plastic matrix. It is usually expressed in terms of milliequivalents (meq) of ion-exchange capacity per gram of dry membrane.

Table 2.3: Main properties of some commercially available homogeneous ion exchange membranes (Xu, 2005)

Membrane	Type	Thickness (mm)	IEC(mol/g(meq/g))	Area resistance (Ωcm^2)	Remarks
Asahi Chemical Industry Co: Japan					
Aciplex K-192	CEM	0.13-0.17	-	1.6-1.9	Univalent selective
Aciplex -501SB	CEM	0.16-0.20	-	1.5-3.0	-
Aciplex A-192	AEM	>015	-	1.8-2.1	Univalent selective
Aciplex-501SB	AEM	0.14-0.18	-	2.0-3.0	-
Aciplex A201	AEM	0.22-0.24	-	3.6-4.2	Desalination
Asahi Glass Co. Ltd, Japan					
Selemion CMV	CEM	0.13-0.15	-	2.0-3.5	Strongly acidic
Selemion AMV	AEM	0.11-0.15	-	1.5-3.0	Strongly basic
Selemion ASV	AEM	011-0.15	-	2.3-3.5	Strongly basic, univalent
Selemion DSV	AEM	0.13-0.17	-	-	Strongly basic, dialysis
Flemion	-	-	-	-	Chlor-alkali
Ionics Inc, USA					
CR61-CMP	CEM	0.58-0.70	2.2-2.5	11.0	ED whey
CR67-HMR	CEM	0.53-0.65	2.1-2.45	7.0-11.0	ED whey
CR67-HMP	-	-	-	-	EDI
AR103QDP	AEM	0.56-0.69	1.95-2.20	14.5	ED whey
AR204SZRA	AEM	0.48-0.66	2.3-2.7	6.2-9.3	EDR
Mega a.s, Czech Republic					
Ralex MH-PES	AEM	0.55 (Dry)	1.8	<8	ED, EDI
Ralex CM-PES	CEM	0.45 (Dry)	2.2	<9	ED,EDI
PCA Polymerchemie Altmeir GmbH, Germany					
PC 100 D	AEM	0.08-0.1	1.2 Quat	5	Small organic anions
PC 200 D	AEM	0.08-0.1	1.3 Quat	2	Medium organic anions
PC Acid 35	AEM	0.08-0.1	1.0 Quat	-	HCl production
PC Acid 60	AEM	0.08-0.1	1.1 Quat	-	Pickling acids (HNO_3/HF)
PC Acid 100	AEM	0.08-0.1	0.57Quat	-	Sulphuric acid production
PC-SK	CEM	-	-	-	Standard CEM
PC-SA	AEM	-	-	-	Standard AEM

2.2   Electrodialysis

2.2.1   Definition

Electrodialysis (ED) is a membrane-based separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution. It can be operated only with solutions at the same temperature to eliminate the energy consumption for the formation of a new phase as distillation process (Luo *et al.*, 2002).

ED is usually considered as a desalination process, but there is much wider scope for this technique because ED is in many cases a powerful separation method when charged compounds have to be separated from a solution (Min-tian *et al.,* 2004). It is an environmentally friendly membrane separation process. It is also an alternative to the chemical treatment process of recovering hydrochloric acid from the hydrolysis mixture. ED is gaining an increasing attention and has been widely investigated in many chemical fields such as production of H_2 and O_2 from water. ED is a membrane separation process in which ionic species are separated from water, macro solutes, and all uncharged solutes. Ions are induced to move by an electrical potential, and separation is facilitated by ion-exchange membranes. Membranes are highly selective, passing either anions or cations and very little of anything else (Perry & Green, 1998).

Electrodialysis has been used in a multitude of applications which include the separation of cations, anions, monovalent from multivalent ions, ionic species of the same or different electrical charge, acids from elements in ionic form, amphoteric elements, compounds of different conductances and degree of dissociation in solution, and ionic species from non dissociated organic compounds (Boateng, 1992).

Figure 2.6 shows the separation technologies which use electricity as the source of power. The technologies are divided into electrolysis and electrodialysis. The difference between an electrolytic and an electrodialysis cell is the configuration of the cell. In electrodialysis, cation and anion exchange membranes are alternated between two electrodes and a repeated cell-pair pattern can be formed, thus several cell pairs can be assembled between the electrodes. In the case of an electrolytic cell unit, the addition of cell pairs requires the addition of electrodes (Morantes, 2004).
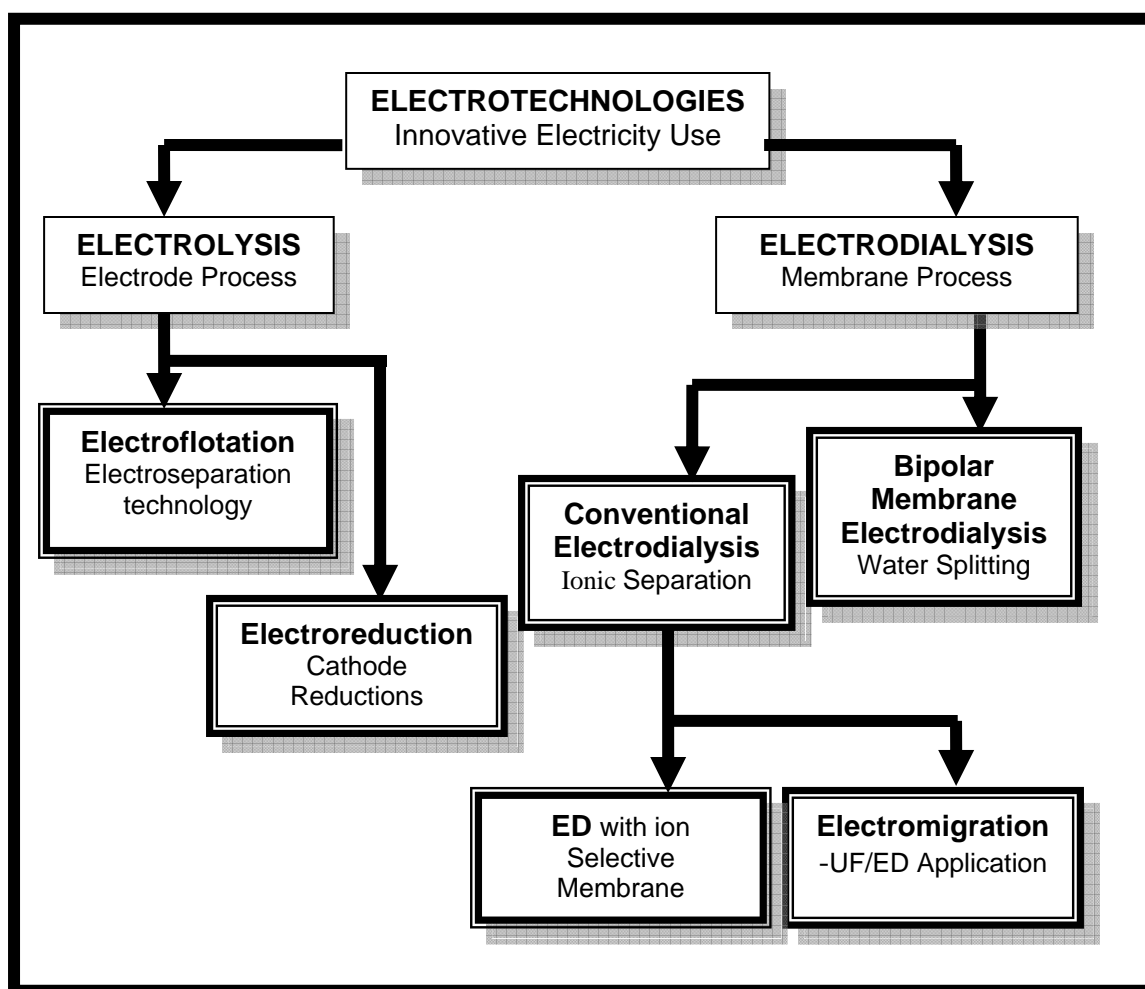

Figure 2.6: Electrotechnologies (Marcotte *et al.*, 2003)