Separation of sulfuric acid from spent acid using membrane based separation process - Electrodialysis

A Thesis submitted to Gujarat Technological University

for the Award of

Doctor of Philosophy in

Chemical Engineering

by

Beena Kanaiyalal Sheth

(Enrollment No: 139997105001)

Under the supervision of

Dr. Kaushik Nath

GUJARAT TECHNOLOGICAL UNIVERSITY

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ABSTRACT

Electrodialysis (ED) has been widely acknowledged as an efficient method for the treatment of acidic effluents generated from various metal processing industries. ED holds much promise in the purification and separation of sulfuric acid from spent acidic liquor wherein the type and cost of electrodes are the major governing factors towards its economic viability at a large scale. Besides, the lean acidic liquor generated electrodialytically also demands the development of an efficient multistage ED process that can not only enrich the lean acidic solution but also render it amenable for further use. The present study investigates some critical aspects of the sulfuric acid separation and concentration through several batch experiments carried out using laboratory-scale ED module. In the first part of the present study, the batch ED process with affordable electrodes such as graphite and SS 316L was tested to separate sulfuric acid from the model spent acidic liquor and its effect on the quality of anolyte was analysed. The SS 316L was observed to be participating in the process and cannot be a suitable electrode as anode under electrodialytic conditions in the presence of sulfuric acid. Conversely, the graphite electrode was found suitable and it could resist corrosion compared to its SS counterpart. Effect of major physico-chemical parameters such as initial catholyte concentration and current density on current efficiency, molar flux, the extent of acid separation and voltage requirements was investigated extensively with a graphite electrode. Graphite worked effectively and efficiently in a certain range of current density and applied voltage under the present experimental conditions.

In the second part of the present study, a cascaded ED process was developed to purify and concentrate sulfuric acid from spent acidic liquor. A cascaded electrodialysis system consisted of six electrodialyzers could increase sulfuric acid concentration up to 28 wt. % with ion exchange membranes namely Selemion AAV, Selemion AMV and IPA. Since higher acid recovery, higher efficiency and lesser electrical energy utilisation are considered to be the key factors in terms of the commercial viability of the process, the performance of the membrane was examined in terms of acid concentration, current efficiency, voltage requirements, and energy consumption. Proton leakage through anion exchange membrane, acid back diffusion, concentration polarization and solution conductivity were considered to be the limiting factors for acid enrichment and their effects were found significant on current efficiency and applied voltage. Major differences were observed in the performance of Selemion AMV membrane with other two AEMs with IPA membrane performed as good as

low proton leakage membrane. Estimation of energy consumed by ED along with economic analysis was carried out and was compared with the conventional evaporation process. On the basis of experimental and computational results, ED was revealed to be a less energy intensive-process and its integration with evaporation was found to be more economical than standalone ED or EV to increase sulfuric acid concentration from 1 to 5 wt. %. An empirical equation was developed to predict molar flux and voltage requirements and it could produce satisfactory results when compared with the experimental values. The findings of the present work may provide useful insights to ED fundamentals, batch and cascaded process performance with a complete set of process parameters along with energy estimations for the sulfuric acid separation and enrichment.

Acknowledgement

First and foremost, I would like to express my sincere gratitude to my research supervisor **Dr. Kaushik Nath**, Professor and Head, Department of Chemical Engineering, G. H. Patel College of Engineering and Technology, Vallabh Vidyanagar. I am deeply thankful to him for his able supervision and unconditional support during every stage across the tenure of this research work. I thank him for his critical observations about my capabilities and limitations, which brought a significant change in my development during this research. I am always thankful to him for reviewing my synopsis, thesis and research papers by giving his valuable time and patience.

I am thankful to my DPC members, **Dr. Sachin Parikh**, Professor and Head, Department of Chemical Engineering, L. D College of Engineering, Ahmedabad and **Dr. Rajagopalan Srinivasan**, Professor, Indian Institute of Technology, Madras for their thoughtful feedback, insightful comments and inspirations. My sincere thanks to them for their kind support, suggestions and able guidance during the entire period of my research.

I am thankful to my Head of the Department, Dr. N. M. Patel, all faculties and supporting staff of the Chemical Engineering Department, VGEC, Chandkheda for their motivation and support. My special thanks to Prof. Haresh K. Dave, faculty, Department of Chemical Engineering, G. H. Patel College of Engineering and Technology, Vallabh Vidyanagar for unconditional support during the tenure of this research.

Finally, my deep and sincere gratitude to my parents, my husband the other family members for their continuous and unparalleled love, help and support. Especially, a lot of love for my children, Krish and Dhairya. I appreciate all their patience and support during this Ph.D. studies.

Beena K Sheth

Date: 07/02/2020 Place: Ahmedabad

Table of Content

List of Abbreviation

AEM	Anion exchange membrane
BPM	Bipolar membrane
CE	Current efficiency
CEM	Cation exchange membrane
CP	Concentration polarization
DD	Diffusion dialysis
DVB	Divinyl benzene
ED	Electrodialysis
EED	Electro-electrodialysis
EV	Evaporation
FE-SEM	Field emission scanning electron microscopy
FTIR	Fourier Transform Infrared Spectroscopy
IEM	Ion exchange membrane
MD	Membrane distillation
RED	Reversal electrodialysis
SX	Solvent extraction

List of Symbols

A_m	Membrane effective area (cm^2)
C_{ao}	Initial anolyte concentration (wt. %)
C_{co}	Initial catholyte concentration (wt. %)
C_{af}	Final anolyte concentration (wt. %)
C_{cf}	Final catholyte concentration (wt. %)
C_{at}	Anolyte concentration with time (wt. %)
C_{ct}	Catholyte concentration with time (wt. %)
dC_c	Catholyte concentration variation with time (C_{ct}-C_{co}) (wt. %)
dC_t	Catholyte and anolyte concentration difference (C_{ct}-C_{at}) (wt. %)
E_{ED}	Energy for electrodialysis (kJ)

E_{EV}	Energy for evaporation (kJ)
F	Faraday constant
I	Current (mA)
I_c	Applied current density (mA cm^{-2})
J_D	Flux due to natural diffusion based on concentration gradient (mol/cm^2 S)
J_m	Flux predicted based on model equation developed (mol/cm^2 S)
J_p	Flux calculated based on experimental data (mol/cm^2 S)
J_u	Flux due to motion/velocity of fluids (mol/cm^2 S)
$J_{Ø}$	Flux due to membrane electric potential (mol/cm^2 S)
$J_{Øa}$	Flux due to applied electric potential (mol/cm^2 S)
K	Kelvin (Temperature)
m	Mobility of ions in solution
R	Absolute Gas constant (J/mol K)
T	Temperature (K)
t	Time
V	Voltage (V)
V_l	Volume of solution (liter)
V_{la}	Volume of anolyte (liter)
V_m	Membrane potential based on concentration difference across the membrane
V_W	Volume of water evaporated (liter)

Greek Letters

μ	Viscosity of solution (cP)
θ	Electrical potential
η	Current efficiency (%)
ρ_w	Density of water (kg $liter^{-1}$)
λ_w	Latent heat of vaporization of water (2260 kJ kg^{-1})

List of Figures

List of Tables

CHAPTER 1

Introduction

Sulfuric acid, referred to as 'king of chemicals' is used extensively in one or the other form, 98% H_2SO_4, Oleum, 33.5% battery acid (used in lead-acid batteries) (pH: 0.5), 62.18% chamber or fertilizer acid (pH about 0.4) and so on in the processing and manufacturing of a plethora of products in chemical industries. Presently it is being produced more than 260 million tons worldwide. By far the largest amount of sulfuric acid is consumed in the manufacturing of fertilizers, and the rest are widely used in metal processing for example in the manufacture of copper and zinc, cleaning the surface of steel sheet, automobile batteries, sulfonating agent, production of cellulose fibres, caprolactam, and in many other industries. Sulfuric acid is very reactive and corrosive. It is soluble in water and ethyl alcohol. Its strong reactivity may ignite organic material (light paper, or other combustible materials) if mixed together. Spent sulphuric acid is categorized as hazardous waste as Sr. No. 26.3 of schedule 1 of Hazardous and other Waste Management rules (HWM 2016). Being a polluting waste, the disposal of the spent conducting solution from the electroplating factories or metal finishing units is a major environmental concern. Iron and steel processing units; wherein hydrochloric acid and sulfuric acid are used as principal acids in large quantities, are the significant contributors of acidic waste streams containing sulfuric acids and other metal impurities. If these waste acids could be recovered and reused in the production processes, a good closed-circuit could be created making the process economical as well as eco-friendly. Many conventional, as well as advanced separation techniques are employed to recover either acid or valuable components from spent acidic liquor.

Separation processes are widely acknowledged as the heart of chemical process, petrochemicals and petroleum refining industries, biochemical, food and pharmaceutical processing units. More than 40% of capital and operating cost lies in separation and purification processes as it is an indispensable part of many downstream operations in chemical and allied process industries. The recovery and separation of sulfuric acid from spent and waste liquor via an environmentally friendly recovery and separation process warrants the reuse of the acid in an effective way.

1.1 Conventional separation routes for sulfuric acid

Sulphuric acid is widely used as an important industrial chemical in iron and steel industries for surface treatment, commonly known as acid pickling because of its relative cost-effectiveness as compared to other acids. Many treatment methods are available to treat waste liquor containing sulfuric acid as one of the components. Conventional technologies such as solvent extraction (SX) (Kesieme et al. 2013), distillation, evaporation (EV), ion exchange (Petkova et al. 1981) and newly developed membrane-based technologies such as membrane distillation (MD) (Li et al. 2012; Feng et al. 2016), diffusion dialysis (DD) (Palatý and Žáková 2004; Li et al. 2012) and electrodialysis (ED) (Cifuentes et al. 2002; Koter and Kultys 2008) have been widely reported in literature for the treatment of spent acidic solutions. However, many of these processes suffer from several drawbacks. For example, adsorption, absorption, distillation, evaporation, and extraction are based on the concept of equilibrium distribution of solutes between the phases. Crystallization is also used for H_2SO_4 and other spent pickling solutions generated from metal finishing industries. In this case, crystallization is based on the solubility relations of water, sulphuric acid, and iron sulfate. This process requires a large amount of energy to freeze out the impurities. In addition to this, removal of heavy metallic ions is difficult as well as an economical method for treating the crystals removed is not available (Regel-Rosocka 2010). The recovery of sulfuric acid using solvent extraction has been also reported as well established and widely used separation technology (Kesieme et al. 2013). This process is principally employed on large scale wherein the concentrations of contaminants are high. It has the major drawback of enhanced downstream processing due to the presence of an additional solvent. Evaporation and distillation are the conventional techniques to purify spent liquor. Though multi-effect evaporator, as well as distillation, is useful for separation/enrichment of acid contents in solution, needs of high thermal energy, complex design, phase change at high temperature and pressure and SO_3 mist eliminator provide constraints to its practical applications. Thermal decomposition can also be used for the treatment of acidic waste by the application of heat (Agrawal and Sahu 2009). The process needs a huge amount of energy in the form of heat, as well as the improper design of the furnace, may result in an appreciable of the amount of heat loss. In essence, these conventional separation techniques demand a considerable amount of energy, external entrainer and additional processing time to recover desired components. Besides, conventional processes like distillation and evaporation

involves phase change at high temperature and pressure and hence may cause thermal pollution.

Advanced separation processes are based on differences in transport rate through some medium under the influence of a driving force resulting from a difference in pressure, concentration, temperature or electrical filed, it is termed as rate governed separation. The membrane is one such medium, separating one phase from another and ensures separation based on the difference of transport of various species through it. Membrane based methods of sulfuric acid recovery include diffusion dialysis, electrodialysis and membrane distillation. Membrane distillation is a combination of membrane separation and distillation which takes place at high temperature and pressure due to the requirement of phase change. It consumes high energy as well as needs auxiliary equipment like reboiler, heat exchange or condenser. Diffusion dialysis works based on sieving principle where smaller particle diffuses faster based on the driving force- a concentration gradient (Luo et al. 2011). A necessary condition of dialysis is that the solute concentration in the recovery stream must be lower than in the feed stream in order to provide a driving force for diffusion. But this condition can be a limitation when the diffusing solute is the desired product, because the product is often recovered at a low concentration. In order to overcome the drawbacks of these techniques, fulfil the increasing energy requirements and environmental safety, processes that are currently in use should be revamped to make them more efficient, economical and environment-friendly. Ion-exchange membranes differ from ion-exchange resins in that ions selectively permeate through membranes by migrating from one site to the next under the influence of an applied field, rather than being adsorbed as by resins. Due to the nature of this separation process, ion-exchange membranes can be put into continuous operation and do not require periodic stripping as is the case with ion-exchange resins (Neuman et al. 1987).

1.2 Significance of Electrodialysis

Conceptually electrodialysis is a combination of electrolysis and dialysis, a powerful technology to separate charged compounds from a solution. It is an electromembrane process in which ions are transported through an ion exchange membrane from one solution to another under the influence of an electrical potential difference across the membrane. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Ion exchange membranes are credited with high

permselectivity, low electrical resistance, good mechanical strength and high chemical stability. Using the right combination of anion exchange and cation exchange membranes the ions of the feed solution can be effectively separated. Two different solutions are produced inside the stack: one more dilute (the diluate) or demineralized and the other more concentrated (the concentrate) than the original solution. It is an environmentally friendly technology for the separation of charged compounds. Electrodialysis (ED) holds much promise in the effective remediation of acidic effluents from industry including many other applications (Agrawal and Sahu 2009; Regel-Rosocka 2010). In ED system separation is accomplished without phase change, resulting in relatively low energy consumption. Phase change takes about 540 kcal/kg heat energy to evaporate one kg of water. ED was reported not only to be feasible and cheaper for acidic wastewater regeneration but also profitable in terms of acid recovery from wastewater (Kroupa et al. 2015). Electrodialytic recovery of acids from mining waste streams and acid mine drainage are reported in a number of studies (Buzzi et al. 2013; Zouhri 2013; Martí-Calatayud et al. 2014; Chekioua and Delimi 2015).

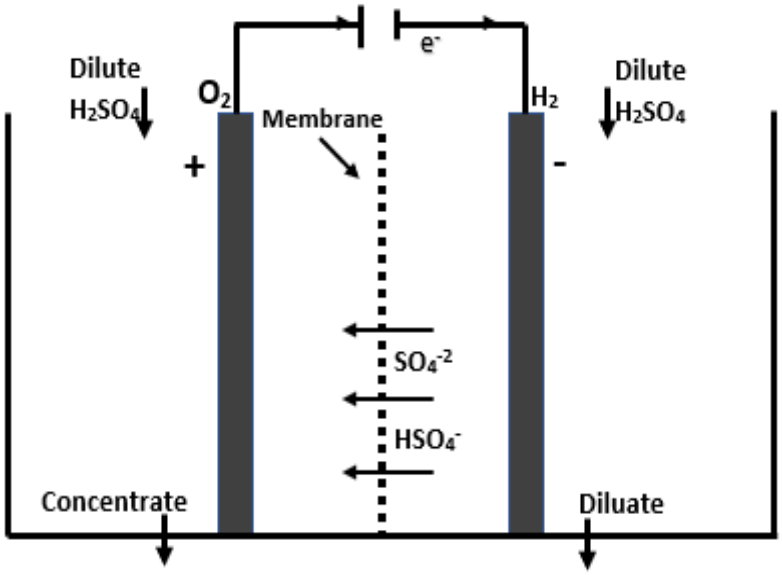


Fig. 1.1 Ion transport through anion exchange membrane

Electrodialytic separation of sulfuric acid from spent liquor is schematically presented in Fig. 1. Dissociation of sulfuric acid generates proton at the anode. Membrane is permeable to anions only and mostly sulfate ions cross from cathodic to anodic side. Generation of proton results in the formation of sulfuric acid in the anode compartment. Diluate and concentrated liquids are produced from anode side and cathode side respectively. Working principle of ED is elaborated in further detail in section 2.1.

1.3 Background of the present work

Disposal of spent pickle liquor is of great public concern in view of stringent environmental regulation as the liquor containing 5-10% of free acid is considered to be unsafe following EPA hazardous waste list (EPA). Metal finishing units particularly iron and steel industries are the significant contributors of waste streams where hydrochloric and sulfuric acids are used as principal acids and the resulting metal salts are ferrous chloride and ferrous sulfate, respectively (Agrawal and Sahu 2009). Recovering the dilute acid is not only profitable to the manufacturer but also imperative to environmental protection (Zhou and Liu 2007). Acids can be recovered using different conventional as well as advanced separation methods amongst which ED is found effective which serves the purpose of purification as well as concentration (Yongtao et al. 2015; Jaroszek et al. 2017; Xie et al. 2018). ED is an electromembrane process holds much promise for the treatment of acidic effluents. Current density, catholyte concentration, and catholyte to anolyte concentration ratio are considered to be the major factors affecting the performance of ED along with the type of electrode and membrane. Current density is considered to be one of the most influencing process variables in ED, and it could be maintained all through the process by varying the applied voltage (Zouhri 2013) which in turn together with current efficiency contributes to the power cost of the treatment (Lewis and Tye 1959).

In Electrodialysis process, the selection of electrodes plays a pivotal role. Despite considerable work in ED for the treatment of a number of wastewaters, development of cost-effective and corrosion free electrodes has become a less focused area of research. The ED process suggested in the literature for acidic waste treatment mostly employed platinum (Cattoir et al. 1999), platinized titanium (Zouhri 2013; Chekioua and Delimi 2015; Kroupa et al. 2015), or titanium coated with titanium oxide (Buzzi et al. 2013) as electrodes. Though effective, the use of costly electrodes may not be economically viable at large scale due to their significant cost contribution, which may exceed more than 90% of the total cost of the ED process unit (Nayar et al. 2015). Along with cost, stability and corrosion resistance are the other major factors affecting the electrode selection (Veerman et al. 2010; Nayar et al. 2015). It has been reported that the stainless steel has good corrosion resistance in acidic solutions, as well as carbon materials due to their chemical and electrochemical characteristics. These are also useful for large scale industrial applications (Iken et al. 2007). In addition, effect of process variables on molar flux, current efficiency, sulfuric acid

separation and applied voltage constitutes an important role in the separation performance of electrodialysis.

Acidic effluent containing metal contents or other impurities can be treated effectively using ED to enhance the concentration of such solutions in order to render them recyclable or reusable. Though multi-effect evaporator system could be useful for the treatment of acidic effluents, drawbacks like high thermal energy requirements, phase change at higher temperature and pressure, risk involvement due to SO_3 mist formation, and complex design set limits to its practical application. Such dilute acid stream could be concentrated initially by ED followed by any conventional techniques such as evaporation thereby reducing the heat load on the evaporation. The energy required to increase the concentration of dilute sulfuric acid by ED can be thought of to be very much lower than the same for evaporation. Supplementation of evaporation with ED can not only be considered as a synergic combination but also an energy-efficient process. Furthermore, ED processes reported in the literature are mostly the processes either for recovery or treatment of solutions with a continuous mode of operation. Scanty information is available wherein simultaneous separation as well concentration is carried out by ED. In addition to this, literature also reports that the enrichment of sulfuric acid solution by ED is affected by the properties of the ion exchange membrane and it is limited to certain value due to its proton leakage characteristics. Yongtao et al. (2015) produced 28.56 wt. % concentrated sulfuric acid by liquid absorption and oxidation of low concentration SO_2 in aqueous solutions as well as electrodialysis enrichment using polyethylene heterogeneous membrane (Yongtao et al. 2015). Asari et al. (2011) reported a concentration of sulfuric acid from 1.4 to 2.9 mol/l at 30 mA/cm2 current density with different ion exchange membranes (AEM) including selemion AAV (Asari et al. 2011). Jaroszek et al. (2017) reported the use of ED process for the production of sulfuric acid and increased its concentration up to 3.5 mol/l using five different types of anion exchange membranes (Jaroszek et al. 2017). Most of the researches have used either low proton leakage or tailored membrane for the given purpose. Multistage electrodialysis process to increase sulfuric acid concentration up to the maximum possible value as well as performance comparison of an indigenous membrane with other AEMs has not been reported with a rigorous determination of process performance parameters.

ED process can be the best alternative option to evaporation for sulfuric acid separation and concentration if developed with cost-effective material of construction of module, type of

electrode and membrane having best qualities with respect to operating time, current efficiency and energy consumption.

1.4 Definition of problem

Presence of sulfuric acid with other metal impurities in waste acidic liquor makes it unusable and non-dischargeable as it affects living and non-living environment and thereby demands its extensive as well as economic reclamation. Compared to conventional separation and concentration methods, ED holds much promise in the treatment of such acidic liquor but employs expensive electrodes that may not be affordable at a large scale. Selection of an appropriate, as well as the affordable electrode, is a great challenge as it affects the quality of anolyte. Limited literature is available reporting use of ED with low-cost electrodes and representing the effect of various physico-chemical parameters on the process performance. Furthermore, development of multistage electrodialysis system for enrichment of lean sulfuric acid solution providing a complete set of process parameters and suggesting a more appropriate and effective membrane is also a major area of research. Systematic experimental and computational studies were performed to find out solutions of the aforementioned problems.

1.5 Objectives and scope of the present study

The present work principally aims at separation and concentration of sulfuric acid form spent acidic liquor using batch electrodialysis as well as cascaded ED system was used with three different types of membranes and two types of electrodes. The main objectives and scope of the present study are appended below:

1 To study the batch electro-membrane separation process and its suitability to recover sulfuric acid from spent acid solution.

2 To investigate the effects of various physico-chemical parameters on electrodialytic recovery of sulfuric acid in a batch process.

3 To study and compare the performance of different commercial anion exchange membranes for enrichment of sulfuric acid in a cascaded electrodialysis.

4 To study the consumption of energy in electrodialysis process.

5 To investigate transport mechanism across the ion exchange membrane and mathematical modeling of the process (Development of an equation relating process performance variables to flux).

1.6 Presentation and layout of the thesis

The present thesis contains six chapters with appropriate sections, subsections, references, appendices and the list of research publications. The first chapter deals with the introduction and significance of the electrodialysis process along with its advantages and limitations in comparison to conventional separation techniques. Problem definition and objectives are described in the first chapter. Chapter 2 describes the theoretical background of the ED process including working principle, industrial application, advantages and limitations. A detailed review of pertinent literature for the separation and purification of spent liquor is presented in chapter 2. Chapter 3 describes the different equipment, glassware, chemicals, electrodes and membranes used to carry out present research work along with the detailed analytical and experimental procedures. This chapter also describes various methodologies of analysis of anolyte and catholyte solutions, membrane characterization and different theoretical equations and terminologies used to determine the effect of various physico-chemical parameters on the ED performance. Chapter 4 describes in detail the results obtained on the basis of experimental and theoretical considerations. Effects of various factors on the ED performance as well as cascaded ED system to concentrate sulfuric acid are evaluated in this chapter. Performance of IPA anion exchange membrane is compared with standard (Selemion AMV) as well as low proton leakage membrane (Selemion AAV). Finally, chapter 5 summarizes the work and evaluates the contribution of the present study with some recommendation for further study.

CHAPTER 2

Literature Review

Membrane technologies have been established as very effective and commercially attractive options for separation and purification processes in the chemical and its allied industries. Membranes are now competitive to conventional techniques, by virtue of the facts that they work without the addition of chemicals, with relatively low energy use, and in a compact modular design. Electrodialysis (ED) is a powerful technology when charged compounds have to be separated from a solution. It is an environmentally friendly alternative to the technology currently in use. Since it removes only ionised species, ED is especially suitable for separating non-ionised components from their ionised counterparts. The requirements of both separation as well as concentration are simultaneously fulfilled by ED. It holds much promise in the effective remediation of acidic effluents from industry, separation of acids from the mixture of acids, production of acid with many other applications. Unlike distillation or evaporation, ED operates without phase change, which results in relatively low energy consumption. Either stand-alone or hybrid/integrated process of ED in combination with other conventional or advance technologies has been found to be efficient and economic options. Despite, the consumption of electrical energy, applications of ED have been increased manifold in the past few decades.

2.1 Working principle of electrodialysis

Electrodialysis method is a combination of electrolysis and dialysis, and it was proposed by Maigrot and Sabates in 1890 (Shaposhnik and Kesore 1997; Koter and Warszawski 2000). It is a powerful technology to separate charged compounds from a solution. ED is an electromembrane process in which ions are transported through an ion exchange membrane from one solution to another under the influence of an electrical potential difference across both anion and cation selective membrane. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Applying a voltage between two end electrodes generated the potential field required for this. During this transportation, anions are able to permeate through anion-selective membranes, but are blocked by the cation-selective membranes. The opposite occurs with cations. As a result,

two different solutions are produced inside the stack: one more dilute (the diluate) or demineralized and the other more concentrated (the concentrate) than the original solution.

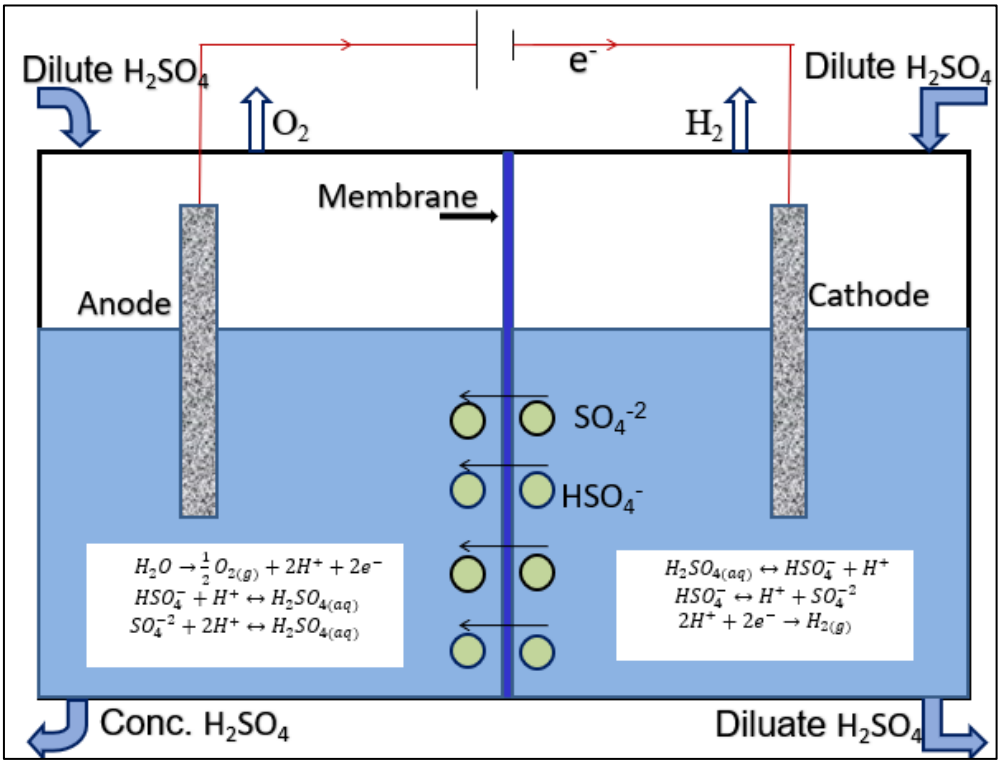


Fig. 2.1 Electrodialysis process mechanism

Fig. 2.1 represents the mechanism and the process particularly for the separation of the sulfuric acid from the spent acidic liquor. Reactions involved therein are shown below,

Cathode side:

$$H_2SO_{4(aq)} \leftrightarrow HSO_4^- + H^+ \quad (2.1)$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{-2} \quad (2.2)$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \quad (2.3)$$

Anode side:

$$H_2O \rightarrow \frac{1}{2}O_{2(g)} + 2H^+ + 2e^- \quad (2.4)$$

$$HSO_4^- + H^+ \leftrightarrow H_2SO_{4(aq)} \quad (2.5)$$

$$SO_4^{-2} + 2H^+ \leftrightarrow H_2SO_{4(aq)} \quad (2.6)$$

Autoprotolysis nature of sulfuric acid forms bisulfate ions and further dissociations generate sulfate ions in aqueous solution. The catholyte is an electrolyte solution of sulfuric acid having z valency of anions. Cathodic reactions are shown by Eqs. (2.1), (2.2) and (2.3). The overall results of these three reactions are the formation of protons and anions at the cathode. As anodic compartment is filled with very dilute sulfuric acid and therefore sulfate, bisulfate, and hydroxyl ions are also present there. The concentration of sulfuric acid is higher in catholyte than in anolyte. As evidenced from equation (2.4), (2.5), and (2.6), protons, generated from the hydrolysis of water, get attached with an influx of sulfate or bisulfate ions crossing the membrane from cathode to anode side, thereby producing acid in the anode side. Protons generated at the anode side also move through the membrane to the cathode side, the phenomena known as proton leakage, which affects the performance of the process. Ultimately protons are generated at the anode and consumed by anions in the anolyte as well as reduced at the cathode with generation of hydrogen and oxygen gas at the cathode and anode respectively. With an ideal perm-selective membrane, there is 1 mol of production of a proton at the anode and 1 mol of reduction of a proton at the cathode when subjected to 1 mol of unit electrical charge field (Cherif and Gavach 1989). In electrodialysis process, the total flux is the contribution of different types of fluxes (discussed in detail in section 2.6) mainly flux due to motion/velocity of fluids, natural diffusion based on the concentration gradient, migration of ions based on membrane electric potential and applied electric potential.

2.2 Significant industrial applications of electrodialysis

There are numerous successful applications of electrodialysis in various areas such as water desalination, wastewater treatment, food and dairy industries, demineralization of whey, deacidification of fruit juices, metallurgy, chemical process industries etc. Fig. 2.2 represents the major applications of ED in various fields. Production of table salt, brackish water desalination and industrial effluent treatment are some applications of ED that has been commercialized at large scale (Noble and Alexander 1995; Baker 2004). Production of ultrapure water, water desalination and pre-concentration of NaCl are the other major application of the conventional ED at commercial scale. ED is also widely used to recover toxic or valuable components from effluents of galvanic and metal surface finishing processes and from dump leaching wastewater (Strathmann 2010).

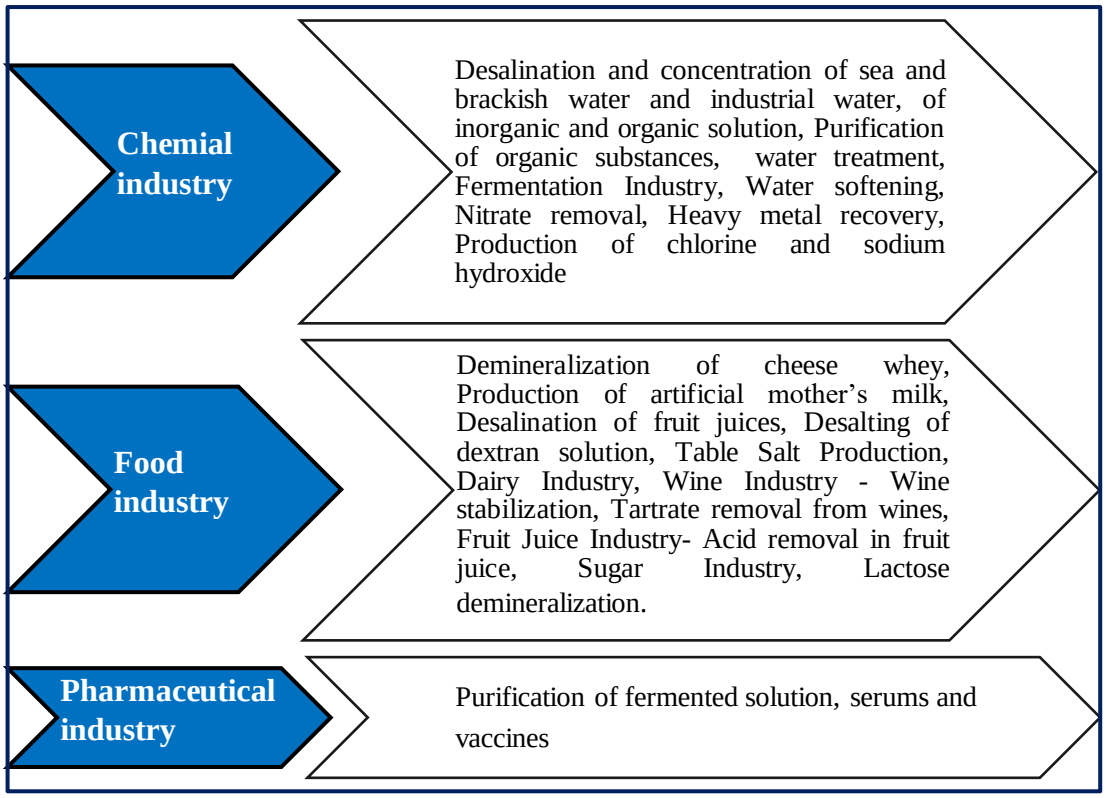


Fig. 2.2 Major applications of electrodialysis

Following section represents the applications of ED particularly in areas wherein sulfuric acid is one of the major components of waste liquor that needs to be treated.

2.2.1 Recovery of acid

Spent pickle liquor, more commonly termed as spent liquor, is traditionally generated from the digestion or extraction of ores with inorganic acids in metallurgical units. The liquor invariably contains residual acid and metal salts of the pickling acid. Amongst a number of metal finishing units, the iron and steel industries in particular, are the significant contributors of such waste streams where hydrochloric and sulfuric acids are used as principal acids and the resulting metal salts are ferrous chloride and ferrous sulfate, respectively (Agrawal and Sahu 2009). One major application of ED is in the treatment of spent acidic liquors. Many successful attempts have been made by various researchers to treat such acidic solutions. Sulfate pickling solution (Bramer and Coull 1955) and pickling liquor (Lewis and Tye 1959) were initially treated by ED before 1960. ED has been a feasible and cheaper application to treat acidic wastewater from the iron and steel industry (Urano et al. 1984). ED recovered almost 90% sulfuric acid from stainless steel decontamination effluent (Cattoir et al. 1999). Spent acidic liquor generated from acid mine drainage, metal finishing units, iron and steel industry has been successfully treated by ED. ED enables not

only separation of acid but also increases the concentration of acid high enough rendering it recyclable or reusable (Regel-Rosocka 2010).

2.2.2 Separation of metal contents/acids from mixture of acids

Prior to the sale to the automobile and major appliances industry, rust, scaling and oxidation from rolled sheet and billets are removed by treatment with sulfuric acid in iron and steelmaking industries. Large quantities of sulfuric acid are used in various metal finishing units (Kultys et al. 2011). Spent acidic liquor generated from such industries contains different acids such as HCl, H_2SO_4 and/or HNO_3 and different metals depending on the kind of treatment required. ED has been successfully applied for the separation of metallic impurities (Cifuentes et al. 2002; Martí-Calatayud et al. 2014; Chekioua and Delimi 2015) from spent acidic liquor. ED has been found to be as an efficient and also suitable on commercial scale to separate various acids such as acetic acid (Koter 2008), nitric acid (Andres et al. 1994), and phosphoric acid (Koter and Kultys 2010) from mixture of acids.

2.2.3 Production of sulfuric acid

It is possible by ED to split waste salt solutions to the corresponding acid and base (Raucq et al. 1993) and therefore it has also been used for the production of sulfuric acid as well as its concentration (Zouhri 2013; Kroupa et al. 2015; Jaroszek et al. 2017). The use of ED to produce purified water and a concentrated solution from an aqueous stream up to some intermediate level has also been evaluated as an economical pre-treatment process to the further purification step in an integrated electrodialysis-evaporation process for the treatment of aqueous process streams containing electrolytes (Rockstraw et al. 1990).

2.2.4 Separation and concentration of solution

The ability of the process to simultaneous separate as well as concentrate the solution makes ED applicable to the production and concentration of sulfuric acid. Simultaneous production and concentration of sulfuric acid from sulfate sodium salt (Zouhri 2013; Jaroszek et al. 2017) have been a successful application of ED. Sulfuric acid was generated and concentrated successfully by liquid absorption and oxidation of low concentration SO_2 in aqueous solutions as well as electrodialysis enrichment. With use of modified/self-made membrane, for example, polyaniline (PANI)/polyvinylidene fluoride (PVDF) membrane, ED has been applied for the sulfuric acid concentration enrichment as high as 63 wt. % (Xie et al. 2018).

2.2.5 Integrated/Hybrid process

Integration of ED with other processes has gained a lot of interest in various applications. The production of high-quality process water for power plants and electronic industry by electrodialysis in combination with other processes such as ion-exchange or reverse osmosis has become a state-of-the-art technology (Strathmann 2004) in recent times. Another application of electrodialysis that was earlier limited regionally to Japan has gained considerable commercial importance. This is the production of table salt from seawater (Noble and Alexander 1995). Electrodialysis membranes can concentrate the salt in seawater to about 18–20% solids, after which the brine is further concentrated by evaporation and the salt recovered by crystallization (Baker 2004). It may be more economical to concentrate the sulfuric acid solution to an intermediate level with electrodialysis, followed by further concentration using evaporation. The combination of ED with evaporation to produce purified water has been an economical application in an integrated electrodialysis-evaporation process for the treatment of aqueous process streams containing electrolytes (Rockstraw et al. 1990). Determination of applicability of ED with another conventional process such as evaporation to enrich sulfuric acid concentration is an area not explored yet, has been considered in present work.

2.3 Electrodialytic separation/recovery of sulfuric acid from spent acidic liquor

Sulfuric acid is produced more than 270 million tons worldwide and used extensively in chemical industries. Because of its low cost and availability, sulfuric acid is extensively used in industry where an acidic or anhydrous condition is required. Sulfuric acid is used in various forms such as dilute, concentrated or oleum as per requirements in reaction or process. Sulfuric acid is used in the manufacturing of fertilizers and various chemicals such as synthetic detergents, dyes and pigments, explosives and drugs. It is widely used to wash impurities out of gasoline and other refinery products as well as in cleaning of metals in metal processing units, e. g. pickling of iron and steel etc. Sulfuric acid serves as the electrolyte in lead-acid batteries used in motor vehicles. Waste liquor generated from such chemical industries contains sulfuric acid as one of the components. Table 2.1 represents some of the industries generating waste acidic liquor containing various chemicals.

Table 2.1 Industries generating spent acidic liquor containing sulfuric acid.

Sr. No.	Industry	Major constituents of waste-streams
1	Fertilizers	Sulfuric acid, ammonia, water etc.
2	Pulp and paper	Sulfuric acid, water, chlorine, hydrochloric acid etc.
3	Petroleum refinery	Sulfuric acid, isobutane, butane etc.
4	Organic and inorganic chemicals	Sulfuric acid, nitric acid, sodium, water, sulphides etc.
5	Pickling of metals	Sulfuric acid, nitric acid, hydrochloric acid, various metals
6	Dyes and intermediates	Sulfuric acid, nitic acid, hydrochloric acid, organic and inorganic compounds, water etc.

Waste generated from chemical industries is generally strong and may contain toxic pollutants as well as organic and inorganic matter in varying degrees of concentration. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply hardly biodegradable. Since these wastes differ from industry to industry in general characteristics, its pre-treatment is required before discharge. Table 2.2 represents the name of the products that consume sulfuric acid and generates waste acidic liquor containing sulfuric acid in different concentrations. Some of the data shown in Table 2.1 and 2.2 are taken from particular industry and hence references are not provided for all.

Table 2.2 Average concentration of sulfuric acid in spent acidic liquor generated from various industries.

Sr. No.	Industry	Sulfuric acid concentration (wt. %)		Ref.
		Inlet stream	Exit stream	
1	Phosphate fertilizers	60-98	35	--
2	Alpha blue pigment	70	25-30	--
3	Fatty alcohol production and detergent manufacturing process	30	20-25	--
4	Alkylation unit (Petroleum refineries)	85-95	5-15	--
5	Titanium white pigment	90-95	10-20	(Tongwen and Weihua 2001)
6	Pickling of metals	5-60	5	(Bramer and Coull 1955), (Lewis and Tye 1959)

The waste liquor thus generated consists of sulfuric acid concentration varying from 5 to 40 wt. % with many other acids and chemicals depending upon the process requirements. Approximately 15 to 20% of the global sulfuric acid produced is being generated as waste

during the production of various chemicals. More than 50 million tons sulfuric acid goes as waste, and recovery of sulfuric acid in pure form is a burning problem.

Disposal of spent pickle liquor is of great public concern in view of stringent environmental regulation as the liquor containing 5-10% of free acid is considered to be unsafe following EPA hazardous waste list (EPA). A considerable cost can be saved if acid is purified/recovered and/or purified acid could be concentrated to a higher level to recycle/reuse. Table 2.3 represents the list of applications of sulfuric acid of various concentrations.

Table 2.3 Source – User mapping for sulfuric acid.

Sr. No.	Sulfuric acid (wt. %)	Applications
1	> 5	Pickling of metals
2	10	Reagent for decolorization, clinical use, laboratory use
3	11-20	Treatment of CPC, Pigment industry
4	21-30	Manufacturing of ammonium sulphate
5	30-33	Battery acid
6	31-40	Hydrolysis of alkoxides to alcohols in detergent mfg.
7	41-50	Polymerization reaction
8	51-60	Extraction of platinum and rhodium from ores
9	62-63	Chamber or fertilizer acid
10	70	Alpha-blue pigment
11	77-78	Tower acid or Glover acid
12	81-90	Alkylation unit, oil refining industries
13	91-98	Catalyst for esterification reactions

Conventional reclamation (Agrawal and Sahu 2009) of the spent liquor includes processes like neutralization-precipitation (López-Delgado et al. 1997), refrigerated crystallization (Özdemir et al. 2006), electrolytic precipitation-deposition (Kerney 1994), ion exchange (Nenov et al. 1997), and relatively older method of solvent extraction (Kesieme et al. 2013). Despite being old none of these processes have achieved widespread acceptance due to cumbersome equipment required, the quantities of treating chemicals including a significant amount of makeup fresh acid consumed and low benefit-cost ratio. Electrodialysis, on the other hand, holds much promise in the treatment of acid effluents from the industry. Work carried out by various researches to recover sulfuric acid from spent liquor using electrodialysis is summarized in Table 2.4.

Table 2.4 Results reported in various studies with the ED and DD using different AEMs.

Sr. No.	Type of feed	Membranes and electrodes used	Results obtained	Reference
1	Waste sulfuric acid (Treating Ilmenite from digestion of Sodium titanate)	MA – 3475, A-101 Anode – Ti coated with Pt Cathode- Hastelloy C	Acid recovery by ED contained very low impurities than by evaporation.	Barney and Hendrix, 1978
2	Waste plating solution H_2SO_4 (From metal cations) Separation of sulfuric acid from contaminants	AG1-X8, Wofatit SBW-anion exchanger	Distribution coefficient for sulfuric acid was greater than that for nickel, copper, iron, zinc and antimony	Petkova et al., 1981
3	Acidic waste-water (Iron and Steel industry)	Selemion AAV, Selemion CMV Pt electrode	Studied optimum operating conditions to recover acid, fouling of membrane with Fe (II) and (III)	Urano et al.,1984
4	H_2SO_4+ glucose + xylose system	Selemion AMV, Selemion CMV Anode – carbon Cathode - stainless steel SUS-27	Use of Nernst-Planck equation. Ionic diffusion reported as rate degerming step. Studied effect of concentration and temperature on limiting current density.	Huang and Juang, 1986
5	H_2SO_4 + glucose (Sugar industry in acid hydrolysis of biomass)	Rohm & Haas Amberlite IR-118 Cation exchange resin	Complete H_2SO_4 recovery and 94% glucose recovery.	Neuman et al., 1987
6	Waste acid (Hydrometallurgy)	Polymeric AEM Anode - Ti-Pt Cathode - Ti-Pt	AEMs-show proton leakage. Use of Nernst-Planck equation. Sulfate ions permeability decreased with anolyte concentration	Cherif et al., 1988
7	Sulfuric acid (Natural and industrial waste water)	Ionics 103 QZL 386 Anode and cathode – platinized titanium	ED was found effective for removing sulfuric acid from waste streams and advantageous over facilitated transport	Simpson and Buckley, 1988
8	Sulfuric acid solution (Waste acid)	RAI R 1035 Anode and cathode – Pt coated Ti	Measured of the trans-membrane flux and used Nernst-Planck electro diffusion equation	Cherif and Gavach , 1989
9	Acidic nickel sulfate stream containing Copper, arsenic, bismuth, antimony and Nickle (Hydrometallurgy)	ACS, CMS, Neosepta ACM Anode – platinum plated titanium Cathode - SS 316	Acid recovery more than 80 %, Acid concentration up to 28 wt. %. Effect of current density on acid extraction, ED was found more energy efficient at lower current densities	Baltazar et al., 1992

Sr. No.	Type of feed	Membranes and electrodes used	Results obtained	Reference
10	Dilute aqueous mixture of sulfuric acid and nitric acid (Acid treatment in chemical process industries)	ARP, CRP, Neosepta, ACS, CMS Anode – platinized titanium Cathode – carbon, SUS 316 SS	Sulfuric acid separation was found possible at room temperature; better results obtained with treated (tailor-made) membrane	Audinos et al., 1993
11	Na_2SO_4 solution	Nafion 117, ARA, BPM Electrode-Platine coated titanium	Production of H_2SO_4 and NaOH	Raucq et al., 1993
12	Mixture of sulfuric acid and nitric acid	ACS, CMS Anode – platinized titanium Cathode –SUS 316 SS	Separation and concentration of acids using selective membrane with reduced proton number to multivalent ions	Andres et al. , 1994
13	Waste sulfuric acid (Metallurgical, Mining, Chemical industries)	Neosepta AFN	Investigated membrane mass transfer coefficient and diffusion coefficient.	Palaty and Zakova, 1996
14	Recovery of acid (Waste water)	ARA Anode and cathode – platinized titanium	Worked on regeneration of acid and base. Determined effect of polarization on proton leakage through AEM	Lorrain et al., 1996
15	Dilute sulfuric acid	ARA Anode and cathode – platinized titanium	Studied proton transport mechanism. Water as well as sulfate ion behaved as mediating agent for proton leakage.	Lorrain et al., 1997
16	Spent sulfuric acid solution (Rinsed water form metal etching)	Neosepta AMX, Neosepta CMX	Reported that the current density should be lower than limiting current density. Current density depends on initial concentration. Recovered acids and estimated energy consumption	Wisniewski and Wisniewska, 1997
17	Waste acid from sulfuric acid production from pyrite containing As, F, Cu, Zn, Fe	AFX and S2O3	Effectively removed of metal cation impurities. Mass transfer coefficient and impurity removing capacity for membranes were compared.	Zhang et al., 1999
18	Stainless steel decontamination effluent	Solvay's AW, Selemion AAV, Neosepta AMH, ACM Anode and cathode – Platinum	Recovered sulfuric acid more than 90%.	Cattoir et al., 1999

Sr. No.	Type of feed	Membranes and electrodes used	Results obtained	Reference
19	Titanium white (pigment) waste liquor	Tailor made membrane	Selectivity and recovery of acid affected by aryl and benzyl substitution and acid composition of feed.	Tongwen and Weihua, 2001
20	Aqueous solution of H_2SO_4 + $CuSO_4$	Neosepta AFN	Membrane used was more permeable to sulfuric acid with the effective rejection of cupric sulfate, operation being more effective at high acid concentration	Palaty and Zakova, 2004
21	Formic acid recovery (Pickling solution from leather industry)	SB-6407, Neosepta AMH, AFN, ACM Anode and cathode - Graphite	Membrane comparison for diffusion dialysis and electrodialysis process, Determined effect of time on current density	Akgemci et al., 2005
22	Preparation and characterization of AEMs	Various IEMs	Reported that the preparation of ion exchange membranes or materials is the most crucial for specific purpose.	Xu, 2005
23	Waste acid + Copper solution (Copper electro-refining industry)	AEM - MA 3475, CEM - MC 3470 Anode and cathode - Platinum	Acid recovered and concentrated up to 50 g/l in 12 h at 45˚C and current density 225 A/m^2 with 5.9-6.5 V.	Cifuentes et al., 2006
24	Mixture of acetic acid and sulfuric acid	Neosepta CMX and ACM	Effect of limiting current density and current efficiency on the separation. Described experimental result by model based on the extended Nernst-Planck equation and the Donnan equilibrium	Koter, 2008
25	Sulfuric acid solution	ACM, Selemion AAV	Determined the current efficiency of membrane electrolysis of sulfuric acid solution, explained transport phenomena by model based on the extended Nernst-Planck equation and the Donnan equilibrium	Koter and Kultys, 2008

Sr. No.	Type of feed	Membranes and electrodes used	Results obtained	Reference
26	Waste anodic aluminum oxidation	DF120	Reported that concentration polarization can be reduced by agitation, acid recovery and H^+ concentration in the recovered acid was affected by flow rate ratio of water to feed.	Xu et al., 2009
27	Spent acidic solution (steel and electroplating industries, metallurgical industries)	Different anion and cation exchange membranes	Review on different possible separation processes. Concept of recycling/reuse of spent wastes is for to convert them as secondary source of acid and metal content.	Agrawal and Sahu, 2009
28	Spent pickling solutions (Steel processing)	Bipolar membrane, IEM	A review on methods of regeneration of spent pickling solutions from steel processing. ED, DD, and crystallization are the best techniques available	Regel-Rosocka, 2010
29	Mixture of sodium and magnesium sulfate (Electrolysis plant cell)	Selemion AAV	The current efficiency reported to be independent of kind of salt on cathode side AAV, Current efficiency hardly exceeded 50%	Kultys et al., 2011
30	Acidic vanadium leaching solution	DF120	Over 84% sulfuric acid recovery efficiency achieved by controlling the flow rate of feed, flow rate ratio, volume, Al and Fe ions concentrations, rejection more than 85%.	Li et al.,2012
31	Mixed industrial waste water (Water treatment plant-coal mine drainage)	HDX 200 AEM, HDX 100 CEM Anode and cathode - Platinum	Recovered water. Contaminant removal efficiency was reported greater than 97%, Scaling of membrane was due to deposition of iron on surface.	Buzzi et al., 2013
32	Sodium Sulfate salt (Metallurgy)	AFN and CMX Anode and cathode - Platinum coated titanium	Generated H_2SO_4 and NaOH. Concentrated H_2SO_4 & NaOH gradually from 0.2 M to 0.8 M at current density 27.77 mA/cm^2.	Zouhri,2013

Sr. No.	Type of feed	Membranes and electrodes used	Results obtained	Reference
33	Magnesium sulfate, Zinc sulfate, Sodium sulfate (Sulfate separation process)	Selemion AAV	Reported that the current efficiency is independent of kind of metal cation present on cathode side of the membrane.	Koter et al., 2014
34	Acid mine drainage (Mining, metallurgy)	Heterogeneous HDX membranes -AEM, CEM Anode-Titanium coated with metal oxide Cathode- AISI 304 stainless steel	Current density affected the recovery of sulfuric acid, observed more recovery at low values of current density.	Martí-Calatayud et al., 2014
35	H_2SO_4 and NaOH recovery from Na_2SO_4	CEM-CM(H) AEM - AM(H)-PP BPM - BM 12-01-P	Production of H_2SO_4 and NaOH by ED was reported to be profitable.	Kroupa et al., 2015
36	Pickling bath (Iron, metallurgy industry)	CMX, AMX, CMV, Nafion 117 Anode - Platinized titanium Cathode - Graphite	Purified sulfuric acid from pickling bath contaminated by Fe (II) ions. On increasing Fe (I) to 20 mA/cm^2 improved efficiency of Fe (II) ions & H_2SO_4 was 70.17% recovered.	Chekioua and Delimi, 2015
37	Production of sulfuric acid by SO_2 absorption in aqueous solutions and ED enrichment (Metallurgy, petroleum industry)	Polyethylene heterogeneous membrane Anode - Ru-Ir-Ti oxide coating on titanium substrate Cathode - Manganese oxide catalyst on 304 chrome-nickel austenitic SS substrate	SO_2 removal rate was 83.4 % with concentration of sulfuric acid of 28.56% by newly developed membrane.	Yongtao et al., 2015
38	Production of concentrated sulfuric acid	Selemion AAV, ANI, ACM etc. Anode and cathode - CF-210, CF-21	Comparison of the applicability of selected anion-exchange membranes for production of sulfuric acid by ED. Maximum concentration of sulfuric acid was 3.5 mol/l by Selemion AAV membrane.	Jaroszek et al., 2017
39	Industrial waste water (1 wt. % sulfuric acid concentration)	PANI/PVDF, AMI-7001, Qianqiu Anode - Ru–Ir–Ti oxide coating on a titanium substrate Cathode - Platinum	63 wt. % of sulfuric acid concentration was obtained by newly developed membrane.	Xie et al., 2018

Bramer and Coull (1955) explored the possibility to electrolyze spent sulfate pickling solution and showed that the important operating variables were catholyte acid concentration, anolyte acid concentration, iron concentration in the catholyte, current density, and velocity of the catholyte past the cathode. They conducted an experiment on ED using cell which was machined from a 5-inch-square block of Plexiglas and was made in three sections and two end sections form the anolyte and catholyte chambers and were separated from the centre section by the permselective membranes (Bramer and Coull 1955). Pickling liquor was treated by Lewis and Tye (1959) with stainless steel electrodes showing the power cost of treatment as a function of current efficiency and the voltage across the cell (Lewis and Tye 1959). Barney and Hendrlx (1978) also calculated power to produce about 50% sulfuric acid and regenerated waste acid by performing a two-stage arrangement which was constructed wherein the waste solution and the concentrate solution would flow counter currently between two stacks arranged hydraulically in series (Barney and Hendrix 1978). Rodrigues et al. (1999) reported the potentials of chromating-bath rinse water treatment by ED whereby optimization of waste reduction and reuse of water and chemical products could be achieved..

Baltazar et al. (1978) described a process to selectively recover sulfuric acid and to concentrate it from an acidic nickel sulphate stream containing copper, arsenic, bismuth and antimony in addition to nickel using electrodialysis process with different membranes. At different values of current densities different acid extraction rates were achieved with more than 80% total acid recovery, proving the electrodialysis process energy-efficient at lower current densities and higher temperatures. They showed that the relationship between acid recovery rate, current density and product acid concentration can be represented by simple mathematical relationships means that the process parameters can be set to give the desired acid recovery and /or product concentration (Baltazar et al. 1992). Even recovered acid contains very law impurities than evaporation when treated by ED (Barney and Hendrix 1978). The recovery of sulfuric acid by electrodialysis is affected by many factors such as type of membrane, type of electrode and process variables. Four different types of membranes were used by Cattoir et al. (1999) to separate sulfuric acid from stainless steel decontamination effluent and recovered approximately 90% of the sulfuric acid. Type of membrane may drastically improve the results of separation (Cattoir et al. 1999). Bipolar ED yielded an acid solution concentrated 63-fold as compared to conventional ED in acid and base purification from water solutions (Wiśniewski et al. 2004). 28.56 wt. % concentrated

sulfuric acid was produced by liquid absorption and oxidation of low concentration SO_2 in aqueous solutions as well as electrodialysis enrichment (Yongtao et al. 2015) whereas the highest concentration was reported to be 3.5 mol/l in application of ED to concentrate sulfuric acid using Selemion AAV membrane (Jaroszek et al. 2017). Xie et al. (2018) increased sulfuric acid concentration as high as 63 wt. % by electrodialysis using a self-made polyaniline (PANI)/polyvinylidene fluoride (PVDF) membrane (Xie et al. 2018). Recovery of acid is also affected by process variables such as current density that ultimately affect the current efficiency of the process and power consumption.

Urano et al. in 1984 studied the optimum operating conditions to recover acid from acidic waste-water released from the iron and steel industry using ED with the newly developed membrane by investigating limiting current density and current efficiency (Urano et al. 1984). Simpson and Buckley (1988) removed sulfuric acid from industrial and mining waste streams (Simpson and Buckley 1988) whereas Buzzi et. al. (2013) recovered water with contaminant removal efficiencies greater than 97% from acid mine drainage (Buzzi et al. 2013). ED when operated at different values of current density affected both acid recovery and current efficiency (Martí-Calatayud et al. 2014) indicating current density as a major variable affecting performance of the process. ED was reported not only to be feasible and cheaper (Urano et al. 1984) for acidic wastewater regeneration, but also profitable in terms of acid recovery from wastewater (Kroupa et al. 2015).

In general, ED can be used to perform several general types of separation such as separation of acid from a mixture of acids and separation of metal contents from spent acidic liquor. In addition, a slightly modified ED can be used for the production of acids and bases from the corresponding salts. Use of low proton leakage membranes or structurally modified membranes in ED has made possible to separate and concentrate sulfuric acid to a higher level.

2.4 Membranes for electrodialysis

Ion-exchange membranes are the most important components of an electrodialysis cell. Ion-exchange membranes are ion-exchange resins in film form. They consist of highly swollen gels carrying fixed positive or negative charges (Noble and Alexander 1995). They usually also contain other polymeric materials to improves mechanical strength and stability. Electrodialysis process uses ion exchange membranes carrying electrical charges to control the transport of ionic species to separate them selectively from a mixture of components

(Strathmann 2004). Performance ED process highly depends on the properties of the AEM. A wide variety of IEMs has been developed to date and used in various membrane separation techniques mainly ED. Table 2.5 represents the list of some manufactures of AEMs with name of their origin.

Table 2.5 Lists of manufactures of ion exchange membranes.

Name of manufacturers of AEM	Name of country	Commercial brand
Asahi glass Co. Ltd.	Japan	Selemion
Asahi Chemical Industry co.	Japan	Aciplex
Tokuyama Co. Astom	Japan	Neosepta
DuPont Co.	USA	Nafion
Ionics, Inc.	USA	AR.., CR..
FuMA Tech. GmbH	Germany	FAS
PCA PolymerchemieAltmeier GmbH	Germany	PC…
LanXess Sybron Chemicals	Germany	Ionac
MEGA a.s.	Czech Republic	Ralex
Solvay, S. A.	Belgium	Morgane
Tianwei Membrane Co. Ltd.	China	TWAED
CSMCRI, Bhavnagar	India	IPA (Indigenous)

The function of ion exchange membrane is determined from the species of the charge of the ion exchange group fixed in the membranes and its distribution and accordingly they are classified based on their function into different categories such as Cation exchange membranes, in which cation exchange groups (negatively charged) exist and cations selectively permeate through the membranes. Anion exchange membranes, in which anion exchange groups (positively charged) exist and anions selectively permeate through the membranes.

Other categories are Amphoteric ion exchange membranes, Bipolar ion-exchange membranes and Mosaic ion exchange membranes (Sata 2010). High permselectivity, low electrical resistance, good mechanical strength and high chemical stability are some desired properties of the membrane. Ion exchange membranes fall into two broad categories: homogeneous and heterogeneous. In homogeneous membranes, the charged groups are uniformly distributed through the membrane matrix. These membranes swell relatively uniformly when exposed to water, the extent of swelling being controlled by their cross-linking density. In heterogeneous membranes, the ion exchange groups are contained in small domains distributed throughout an inert support matrix, which provides mechanical strength. Heterogeneous membranes can be made by dispersing finely ground ion exchange

particles in a polymer support matrix. Because of the difference in the degree of swelling between the ion exchange portion and the inert portion of heterogeneous membranes, mechanical failure, leading to leaks at the boundary between the two domains, can be a problem (Baker 2004).

The aim of present work is to transfer the sulfate ions only through ion exchange membrane and therefore different AEMs have been used in the present study. Anion transfer membranes, which are electrically conductive membranes that allow only negatively charged ions to pass through. Usually, the membrane matrix has fixed positive charges from quaternary ammonium groups which repel positive ions. Moieties used as fixed charges in anion-exchange membranes fixed charges may be: $-NH_3^+$, $-RNH_2^+$, $-R_2NH^+$, $-R_3N^+$, $-R_3P^+$, $-R_2S^+$ (Noble and Alexander 1995; Xu 2005). These different ionic groups have significant effects on the selectivity and electrical resistance of the ion-exchange membrane. Tongwen and Weihua (2001) recovered sulfuric acid from waste liquor and studied the effect of some important factors such as ion exchange capacity, content of benzyl-halogen and the relative compositions of the liquor. It was found that the acid recovery rate was increased by benzyl substitution, while the selectivity of the membrane was improved by substitution of aryl (Tongwen and Weihua 2001). By adjusting the proper balance between substitutions and adjusting the feed composition, higher selectivity and acid recovery can be achieved.

Generally, ion exchange membranes contain a high concentration of fixed ionic groups, typically 3–4 meq/g or more. AEMs swell when they are placed in water because of the tendency of these ionic groups to absorb water. Charge repulsion of the ionic groups can cause the membrane to swell excessively. This is why the most ion exchange membranes are highly cross-linked to limit swelling. However, high cross-linking densities make polymers brittle, so the membranes are usually stored and handled wet to allow absorbed water to plasticize the membrane. Most ion exchange membranes are produced as homogenous films 50–200 μm thick. Typically, the membrane is reinforced by casting onto a net or fabric to maintain the shape and to minimize swelling (Baker 2004). Anion exchange membranes are usually monopolar since they are permeable to a single type of ions only. Ion-exchange polymers, such as polystyrene sulphonic acid, are water soluble, so cross-linking with divinylbenzene (DVB) is used to prevent dissolution of ion-permeable membranes. As the degree of cross-linking is increased, the membrane selectivity, stability, and electrical resistance increase. There is a positive effect on membrane selectivity and conductivity as the fixed-charge density is increased but that also increases membrane swelling. Therefore,

a compromise among selectivity, electrical resistance, and dimensional stability has to be achieved by controlling appropriately cross-linking and fixed-charge densities (Noble and Alexander 1995).

2.4.1 Proton leakage through membrane and concentration of sulfuric acid

Proton leakage characteristic of ion exchange membranes has been a great issue towards the application of ED to concentrate an acidic solution that adversely affects the performance of the process. ED process mainly uses polymeric ion-exchange membranes. Proton leakage is a major problem associated with most commercial anion-exchange membranes, which makes them unsuitable to use to recover sulfuric acid (Cherif et al. 1988).

By means of traditional membranes, it is not possible to apply ED in the recovery of acid in order to reuse the acid because of high proton leakage through the IEMs. In general, since protons permeate easily through an IEM, acids cannot be concentrated to more than a certain level by ED with high efficiency. Recently developed membranes exhibit low proton permeabilities and enable efficient acid concentration. By modifying the membrane cross-linking agent and membrane structure, proton leakage can be reduced to a great extent and acid can be concentrated to a higher value (Noble and Alexander 1995; Strathmann 2004). Table 2.6 represents the information of such membranes that are either low proton leakage, tailor-made or modified by the researcher and used in the process that improved performance of acid enrichment process by electrodialysis drastically.

Sulfuric acid recovery by ED cannot be developed on an industrial scale because of the proton leakage of polymeric anion exchange membranes which has been found up to now. Proton leakage through a RAI R1035 anion exchange membrane was studied by Cherif et al. in 1988 and showed that the proton leakage is a major problem associated with most commercial anion-exchange membranes, which makes them unsuitable to use to recover sulfuric acid. Generally, the acid concentration reaches a limiting value at which the current efficiency falls to zero (Cherif et al. 1988). In order to study the proton leakage through the membrane, transport properties of membranes were studied by Baltazar et.al. (1992) using different AEMs, cation exchange membranes (CEM) and bipolar membranes (BPM) in treatment of spent liquor containing sulfuric acid, copper, arsenic, bismuth, and nickel. They showed that the characteristic of ion exchange membrane used plays an important role in the recovery of acid (Baltazar et al. 1992). Since AEMs are made of polymeric materials, their

swollen, as well as proton leakage characteristic, affect the performance of the separation process by ED.

Table 2.6 Concentration of sulfuric acid by various AEMs in ED process.

Sr. No.	Feed	ED Configuration	Membranes used	Anode	Cathode	Concentration of Sulfuric acid obtained	Reference
1	Acidic nickel sulfate stream (15-18 wt. %)	Mini-pilot scale (Tokuyama Soda of Japan)	AMH, ACS, CMS, ACM, Nafion	Platinum-plated titanium	316SS	28 wt. %	Baltazar et al., 1992
2	Copper electrorefining solution	Lab scale six compartments Electrohydrolysis cell	Ionac MA3475, Ionac MC3470	Platinum	Platinum	0.5 mol/L (≈5 wt. %) at 225 A/m^2 current density in 12 hours	Cifuentes et al., 2006
3	Model sulfuric acid solution (5 wt. %)	ED set up	Selemion AAV GMA, Selemion CMV, Nafion 117	-----		2.9 mol/L at 30 mA/cm^2 current density	Asari et al., 2011
4	Acid mine drainage (0.7 wt. %)	Three compartment ED cells with re-circulation of solution	AEM (HDX 200), CEM (HDX 100)	Titanium coated with metal oxide	AISI 304 stainless steel	0.25 mol/L (≈2.5 wt. %) at 15 mA/cm^2 current density in 10 hours	Martí-Calatayud et al., 2014
5	Production of sulfuric acid by SO_2	ED reactor	Polyethylene heterogeneous membrane	Ru-Ir-Ti oxide coating on titanium substrate	Manganese oxide catalyst on 304 chrome-nickel austenitic SS substrate	28.56 wt. %	Yongtao et al., 2015
6	Concentration of sulfuric acid solution (0.5 mol/L)	EDR-Z flat sheet electrodialyzer	AAV, ACM, AM-PP, AMI 7001S, FAB	CF-210, CF-21		3.5 mol/L in 10 hours	Jaroszek et al., 2017
7	Industrial waste water (1 wt. %)	Continuous injection of catholyte	PANI/PVDF, AMI-7001, Qianqiu	Ru–Ir–Ti oxide coating on a titanium substrate	Platinum	63 wt. % (9.7 mol/L) at 40 mA/cm^2 current density in 180 hours	Xie et al., 2018
8	Model sulfuric acid solution (5 wt. %)	Acrylic flat sheet ED module, no solution re-circulation, no any moving element	IPA, Selemion AAV, Selemion AMV	Graphite	Graphite	27.93 wt. % at 20 mA/cm^2 in 67 hours with IPA membrane	Present study, 2018

It has been reported that the separation can be improved if the membrane is treated prior to its use. Possibility of separation and concentration of dilute aqueous mixtures of sulfuric and nitric acids was observed more when used treated ion exchange membranes (Audinos et al. 1993). In 1996 Lorrain et. al. studied the mechanism of transport of sulfuric acid through the membrane on the basis of the proton transport number and proved that proton leakage

adversely affects the recovery of the acid (Lorrain et al. 1996). In 1997 they studied water present in all ion exchange membranes acts as an excellent mediating agent for the proton leakage and represented a transport mechanism of ions through ARA membrane (Lorrain et al. 1997). The proton leakage was quantified from the value of the proton transport number. Proton leakage characteristic of an ion exchange membranes has been a great issue towards the application of ED to concentrate an acidic solution.

As shown in Table 2.6, Baltazar et al. (1992) reported the selective recovery of sulfuric acid about 28 wt. % from acidic nickel stream by ED (Baltazar et al. 1992). Sulfuric acid with a concentration of about 5 wt. % was obtained by Cifuents et al. (2006) using a six-compartment electrohydrolysis cell in 12 h operation at and a cell current density of 225 A/m^2 with a cell voltage of 5.9–6.5 V (Cifuentes et al. 2006). Yongtao et al. (2015) produced 28.56 wt. % concentrated sulfuric acid by liquid absorption and oxidation of low concentration SO_2 in aqueous solutions as well as electrodialysis enrichment using polyethylene heterogeneous membrane (Yongtao et al. 2015). Asari et al. reported a concentration of sulfuric acid from 1.4 to 2.9 mol/l at 30 mA/cm^2 current density with different AEMs including selemion AAV (Asari et al. 2011). Low proton leakage membranes such as selemion AAV has been found to be the best for the concentration of sulfuric acid. Selemion AAV membrane has been reported as more suitable amongst five different types of membranes to concentrate sulfuric acid up to 3.5 mol/l (Jaroszek et al. 2017). Structurally/surface-modified membranes have shown better results when applied to concentrate solution. Modification in membrane structure and cross-linking has greatly resolved the issue of proton leakage and it has now become possible to concentrate sulfuric acid solution up to a higher level as high as 63 wt. % (Xie et al. 2018). This literature review concludes that the best membranes for separation or concentration of sulfuric acid solutions are those in which the sorption of acid and diffusion of protons are minimized. Performance of IPA (an indigenous membrane) to concentrate sulfuric acid has not been reported by any researcher yet. The present study used Selemion AAV, Selemion AMV and IPA membranes for acid enrichment process. The characteristics of these membranes are given in detail in the Materials and Methods section 3.3.

In addition to this, as shown in Table 2.6, sulfuric acid was concentrated using different configurations and modules of ED process such as ED reactor, mini pilot plant, 3-compartment ED cell or 6- compartment electrohydrolysis (EH) cell etc. wherein solution was circulated using a pump. Along with this, various membranes and different metals as

electrodes such as platinum, titanium, electrode coated with some other materials were used. The acid enrichment by ED is influenced by a number of physico-chemical factors and also limited to certain values. ED configuration such as batch process or process with recirculation of solution, acid back diffusion (Jaroszek et al. 2017), concentration polarization (Tanaka 2003; Strathmann 2004; Le 2012; La Cerva et al. 2018), properties of membrane such proton leakage, acid resistance, thickness of the membrane, ion exchange capacity and material of electrode affects the acid enrichment process and other process performance parameters. Many of these factors contribute to the current efficiency (Akgemci et al. 2005) and power consumption (Strathmann 2004) that together affect the cost of the system. Use of simple batch ED process instead of complex equipment and use of cost-effective electrodes may considerably reduce costing of the system. The present work is also aimed in making economical ED system by using low-cost electrodes, acrylic ED module and an IPA anion exchange membrane with no moving elements present in the system.

2.4.2 Characterizations of membrane

The ion-exchange membranes used in electrodialysis are essentially sheets of ion-exchange resins either homogenous or heterogeneous in structure, and their characterisation is closely related to their preparation. A microscopic examination yields information on whether or not a membrane is homogeneous or heterogeneous. Mechanical and electrical properties, their permselectivity and chemical stability are the several important terms used to classify the ion exchange membranes. The mechanical characterization of ion-exchange membranes includes the determination of thickness, swelling, dimensional stability, tensile strength and hydraulic permeability. Fixed charge density, the electrical resistance, the ion permselectivity, and the transport of non-ionic components such as water or of other neutral molecules are some desired electrochemical properties to characterize a membrane (Strathmann 2004). Most of the aforesaid properties of the membranes used in present study are available and well determined in several studies.

Scanning electron microscopy (SEM) is one of the most accepted and extensively used techniques for the membrane characterization. Pristine and used membrane topography can be studied and compared from the morphology of the surface and cross sections obtained from SEM analysis (Le et al. 2009). Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. It offers quantitative and qualitative analysis for organic and inorganic samples. FTIR

spectroscopy is a widespread, relatively cheap technique for studying the structure of compounds through chemical bond vibrations. Interpretation of the FTIR spectrum can be of great help in determining the presence of functional groups in the ion-exchange membrane specimen (Le 2013).

Though characterization of membrane is not the objective of the present work, membrane functional groups as well as surface and cross-sections topography has been analysed by FTIR and FESEM analysis respectively and compared for all the membranes used in present study.

2.5 Parameters affecting electrodialysis performance

The extent of acid separation, current efficiency, molar flux and the external driving force required are major parameters used to mark the performance of ED processes. Performance of electrodialytic separation of sulfuric acid from spent acidic liquor is significantly affected by process variables such as initial catholyte concentration, initial anolyte concentration, catholyte and anolyte concentration difference and current density. In addition to this, the role of electrode material and membrane type is imperative on process performance as they are in direct contact with the feed solution. Following subsections describe the effects of few such variables on the performance of ED.

2.5.1 Material of electrodes

Electrodes are required to create an electric field in order to drive the migration of ions present in solution to be treated in electrodialysis. Generally, metal electrodes are selected for this purpose. Material of the electrode selected must be compatible with the module of the process and feed to be treated. If electrodes are participating in the process, their selection depends upon the type of feed and process performance variables, etc. If the purpose of an electrode is just to create an electric field, they must be inert or noble metals.

In ED, an external voltage is applied between two electrodes to generate an ionic current through the membrane. Anodes are positively charged and cathodes are negatively charged electrodes used in a variety of electrochemical processes such as corrosion protection and electroplating, components in batteries, fuel cells, and electrochemical devices, electrolysis systems, electrowinning, electron emission, and other specialized processes. Conductivity and corrosion resistance are important properties of electrode materials which are determined by inherent characteristics of the material. Conductivity is the measure of a material's ability to carry or conduct an electric current. Corrosion resistance is the

material's ability to resist chemical decay. A material that has little corrosion resistance degrades rapidly in corrosive environments resulting in a shorter lifespan. Higher conductive electrode utilizes lesser power in ED and higher corrosion resistance material can last longer in electrodialytic separation of acidic solution. Therefore, the selection of electrodes plays a pivotal role in ED. Cost and chemical properties of electrode material affect the performance as well as cost of the process. Wide variety of materials has been used till date in various electromembrane processes. Table 2.4 and 2.6, both represent a different kind of electrodes used in ED process for separation and concentration of sulfuric acid. The ED process suggested in the literature for acidic waste treatment mostly employed platinum (Cattoir et al. 1999), platinized titanium (Zouhri 2013; Chekioua and Delimi 2015; Kroupa et al. 2015), or titanium coated with titanium oxide (Buzzi et al. 2013) as electrodes. Platinum accelerates corrosion much higher to graphite comparatively as well as not resistant to certain acids (Tanaka 2003; SIROMA et al. 2007). Platinum group metals are known for their high resistance to corrosion. Platinum is costly metal with the necessity of high purification index and having life span up to 5 years (Veerman et al. 2010). Though effective, the use of costly electrodes may not be economically viable at large scale due to their significant cost contribution, which may exceed more than 90% of the total cost of the ED process unit (Nayar et al. 2015).Along with cost, stability and corrosion resistance are the other major factors affecting the electrode selection. Despite considerable work in ED for the treatment of a number of wastewaters, development of cost-effective and corrosion-free electrodes has become a less focused area of research.

Graphite can be made from coke and other residues of carbon industry which can be cost-effective and give higher efficiency. The deposition of salts upon graphite electrode is a disadvantage which can be solved by different techniques such as reversal electrodialysis (RED) and other possible ways. Graphite has higher redox potential because of having a good oxidizing tendency. Rabah et al. (1981) showed that graphite electrode prepared out of coke at high temperatures are comparatively more resistant to wear than light electrodes because of the lower pore volume and less internal surface area in the former (Rabah et al. 1981a). Following next they showed that dense electrodes with a micropore or mesopore system are more stable than graphite having wider pores to the attack of the corrosive effect of the electrolyte. It was reported that impregnation of graphite with coal tar pitch increased the lifetime of graphite as anode by a factor of 3.2 times (Rabah et al. 1981b). Stainless steel having good corrosion resistance in acidic solutions, as well as carbon materials due to their

chemical and electrochemical characteristics are also effective for industrial applications (Iken et al. 2007). Materials such as Teflon, Platinum, graphite and SS 316L has been studied as electrodes and then selected on the basis of their cost and conductivity in present work.

2.5.2 Catholyte concentration

Spent acidic liquor generated from various industries differs in composition depending upon the process and downstream operations. Such type of liquor may contain various acids, organic and inorganic compounds, metal contents etc. Concentration or composition of feed solution not only affect process performance parameters, but also the lifespan of a membrane that ultimately contributes to the costing of the process. Composition or concentration of feed or catholyte solution greatly affects the performance of electrodialytic separation of sulfuric acid from spent acidic liquor in terms of process performance parameters such as molar flux, current efficiency and the external force required to push the ions.

Each membrane has its characteristic and capacity to withstand acidic solution. Very high pH or higher concentration of acid may damage the membrane. It is therefore vital to select membrane wisely and operate it in a certain concentration range. Membrane separation processes, therefore, require pre-treatment of feed solution as and when required. On the contrary, under the influence of the electric field, very dilute solution due to water splitting and uncontrollable rise in current may also damage the membrane. This enforces the researcher for the determination of limiting current density. As far as molar flux is concerned, it is a function of the initial concentration of solution, so a higher concentration of acid in catholyte generates higher molar fluxes as well as current efficiency.

A solution of formic acid was concentrated by Luo et.al. using ED in 2002. The effects of concentration, electric current density, and concentration difference between the concentrated side and the dilute side were studied. Increase in initial concentration increased current efficiency to a certain value and then decreased trend was observed (Luo et al. 2002). It is worthwhile to mention that current efficiency increased with increasing solution concentration till the values reached to maximum current efficiency (Luo et al. 2002; Natália Káňavová and Lubomír Machuča 2014). The concentration of feed affects both flux rate as well as the efficiency of the process. High current efficiencies were observed (>80 %) by Luo et.al at higher acid concentrations Increase in anolyte to catholyte ratio led to a reduction in current efficiency as well as concentration ratio (Luo et al. 2002). Possibility of eliminating the iron ions present as impurity in sulfuric acid solution was reported by

Chekioua and Delimi et al. (2015) showing positive effect of higher concentrations of ions in feed solution on the effectiveness of the treatment (Chekioua and Delimi 2015). Molar flux as well as current efficiencies both get affected by upstream and downstream acid concentrations (Jaroszek et al. 2017). Initial catholyte concentration is a major influencing variable in the ED process. It has been reported that the membrane resistance is considerably lower than the resistance offered by dilute solution due to relatively high ionic concentration in the membrane (Strathmann 2004). The resistance provided by the dilute acidic solution is more and hence requires higher applied voltage. Unlike this, at higher initial concentration, the number of ions present in the solution being higher, their conductivity increased leads to requirements of lower applied voltage. It is appropriate to conclude that higher acid concentrations can provide higher efficiency with lower applied voltage and consequently reduce costing of the system.

2.5.3 Current density

Current density is basically the number of ions crossing the membrane per unit area of the membrane. Since the ions moving through the membrane carry current with them, the current density is measured in mA/cm^2. Current density is a major variable influencing the process performance and is maintained constant by controlling voltage variation. Current density affects the molar flux, current efficiency and itself gets controlled by the applied voltage.

The molar flux through ion exchange membrane depends upon the current flowing between anode and cathode. Higher the current density, more the number of ions transferred and therefore higher the flux. It was reported by Luo et. al. in 2002 that the mass flux increases with an increase in current density (Luo et al. 2002) and therefore lesser time is required for the given separation. Baltazar et al. (1992) described a process to selectively recover sulfuric acid and to concentrate it from an acidic nickel sulphate stream containing copper, arsenic, bismuth and antimony in addition to nickel using ED process with different membranes. At different values of current densities different acid extraction rates were achieved with more than 80% total acid recovery, proving the ED as an process energy-efficient process at lower current densities and higher temperatures (Baltazar et al. 1992). Electrodialytic recovery of acids from mining waste streams and acid mine drainage at specific current densities has been reported in several studies (Buzzi et al. 2013; Zouhri 2013; Martí-Calatayud et al. 2014; Chekioua and Delimi 2015). Martí-Calatayud et al. (2014) recovered sulfuric acid from acid mine drainage means of 3-compartment electrodialysis cell, at different values of current

densities such as 5, 10 and 15 mA cm^{-2} using CEM and AEM along with the removal of Fe (III) ions as a result of the co-ion exclusion mechanism in the membranes. They evaluated the energy efficiency of sulfate transport through the AEM by means of calculating the current efficiency and specific energy consumption values. The current efficiency values of the anion-exchange membrane at different current densities were reported approximately constant with time (Martí-Calatayud et al. 2014).

Current efficiency also depends upon the type of AEM used. Though Selemion AAV is a low proton leakage membrane, in the electric transport, the Selemion AAV membrane does not block the leakage of protons efficiently; the current efficiency of H_2SO_4 removal from the cathode side of the AAV hardly exceeds 50%. Additionally, the current efficiency practically does not depend on the kind of salt present on the cathode side of the Selemion AAV (Kultys et al. 2011; Koter et al. 2014). Chekioua and Delimi used ED to remove the iron (II) ions of sulfuric acid pickling bath. They reported that the increase in the current density of 1 to 20 mA/cm^2 caused an increase of the purification rate of 7.43 to 66.32%. However, the increase in density up to 30 mA cm^2 led to a reduction of the purification rate at 60.49%. Beyond this value of current density, the formation of a deposit on the surface of the membrane was observed (Chekioua and Delimi 2015).

Furthermore, the limiting current density plays an important role in deciding the operating range of current density as it may cause damage to the membrane and electrode material. Luo et al. (2002) used ED process to concentrate a formic acid solution and observed that the overall current efficiency increased until a maximum value is reached, and then decreases with an increase of current density. The main reason is that if the current is less than the limiting current density, the increase of current density will not cause negative effects such as higher electrical resistance, co-ion leakage through the ion exchange membrane, and water splitting on the surface of the membranes. Therefore, the overall current efficiency increases with an increase in the current density. They reported that the limiting current density is not a certain value, it changes with the working system and the properties of the membranes (Luo et al. 2002). S. Koter (2008) separated the mixture of sulfuric acid and acetic acid using two different membranes, CMX and ACM. They proved that the efficiency of retention of acetic acid is high (>0.9) when the process is run below the limiting current density (Koter 2008).

Current density, is considered to be one of the most influencing process variables in ED, and it could be maintained all through the process by varying the applied voltage (Zouhri 2013)

which in turn together with current efficiency contributes to the power cost of the treatment (Lewis and Tye 1959). Increase in current density needs an increase in applied voltage. A sharp increase in applied voltage was observed with time with an increase in current density by Cifuentes et al. (2002) in electrodialysis of aqueous H_2SO_4–$CuSO_4$ electrolytes with metallic impurities (Cifuentes et al. 2002). Higher current densities are maintained by applying a higher potential difference causing migration of the greater number of ions from catholyte to anolyte. It is necessary to determine the precise range of current density in order to maximize the process efficiency, molar flux and determine the range of applied voltage required for estimation of consumption of energy.

2.6 Transport mechanism and modeling of the process

The driving force for the demineralization process is the difference in the chemical potential of the species on either side of the membrane in the membrane-based separation processes where no current is applied. The equilibrium position may be shifted by the passage of a current through the membrane, in which instance the driving force becomes the applied electric potential (Simpson and Buckley 1988). In order to achieve separation, ions must be transported from one solution to other through the ion exchange membrane. Kinetic and thermodynamic parameters are considered to determine the transport rate of these ions. The kinetic parameters are expressed by the mobility or diffusivity of the ions in the membrane matrix and the electrolyte solution. The thermodynamic parameters are expressed by the driving forces which must be applied to overcome the friction a component experiences while being moved through the solution or the membrane (Strathmann 2004). As far as the movement of ions through a membrane is considered, the overall transfer of ions or ionic flux is a result of a combination of fluxes due to three different modes of transport. Flux due to diffusion, convection and migration of ions.

When solutions of different concentrations are separated by an interface then molecules will move from more concentrated side to the less concentrated side simply because of the difference in number of molecules. This concept was first recognized by Fick theoretically and experimentally in 1855 (Baker 2004). Gradients in the chemical potential of a component under isothermal conditions can arise from gradients in concentration or pressure. The dominant term for molecules or ions transported through an ion-exchange membrane or in a solution by diffusion is the concentration gradient. For the diffusion of ions, it is mandatory that the electroneutrality requirement is fulfilled, i.e. cations and anions have to

diffuse in the same direction (Strathmann 2004). Diffusive flux through the membrane is basically the derivation of Fick's law expressed by Eqn. (2.7)

$$J_D = -D\frac{dC}{dx} \qquad (2.7)$$

Where, J_D is diffusive flux through membrane, D is diffusion coefficient of particular ions through the membrane, C is the concentration of solution, and x is the thickness of the membrane.

Convection is a movement of mass due to a mechanical force, i.e., in general, a hydrostatic pressure difference. Convective transport is generally less important in homogeneous solid materials such as ion-exchange membranes. It is, however, dominant in porous structures and stirred solutions (Strathmann 2004; Koter and Kultys 2010; Koter et al. 2014).In the studied batch ED process, the contribution of convective flux is zero.

Migration is a movement of ions/charged species due to an electrical potential gradient. An electrical potential gradient is usually established by applying a voltage difference between two electrodes dipping into an electrolyte solution. The positively charged cations migrate towards the negatively charged cathode and the negatively charged anions migrate towards the positively charged anode, i. e. cations and anions are transported in opposite directions (Koter and Kultys 2010; Tedesco et al. 2016).

In electrodialysis process the total flux is the contribution of three different types of fluxes and is a summation of fluxes due to diffusion, convection and migration of ions represented by Eqn. (2.8).

$$J = J_v + J_D + J_\theta \qquad (2.8)$$

Where J_D, J_V and J_θ are flux due to convection, diffusion and migration.

Under the influence of an electric field, flux is calculated with the help of extended Nernst-Planck equation (Koter and Kultys 2010; Koter et al. 2014; Tedesco et al. 2016). It is basically a physical reformulation of Fick's macroscale diffusion law, extended to the motion of charged particles. Nernst-Planck equation is valid for both in solution and in the membranes (Tedesco et al. 2016). It is represented by Eqn. (2.9)

$$J = J_v + \left(-D\,\frac{dC}{dx} - z\,C\,\frac{dV}{dx}\right) \qquad (2.9)$$

Where z is valence number of ions, C is the concentration of ions and dV is the electric potential difference.

The principle of ED is based on the selective transport of cations and anions through IEM, under the influence of an applied voltage. The ionic current is generated through IEM by applying an external voltage between cathode and anode. Ion exchange membrane allows only the passage of counterions and therefore, an AEM allows only anions to pass through the membrane. Transport phenomena in ED involve all the three types of fluxes namely diffusive, convective and electro-migrative through the membranes. Since the membrane does not behave ideally, along with the desired ions, co-ions and water can cross the membrane and reduces the process performance and makes the modeling of transport phenomena in ED complex. Till now different modeling approaches have been proposed in the literature to describe ion transport in ED, but Nernst-Planck approach is the most common when water transport is neglected (Tedesco et al. 2016).

Modeling of the transport mechanism of electro-transport of sulfuric acid requires the knowledge of parameters such as sorbed acid and ratio between the diffusion coefficients of the proton and of the sulfate ion in the membrane if the Nernst-Planck electro-diffusion equation is to be applied for the comparison of experimental results (Cherif and Gavach 1989). In 1996 Yves Lorrain et. al. studied the mechanism of transport of sulfuric acid through the membrane on the basis of the proton transport number and proved that proton leakage adversely affects the recovery of the acid (Lorrain et al. 1996). In 1997 they studied water present in all ion exchange membranes acts as an excellent mediating agent for the proton leakage and represented a transport mechanism of ions through ARA membrane. They presented a specific mechanism of proton transport taking into account the nature of the sulfate ion which behaves as a proton acceptor mediating the proton leakage (Lorrain et al. 1997).

Modeling of the separation of acetic acid from mixture of acetic acid and sulfuric acid by the electro-electrodialysis (EED) method using Neosepta membranes CMX and ACM was represented by S. Koter in 2008. They used extended Nernst-Planck equation and the Donnan equilibrium to fit the experimental data considering selectivity of AEM, the concentration of fixed charges of the selected membrane and the pore factor as main fitting parameters (Koter 2008). In addition to these parameters, concentration polarization that reflects the hydrodynamic conditions in the membrane module was added as another important parameter to model the electric transport of sulfuric acid through AEM. In the

same year, Koter et al. (2008) described the model based on extended Nernst-Planck equation and the Donnan equilibrium for the electric transport of sulfuric acid through selemion AAV membrane in aqueous solutions considering the effect of concentration polarization (Koter and Kultys 2008). In 2014 they extended their work to modeling the transport of sulfuric acid and its sulfates ($MgSO_4$, $ZnSO_4$, Na_2SO_4) through an anion-exchange membrane. They reported that the assumption of full dissociation of metal sulfate is insufficient and the metal cation-sulfate anion association should be taken into account (Koter et al. 2014). Nernst-Planck equation is well-known and important in modelling the transport mechanism of sulfuric acid through AEM which requires the information of membrane parameters such as fixed charge density, porosity, amount of sorbed acid and concentration polarization, etc. In addition, it requires knowledge of diffusion coefficients of ions in solutions and within the membranes. Nernst-Planck equation is used for the calculation of molar flux which is a function of diffusivity, ion concentration, temperature, electric potential difference and membrane thickness.

2.7 Energy and cost considerations

In electrodialytic separation of sulfuric acid through the membrane, two different types of energies contribute to the total energy requirements: (1) the electrical energy to transfer the ions from one solution through the membrane into the other solution and (2) the energy required to pump the solutions through the ED cell (Noble and Alexander 1995). Since the solution is not pumped through the ED cell, convective flux, as well as pumping energy required both are assumed to be zero in present work. Energy consumed to perform the separation is the key factor determining the overall efficiency of an ED process.

The energy required by the process depends on the overall cell voltage (Cifuentes et al. 2002) represented by Eq. (2.10),

$$W = VIt \qquad (2.10)$$

Where W is the energy required, V is the cell voltage, I is the current and t is the time.

The cell voltage is affected by factors such as solution resistance and current density (Described in detail in section 2.5.3). Increase in current density or decrease in solution conductivity increases the demand of cell voltage and hence needs higher electricity consumption. An experimental investigation into the batch electrodialysis process for removal of sodium sulfate from magnesium stearate aqueous slurry was carried out by

Masigol et al. in 2102 (Masigol et al. 2012). They calculated the specific power consumption (SPC), the energy needed for the recovery of one mole Na^+ ions from the feed solution. Enhanced flux rates were obtained with the increase in applied voltage, but higher voltages led to higher SPC because of energy dissipation in the form of heat generation. In the electrodialysis process of recovery of lithium ions from sodium-contaminated lithium bromide solution, specific electricity consumption (SEC) was described as electric energy needed for recovery of one mol of Li^+ from the feed solution was calculated. It was reported that, though recovery rate and current density was enhanced by a higher applied voltage, it increased specific electricity consumption too (Parsa et al. 2015).

It is extremely important to determine the variables affecting the applied voltage of the process such as current density and solution concentration in order to determine the energy consumption and thereby operating cost of the system. In present work, based on rigorous experimental work, applied voltage range has been determined for separation of sulfuric acid from its dilute solution in a batch ED process as well as for enrichment of sulfuric acid solution using cascaded ED process. Energy consumed during process was estimated and compared for three different membranes.

2.8 Limitations of electrodialysis

Though electrodialysis has been used since years for the separation of charged species from solution, it has some inherent limitations. It is efficient at removing low molecular weight ionic components from a feed stream. High molecular weight, non-charged and less mobile ionic species will not be significantly removed by ED. Organic matter, colloids and SiO_2 cannot be removed by ED system. When extremely low salt concentrations are required in the product and with sparingly conductive feeds, ED becomes less economical. With fewer ions present in the very dilute solution to carry current, both ion transport and energy efficiency greatly declines and hence current density becomes limited and current efficiency decreases as the feed concentration becomes lower. Consequently, comparatively large membrane areas are required to satisfy capacity requirements for low concentration feed solutions. Feedwater pre-treatment is necessary to prevent ED stacks fouling. ED process requires feed pre-treatment to remove species that coat, precipitate onto or foul the surface of the AEMs. In addition to this, since ED cannot remove neutral toxic components such as viruses or bacteria, it requires post-treatment procedure also when used as potable water supply. Furthermore, elaborate controls are required, and keeping them at optimum

condition can be difficult. Selection of materials of construction for membranes and stack is important to ensure compatibility with the feed stream. ED, when operated batch-wise with stagnant feed, the formation of concentration polarization can greatly limit the transport of ions through the membrane and leads to increase in applied force with a reduction in current efficiency and increase in operating cost. ED may be a costly option when used to concentrate a solution. ED applications are affected by some key problems such as high operating cost, scaling and fouling of the membrane.

2.9 Research gap and challenges

Presence of sulfuric acid with other metal impurities in waste acidic liquor makes it unusable and non-dischargeable as it affects living and non-living environment and thereby demands its extensive as well as economic reclamation. Electrodialysis has been emphasized as an effective and eco-friendly separation technique when compared to other conventional as well as membrane separation techniques. ED holds much promise in the treatment of such acidic liquor but the use of costly metals as electrodes may make it economically unviable at large scale. Electrode material also affects the quality of anolyte and hence the purity of sulfuric acid obtained. Selection of an appropriate, as well as affordable electrode, is a great challenge in ED processes. Limited information is available in literature reporting use of ED with cost-effective electrodes and representing the effect of various physico-chemical parameters on the process performance. Therefore, in the present study, electrodialytic separation of sulfuric acid has been carried out using graphite and SS 316L as low-cost electrodes and their effects on quality of anolyte along with rigorous estimation of effects of process variables such as catholyte concentration and current density on molar flux, current efficiency and applied voltage have been investigated.

Acidic effluent containing metal contents or other impurities can be treated effectively using ED to obtain impurity-free acidic solution. It is essential to enhance the concentration of such a solution in order to render it recyclable or reusable. Though multi effect evaporator system is useful for the treatment of acidic effluents, some inherent problems associated with it such as phase change at high temperature and pressure, high thermal energy consumption set limits to its applications. Such dilute acid stream could be concentrated initially by ED followed by any conventional techniques such as evaporation thereby reducing the heat load on the evaporation. The energy required to increase the concentration of dilute sulfuric acid by ED has been found out to be much lower than the same for evaporation. Supplementation

of evaporation with ED can not only be considered as a synergic combination but also an energy-efficient process. Taking this into consideration, in present work, integration of ED with evaporation has been carried out and evaluated the performance of ED-EV integrated process in terms of energy and cost.

Furthermore, enrichment of sulfuric acid solution using ED is affected by the properties of the anion exchange membrane and it is limited to certain value due to proton leakage characteristics of AEM. Although the literature has reported the performance of many AEMs to enhance the acid concentration, still there is need to evaluate the performance of ED with a new membrane that has not been tried so far for such applications. Most of the researchers have used either low proton leakage or tailored membrane for the given purpose. Multistage electrodialysis process to increase sulfuric acid concentration up to maximum possible value using IPA (indigenous) anion exchange membrane has not been reported with a rigorous determination of process performance parameters. Taking this into consideration a cascaded ED system has been designed with graphite electrode to enrich the sulfuric acid concentration from model solution. In addition, IPA membrane performance is evaluated and compared with standard and low proton leakage membrane on the basis of experimental results.

CHAPTER 3

Materials and Methods

3.1 Materials used

3.1.1 Equipment and instruments

High precision digital balance (MAB 250, WENSAR), Multiple power supply (PSD3304). Digital conductivity meter (Chemiline digital conductivity meter CL 220, Aqua Mart, Kolkata, India), Fourier transform Infrared spectroscope (Spectrum GX Model; Perkin Elmer, USA), Field emission scanning electron microscope (JEOLFE-SEM, JSM-6701F), Ammeter, Thermometer.

3.1.2 Glassware/plasticware

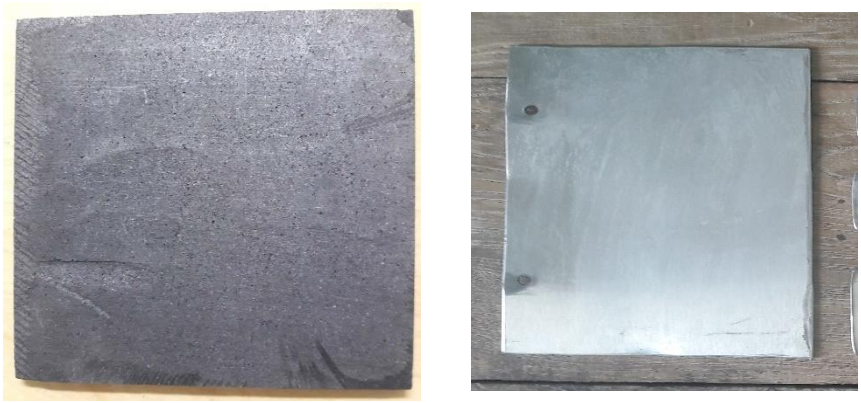
Acrylic electrodialysis module (total volume 500 ml), Volumetric flask (50 ml to 1 L), measuring cylinder (10 ml to 1000 ml), Beaker (50 ml to 1000 ml), conical flask (50 ml to 250 ml), round bottom flask (500 ml to 1 L), thermometer, pipette, specific gravity bottle, glass rod, sampling bottles, burette, pipette, dropper, stand, silicon jelly, plastics corks, thermocol sheet, Teflon tap, packing material.

3.1.3 Chemicals and electrodes

Various chemicals (AR grade) such as sulfuric acid (H_2SO_4), Sodium hydroxide (NaOH), Deionized water (H_2O), Phenolphthalein, and Potassium Thiocyanate used in the present study were purchased/procured from M/s S. D. Fine-Chem, Mumbai, India. The chemicals were used as received from the supplier and stock solutions of potassium thiocyanate and sulfuric acid were prepared with deionized water having a conductivity of 20 µS cm^{-1}, produced from a reverse osmosis system. The physical properties of the sulfuric acid, sodium hydroxide and deionized water are presented in Table 3.1. Commercially available SS 316L and graphite sheets were used as electrodes. The images of electrodes used in the present study are shown in Fig. 3.1.

Table 3.1 Physical properties of sulfuric acid, sodium hydroxide and water.

Physical property	Sulfuric acid	Water	Sodium hydroxide
Chemical Formula	H_2SO_4	H_2O	NaOH
IUPAC name	Sulfuric acid	Water, Oxidane	Sodium hydroxide
Other names	Oil of vitriol	Hydrogen oxide	Caustic soda, Lye, Sodium hydrate
Molecular weight	98.079 g/mol	18.0 g/mol	39.9971 g/mol
Appearance	Clear, colorless, liquid	Colourless liquid	White, waxy, opaque crystals
Odour	Odourless	None	Odourless
Taste	Sour	--	Bitter
Density	1.84 g/cm^3	1.0 g/cm^3	2.13 g/cm^3
Melting Point	10 °C, 283 K	0 °C, 273 K	318°C, 591 K
Boiling Point	337 °C, 610 K	100°C, 373 K	1388 °C, 1661 K
Solubility in Water	miscible	--	1 kg/L at 25 °C
Acidity	−3, 1.99	7.0	--
Basicity	--	--	-56
Refractive index	--	1.3330	1.3576
Viscosity	26.7 cP (20 °C)	0.890 cP	87 cP (50 wt. %) (25 °C)
Flash Point	Non-flammable	Non-flammable	--



Graphite SS 316L

Fig. 3.1 Images of electrodes used in the present study

3.1.4 Software

Microsoft Excel (Windows 2010) and ORIGINLAB (2017 SR2) were used to construct the different plots of experimental data points. An equation was developed based on experimental results using MATLAB programming (MATLAB R2018a, version 2018 in a symbolic mathematics tool box).

3.2 Membranes used

Four different types of anion exchange membranes were tested under electrodialytic conditions in the present study. Selemion AMV and Selemion AAV membranes were imported from Asahi Glass Chemicals, AGC Engineering Co. Ltd., Chiba, Japan. Selemion AMV is the standard, high basic ion exchange membrane whereas Selemion AAV is the low proton leakage, weak basic anion exchange membrane. Images of Selemion AAV and Selemion AMV are shown in Fig. 3.2 (a) and (b) respectively.

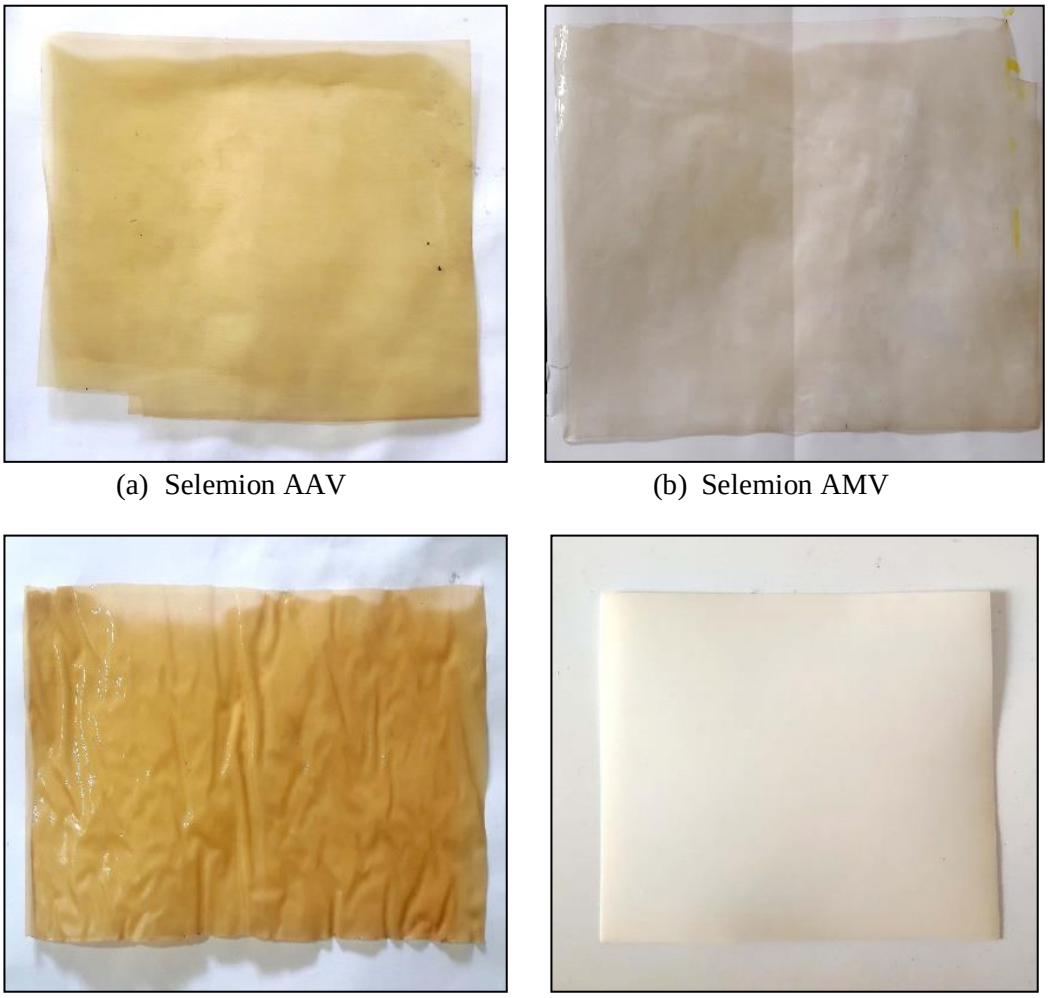
Table 3.2 Characteristics of the membranes used in the present study.

Membrane / type	Structural properties (functional groups)	Ion-exchange capacity (meq/g)	Thickness (mm)	Mechanical strength (kg/cm2)
Selemion AAV / Low proton leakage	4-vinylpyridinium	0.95	0.12	1.5 to 2
Selemion AMV / Standard	Anion PS/butadiene (polystyrene copolymer)	1.9	0.11	3 to 5
IPA (Interpolymer anion-exchange) / Homogeneous	Anion LDCE/HDPE (styrene-divinylbenzene)	0.8-0.9	0.16-0.18	--
AMI-7001S / Heterogeneous	Gel polystyrene crosslinked with divinylbenzene (Quaternary Ammonium)	1.3±0.1	0.45±0.025	5.6

IPA (interpolymer anion-exchange) membrane as shown in Fig. 3.2 (c) was provided by Membrane Division, Central Salt and Marine Chemicals Research Institute (CSMCRI),

Bhavnagar, India. AMI 7001S as shown in Fig. 3.2 (d) is a heterogeneous, anion exchange membrane imported from Membrane International Inc., USA.

All the membranes were stored in distilled water to prevent rupture except AMI 7001S. The details of the purchased commercial anion exchange membranes used in the present study are presented in Table 3.2.



(a) Selemion AAV (b) Selemion AMV

(c) IPA (d) AMI7001S

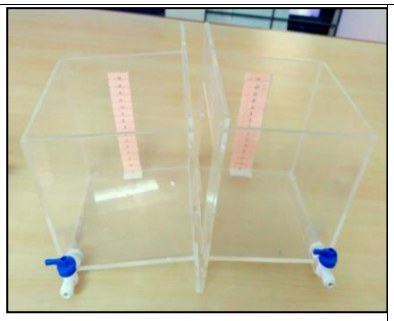
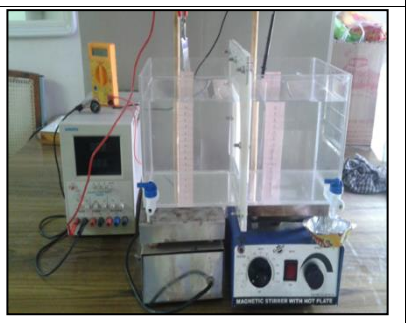
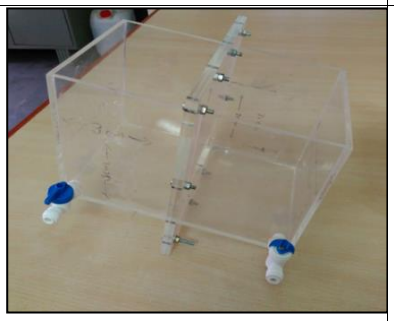
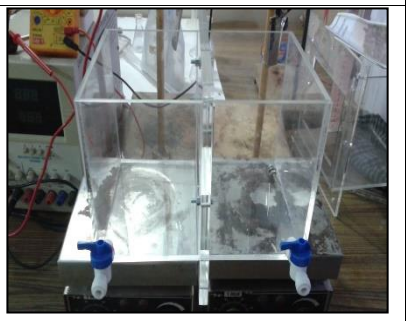
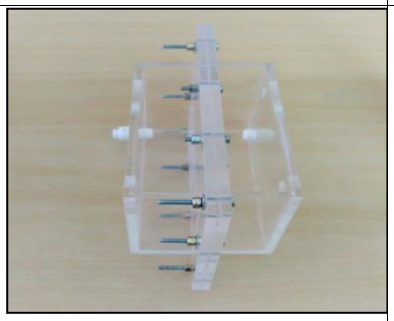
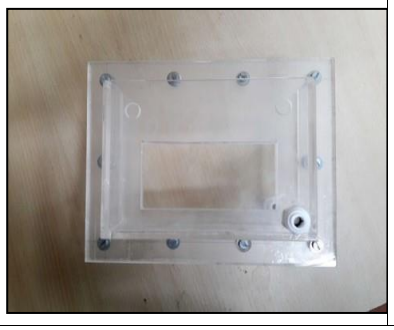
Fig. 3.2 Images of the pristine membranes used in the present study

3.3 Experimental set-up and operating conditions

Electrodialysis module was made up of acrylic material which was transparent as well as suitable for the range of sulfuric acid solutions used in present study. Modules of different sizes were tried and based on analysis of experimental results they were modified. The detailed description of all the modules used in present study is given in Table 3.3. The first module, as shown in Table 3.3, Module 1 was constructed to have a large capacity of 8 liter

with an effective membrane area of 161 cm^2. The capacity of Module 2 was 3 liter and effective membrane area of 63.5 cm^2 and finally, the size of Module 3 was constructed to have a capacity of 550 ml and effective membrane area of 49.5 cm^2.

Table 3.3 Specifications of different sized ED modules used in the present study.

Sr. No.	Modules and dimensions	Module and Experimental set up photos
1	Module 1 Length: 16 cm Breadth: 17 cm Height: 17 cm Effective membrane area: 161 cm^2	 
2	Module 2 Length: 11 cm Breadth: 14.5 cm Height: 14.5 cm Effective membrane area: 63.5 cm^2	 
3	Module 3 Length: 03 cm Breadth: 14 cm Height: 10 cm Effective membrane area: 49.5 cm^2	  

3.3.1 Batch electrodialysis process

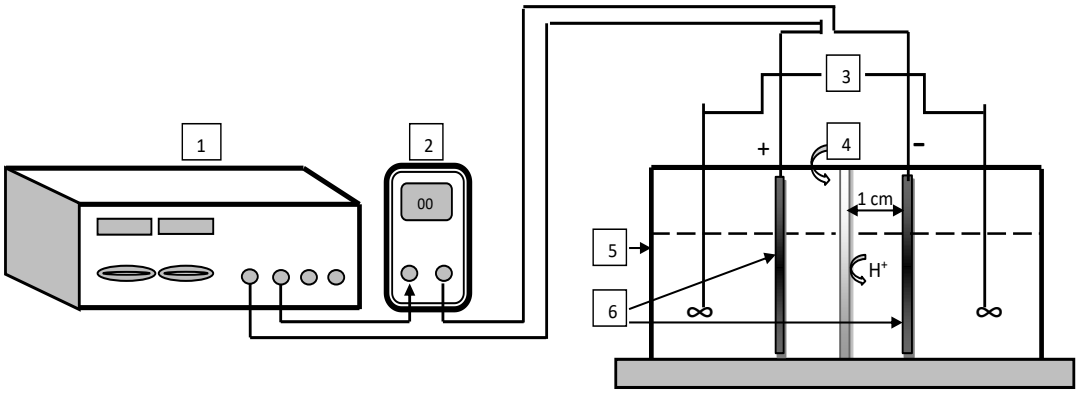


Fig. 3.3 Schematic representation of experimental set up used in the present study (1. DC power supply 2. Ammeter 3. Stirrer 4. Membrane 5. ED module 6. Electrodes)

The batch ED experimental set-up, as shown in Fig. 3.3, consisted of a two-compartment cell having the similar volume on both the side, partitioned by AEM with an effective area of 49.5 cm^2. Commercially available sheets of SS 316L and graphite having the same surface area were used as electrodes.

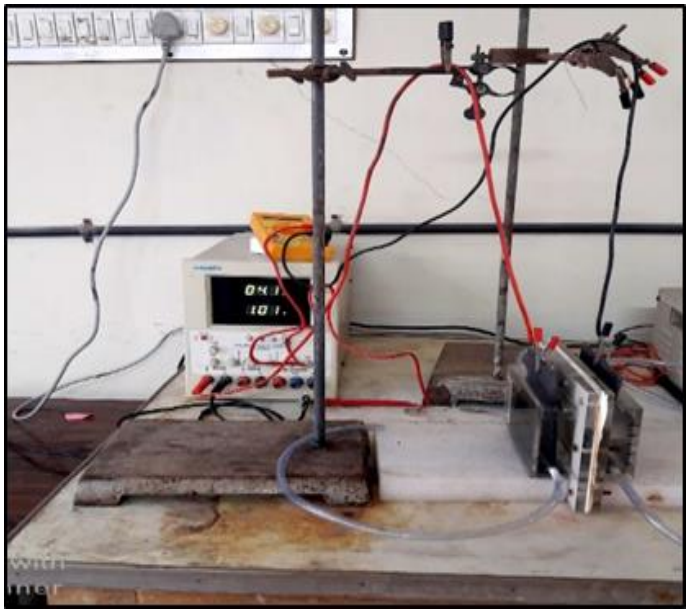
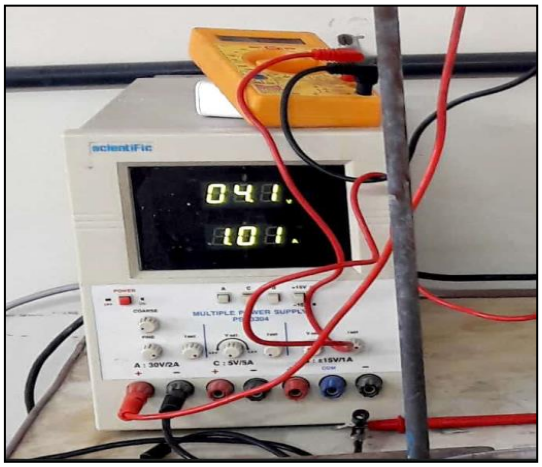


Fig. 3.4 Photograph of lab-scale batch ED experimental set up used in the present study

Photo of laboratory-scale experimental set up used to conduct batch ED experiments is shown in Fig. 3.4. The main instruments used in the present study are shown in Fig. 3.5.



(a) PSD3304, Multiple power supply

(b) TESTRONIX, DC power supply

(c) CL220, Chemiline conductivity meter

(d) DT83OD, Digital multimeter

Fig. 3.5 Various instruments used in the present study

Experiments were performed with different initial catholyte concentration for a wide range of current density from 2 to 50 mA cm^{-2} which was maintained constant by controlling the applied voltage using Multiple power supply as shown in Fig. 3.5 (a) model-PSD3304 and (b) TESTRONIX. The sulfuric acid concentration in anolyte and catholyte was analysed at regular intervals by conductivity analysis using Chemiline digital conductivity meter CL 220 as shown in Fig. 3.5 (c) supplied by Aqua Mart, Kolkata, India. and titrimetrically using 0.1 N NaOH solutions. An actual current flowing through the process during an experiment is measured by digital multimeter DT83OD shown in Fig. 3.5 (d). Homogeneity of the solution was maintained by providing frequent stirring in both the compartments. A qualitative analytical test was performed to determine the presence of iron ($Fe^{3+)}$ in the anolyte solution using a standard potassium thiocyanate solution (Vogel 1979). Table 3.4 represents the experimental operating parameter considered for batch ED process study.

Table 3.4 Experimental operating parameter considered for the batch ED process study.

Batch ED process	Range of variables
Initial catholyte concentration (wt. %)	1 to 5
Initial anolyte concentration (wt. %)	1 to 5
Current density (mA cm^{-2})	2 to 40
Applied voltage (V)	2 to 12
Electrodes	SS 316 L, Graphite
Membrane	Selemion AAV

3.3.2 Cascaded electrodialysis process

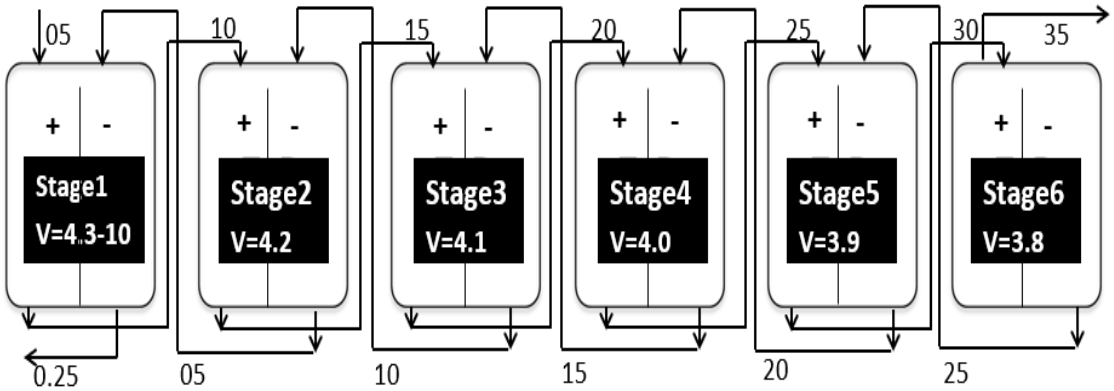


Fig. 3.6 Schematic diagram for the cascaded electrodialysis system; numbers indicate sulfuric acid concentration by weight %.

A proposed cascaded ED system schematic diagram is shown in Fig. 3.6. A 5 wt. % synthetic solution of sulfuric acid was taken as an initial feedstock. Each electrodialyzer consisted of an acrylic module having dimensions and membrane effective area similar to the batch scale ED module. Each experiment was started with equal volume and concentration of anolyte and catholyte solution with graphite electrodes and operated at a constant current density of 20.2 mA/cm^2. Each experiment was run for more than 15 hours and analysis of anolyte and catholyte concentrations were carried out at regular time interval. Table 3.5 represents the experimental operating parameter considered for cascaded ED process study.

Table 3.5 Experimental operating parameter considered for cascaded ED process study.

Cascaded ED process	Range of variables
Initial catholyte concentration (wt. %)	5 to 30
Initial anolyte concentration (wt. %.)	5 to 30
Stage wise concentration increment (wt. %)	5
Current density (mA cm^{-2})	20
Applied voltage (V)	3 to 5
Electrode	Graphite
Membranes	Selemion AMV, Selemion AAV, IPA

3.4 Determination of process performance parameters

3.4.1 Experimental molar flux (J_P)

Under the influence of an electric field, sulfate ions transfer to the anode compartment and get attached with the proton formed due to hydrolysis of water and anolyte become concentrated in terms of sulfuric acid. A common measure of ion transport from catholyte to anolyte per unit time and the unit surface of the membrane is the flux. Flux through membrane depends upon the process variables such as current density and initial concentration as well as the type of membrane. A thin membrane, comparatively, with higher ion-exchange capacity can generate higher molar flux. Particularly, in electrodialytic separation of sulfuric acid from a solution, it can be expressed as the net flux of sulfate ions crossing the membrane and is directly related to the variation in the amount of sulfuric acid in either catholyte or anolyte over the experimental time interval (Masigol et al. 2012; Parsa et al. 2015). In the present study, experimental molar flux was calculated using Eq. (3.1).

$$J_p = \frac{1}{A_m V_l} \int_0^t \frac{dC_c}{dt} \qquad (3.1)$$

Where A_m is the effective membrane area, V_l is the volume of the solution in catholyte, C_c is the sulfuric acid concentration in catholyte and t is the time.

3.4.2 Current efficiency (η)

Faraday's law is the basis for determining the amount of electrical current needed in an ED process to transfer a specific quantity of salt. It states that the passage 1 Faraday charge will transfer 1 g equivalent of salt. Current efficiency refers to the percentage of total current that

is used effectively for transferring ions. Current efficiency is affected by catholyte concentration, anolyte concentration and mainly current density. Current efficiency is an important parameter to be calculated to evaluate the performance of the process since it contributes to the energy consumption and cost of the process.

Current efficiency is the actual current utilized for the movement of ions from catholyte to anolyte per current supplied (Koter and Kultys 2008; Nur Afifah et al. 2018). It was calculated using Eq. (3.2).

$$\eta = \frac{z\,F\,(C_{co} - C_{cf})}{I\,t} \qquad (3.2)$$

Where z is the valence number of ions, C_{co} is the initial catholyte concentration, C_{cf} is the final catholyte concentration, F is the faraday constant, I is the current supplied.

3.4.3 Sulfuric acid separation (%)

In the ED process, as sulfate ions move to the anolyte makes the catholyte depleted in terms of sulfuric acid concentration. This separation of sulfuric acid from catholyte is measured in terms of % separation. Separation/movement of sulfuric acid through the membrane depends on the feed concentration, process variables, membrane properties and characteristics. With a single type of AEM, flux is mostly influenced by the current density. Sulfuric acid separation in terms of sulfuric acid wt. % reduction in catholyte in given time extent is obtained from the following Eq. (3.3) (Buzzi et al. 2013; Parsa et al. 2015; Nur Afifah et al. 2018).

$$\frac{C_{co} - C_{cf}}{C_{co}} \times 100 \qquad (3.3)$$

3.4.4 Energy Consumption

In electrodialytic separation of sulfuric acid through the membrane, two different types of energies contribute to the total energy requirements: (1) the electrical energy to transfer the ions from one solution through the membrane into the other solution and (2) the energy required to pump the solutions through the ED cell (Noble and Alexander 1995). Since the solution is not pumped through the ED cell, convective flux, as well as pumping energy required, are assumed to be zero in present work.

The energy required in the ED process is the specific power consumption (SPC) which can be described as the energy needed for recovery of one mole of ions from feed solution

(Masigol et al. 2012; Parsa et al. 2015).The energy (E_{ED}) required to increase anolyte concentration by ED was calculated using Eq. (3.4) to obtain its value in kJ per liter of final anolyte solution (V_{la}) (Cattoir et al. 1999; Zouhri 2013; Kroupa et al. 2015). Whereas the energy required for the same by evaporation (E_{EV}) is calculated theoretically using Eq. (3.5) on the basis of latent heat of vaporization of water (λ_w), density of water (ρ_w) and volume of water evaporated (V_w) for the concentrated solution (V_l).

$$E_{ED} = \frac{V\ I\ t}{V_{la}} \qquad (3.4)$$

$$E_{EV} = \frac{V_w\ \rho_w \lambda_w}{V_l} \qquad (3.5)$$

3.4.5 Diffusive flux (J_D)

Diffusive flux through the membrane is basically the derivation of Fick's law. Diffusive flux (Urano et al. 1984; Tedesco et al. 2016) through the membrane was calculated using Eq. (3.6).

$$J_D = -D\frac{dC_t}{dx} \qquad (3.6)$$

Where, D is diffusion coefficient of particular ions, dC_t is catholyte and anolyte initial concentration difference, and x is the thickness of the membrane.

3.4.6 Flux due to membrane electric potential ($J_ø$)

Flux through the membrane due to membrane electric potential generated based on concentration gradient (Pourcelly et al. 1994; Tedesco et al. 2016)was evaluated by Eq. (3.7).

$$J_\theta = \frac{-DzFC_{co}\left(\frac{dV_m}{dx}\right)}{RT} \qquad (3.7)$$

Where Vm is the membrane potential represented by Eq. (3.8),

$$V_m = \frac{RT}{zF} ln \frac{C_{co}}{C_{ao}} \qquad (3.8)$$

Where, C_{co} and C_{ao} are the initial catholyte and anolyte concentrations.

The Nernst-Planck equation (Koter and Kultys 2008; Koter et al. 2014) which is a result of the combined effect of the concentration gradient and an electric field is represented by Eq. (3.9) as below,

$$J = -D\left(\frac{dC_t}{dx} + \frac{zFC\left(\frac{dV_m}{dx}\right)}{RT}\right) \qquad (3.9)$$

3.4.7 FTIR analysis of the membrane

The presence of organic functional groups on the membrane surface was analysed by the Fourier transform infrared spectroscopy (Perkin Elmer Spectrum GX) using a wave number range of 400 – 4000 cm^{-1} at a resolution of 4.0 cm^{-1} with an acquisition time of 1 min. Wet samples were prepared by thoroughly cleaning pristine membrane coupons with deionized water and soaking them in a water bath for 24 h. The dried samples were sandwiched into a special folder and fixed with transparent tape for absorption measurement. The sampling chamber was continuously purged with nitrogen gas at a flow rate of 10 mL min^{-1} to avoid signal interference from the surrounding moisture and CO_2. At least 2 replicates were obtained for every sample type without applying any baseline corrections.

3.4.8 FE-SEM analysis of the membrane

The outer surface topologies of the AAV membrane was investigated via field emission scanning electron microscopy (FE-SEM) using JEOLFE-SEM (JSM-6701F) at 5 kV. For cross-sectional analysis, cryogenically fractured membrane samples under liquid N_2 were freeze-dried overnight and sputtered with a thin layer of platinum using JEOL JFC-1600 auto fine coater.

CHAPTER 4

Results and Discussions

Electrodialytic separation of sulfuric acid from model spent acidic solution was carried out using a simple two compartment ED module with different electrodes and membranes. Low-cost electrodes such as graphite and SS 316L were tested under electrodialytic conditions for acid separation and their effect on anolyte quality was investigated. Rigorous experiments were performed using batch electrodialysis for a wide range of process variables with the graphite electrode. Effect of various physico-chemical parameters such as initial catholyte concentration, current density on molar flux, current efficiency, the extent of sulfuric acid separation and voltage requirements were studied. A cascaded electrodialysis system consisted of six electrodialyzer was operated at a constant current density of 20 mA cm^{-2} (a value found appropriate based on batch ED experimental results) and was proposed for the enrichment of sulfuric acid concentration. Selemion AAV, Selemion AMV and IPA membranes were used in this study and their performance to increase acid concentration, operating time, current efficiency, voltage requirements and energy consumption was examined. Estimation of energy consumed by ED process along with economic analysis was carried out and compared with the conventional evaporation process. Experimental observations and findings of the present work are discussed in the following subsections.

4.1 Selection of an electrodialysis module

The electrodialysis module was made up of acrylic material which was transparent as well as suitable with dilute sulfuric acid solutions. Modules of different sizes were fabricated and a few of these were modified subsequently based on the obtained results. Specifications of different dimensions of ED modules used in the present study are discussed in Table 3.3. Stack (ED cell) construction, the feed flow velocities and mode of operation are some of the important design parameters that have been considered while designing an ED process (Strathmann 2004). The first module had a very large volume of 8 liter capacity with effective membrane area and electrode surface area of 161 cm^2 and 110 cm^2 respectively. Experiments were initially performed in batch mode with module 1. Anode and cathode side compartments were initially filled with 2 wt. % sulfuric acid solution and applied voltage was about 2 V. Under these set of conditions, no change in anolyte concentration was

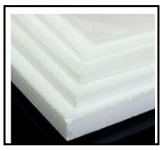
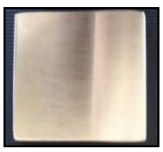
observed. The same results were obtained even with 10 wt. % of initial anolyte and catholyte concentrations. Therefore, module 1 was modified to module 2. Negligible separation of acid from catholyte to anolyte was observed even after prolonged operating time and at a high voltage of about 5 V. In order to achieve separation, the module 2 was once again modified to have a compact cell, lesser volume and higher membrane effective surface area. The second module capacity was 3 liter and effective membrane area of 63.5 cm^2 and finally, the size of module 3 was reduced to have 550 ml capacity and effective membrane surface area of 49.5 cm^2. When experiments were carried out with module 3, more satisfactory results were obtained. Remaining experiments were performed batch-wise using module 3.

4.2 Selection of electrode material

Electrodialytic separation of sulfuric acid from spent acidic liquor is not only influenced by process variables like applied voltage, current density, and initial catholyte concentration but also by other factors like material of construction of the module and electrodes. The selection of an appropriate electrode is an important factor when it is to be used in ED dealing with acidic solutions. Despite considerable work in ED for the treatment of a number of wastewater, the development of cost-effective and corrosion-free electrodes has become a less focused area of research. Initially, four different types of electrodes were considered to be studied. These were compared on the basis of cost, corrosion resistance, electrical conductivity and stability in sulfuric acid solution. A detailed comparison of electrodes is given in Table 4.1.

As shown in Table 4.1, the cost of platinum mesh sized 10 cm×10 cm is very high about 7000/- Rs. in comparison with other electrodes. Though it has high stability in sulfuric acid solution and higher conductivity of 9.43×10^6 S/m, its cost contribution may be significant to the cost of the whole ED unit. The ED process suggested in the literature for acidic waste treatment mostly employed platinum (Cattoir et al. 1999), platinized titanium (Zouhri 2013; Chekioua and Delimi 2015; Kroupa et al. 2015), or titanium coated with titanium oxide (Buzzi et al. 2013) as electrodes.

Table 4.1 Different electrodes studied in the present work.

Electrode Material	Electrode Image	Conductivity κ (S/m) at 20 °C	Price (Rs.)/piece	Characteristics
Platinum		9.43×10^{6}	7000 (25000 Rs. /10 gm)	Inert, High conductivity, High resistance in acidic solution
Teflon		10^{-25} to 10^{-23}	150	Inert, Highly Poor conductivity, High resistance in acidic solution
SS 316L		1.45×10^{6}	100	Good conductivity, Good resistance in acidic solution
Graphite		2 to 3×10^{5}	300	Inert, Good conductivity, Good resistance in acidic solution

Though effective, the use of costly electrodes may not be economically viable at large scale due to their significant cost contribution, which may exceed more than 90% of the total cost of the ED process unit (Nayar et al. 2015). The aim of the present work was to develop an economic process and therefore on the basis of cost comparison the platinum electrode was not selected in the present work. Teflon has very high resistance in acidic solution and its cost is also lesser but due to the very low value of conductivity 10^{-25} to 10^{-23} S/m, it cannot work under electrodialytic conditions and hence was not used either. Along with the cost, stability and corrosion resistance are the other major factors affecting the electrode selection (Veerman et al. 2010; Nayar et al. 2015). It has been reported that the stainless steel has good corrosion resistance in acidic solutions, as well as carbon materials due to their chemical and electrochemical characteristics are also effective for industrial applications (Iken et al. 2007). Electrical conductivity, resistance in corrosive medium and cost of SS 316L and graphite as electrode material are found appropriate to be tested under electrodialytic conditions in the present study.

4.3 Batch electrodialysis process

Electrodialytic separation of sulfuric acid from its dilute solution was carried out batch-wise using graphite and SS 316L as electrodes. Initially, experiments were conducted with constant initial catholyte concentration ranging from 1 to 5 wt. % to determine the effect of current density. Then experiments were performed with different initial catholyte concentration for a wide range of current density from 2 to 50 mA cm^{-2} which was maintained constant by controlling the applied voltage.

The extent of acid separation, current efficiency, molar flux and the external driving force required are major parameters used to mark the performance of ED processes. These parameters are affected by several factors such as initial catholyte concentration, initial anolyte concentration, catholyte and anolyte concentration difference and current density. In addition to these process variables, the role of electrode material and membrane type is imperative on process performance as they are in direct contact with the feed solution. The following subsections describe the effects of electrode material, catholyte concentration, current density and concentration difference on the basis of experimental results.

4.3.1 Effect of electrode material

Table 4.2 Responses of graphite and SS 316L electrodes observed in the present study of electrodialytic separation of spent sulfuric acid.

Sr. No.	Applied voltage (V)	Applied current density (mA cm^{-2})	Initial catholyte concentration (wt. %)	Initial anolyte concentration (wt. %)	Electrode observations	
					Graphite	SS 316 L
1	2 - 3	2.02	1±0.15	1±0.15	No carbon particles precipitation	Anolyte color turned yellow
2	2 - 12	2.02 - 30.3	1±0.15 - 4.4±0.05	1±0.15	No carbon particles precipitation	--
3	4.5 - 12	>30.3	2.26±0.15 - 4.4±0.05	2.26±0.15 - 4.4±0.05	Anode disintegration, precipitation of carbon particles	--

In the present study, SS 316L and graphite electrodes were used for a range of current density, applied voltage, catholyte and anolyte concentration. Table 4.2 summarizes the relative performance of two different electrodes used under present experimental conditions.

4.3.1.1 Effect of SS 316L

A perusal of Table 4.2 indicates that in the presence of SS 316L electrode there was an increase in the anolyte concentration and its color changed to yellow. Similar observations were made in the experiments at other operating conditions as well. When anolyte sample was examined with potassium thiocyanate reagent, the solution turned blood-red indicating oxidation on the surface of SS 316L and confirming the presence of ferric ions (Vogel 1979). No such observations were reported when SS 316L was used as a cathode. It can be concluded from these observations that the SS 316L cannot be a suitable electrode as an anode in the electrodialytic separation of sulfuric acid.

4.3.1.2 Effect of Graphite

The performance of graphite anode was satisfactory up to the current density of 30 mA cm^{-2}. But at a higher current density above 30 mA cm^{-2} and a higher voltage within the range of 4.5 - 12 V, graphite particles started crumbling down turning anolyte black and rendered the electrode unusable. Similar observation for graphite as the anode was reported by other researchers (Rabah et al. 1981a; SIROMA et al. 2007). The wear of graphite was plausibly due to the attack of atomic oxygen in the presence of sulfuric acid solution. Coking of graphite could not be ruled out as it might be responsible for detaching the graphite particles from the surface resulting in the loss of material. Iken et al. (2007) also analysed corrosion behavior of graphite and stainless-steel electrodes in presence of phosphoric acid and confirmed that graphite had better corrosion resistance than stainless steel (Iken et al. 2007). Taken together these observations imply that the graphite could be a better corrosion-resistant electrode than SS 316L under the present experimental conditions.

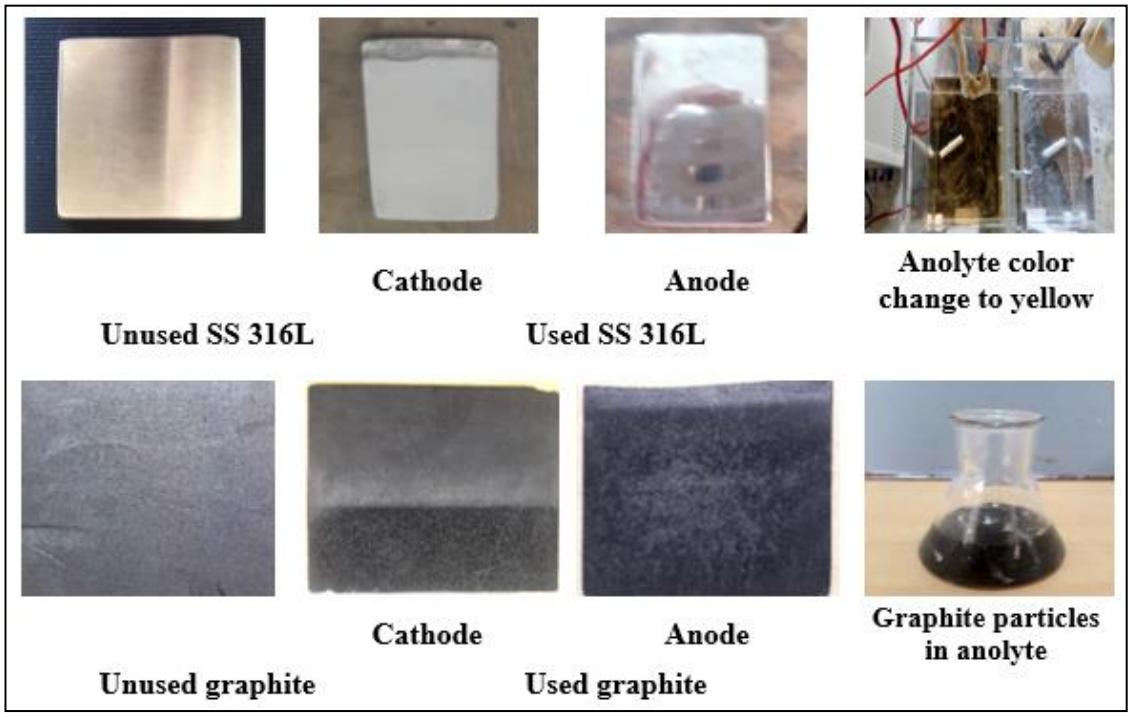


Fig. 4.1 Images of electrodes used in the present study

Fig. 4.1 presents the visuals of unused and used SS 316L and graphite electrodes. The image of the electrode at the top is of the unused SS 316L where the sharp edges and a polished floor are visible. After prolonged use in the ED cell, the electrode edges and floor underwent corrosion as seen in the top right image. It is noteworthy to mention that the anode electrode got more corroded in comparison to its cathode counterpart. A similar phenomenon was noticed for a graphite electrode in the lowest part of Fig. 4.1. In the present study, the graphite electrode was found suitable and it could resist corrosion compared to the SS 316L. Graphite could have been a good source of electrode if it could be developed in a cost-effective way. Improvements in the ED process performance with surface-modified electrodes or coating on the surface constitutes a future scope for research (Rabah et al. 1981b).

4.3.2 Effect of initial catholyte concentration (C_{co})

In the electrodialytic separation of acids, ions move from catholyte to anolyte through an anion exchange membrane. Feed concentration or catholyte concentration is a major variable affecting the performance of the system. Flux through the membrane, applied voltage and current efficiency varies with the initial catholyte concentration. Very dilute acid concentration may provide very high electrical resistance and sometimes may become a reason for reaching a limiting current density to damage the membrane. On the contrary, a

very high concentration of acid may also damage the membrane. It is, therefore, necessary to check the performance of the process in an appropriate range of acid concentration. Initially, the batch ED was operated in the sulfuric acid concentration range from 1 to 5 wt. % and determined its effect on process performance parameters that are described in the following subsections.

4.3.2.1 Effect of initial catholyte concentration on molar flux

Initial catholyte concentration can significantly affect the performance of the ED process. The effect of initial catholyte concentration on molar flux (J_p) at constant current density is presented in Fig. 4.2. It shows that the flux increased almost linearly with initial catholyte concentration for current densities 10 mA cm^{-2} and above, however for lower current densities there was a negligible enhancement. For the current density of 10 mA cm^{-2}, the maximum increase of molar flux with increasing catholyte concentration was estimated to be 3.6×10^{-8} mol cm^{-2} s^{-1}, whereas for the current density of 20 mA cm^{-2} and 30 mA cm^{-2} maximum increase of molar fluxes were 7.15×10^{-8} mol cm^{-2} s^{-1} and 10.5×10^{-8} mol cm^{-2} s^{-1} respectively. At very lower values of current density, 2 and 4 mA cm^{-2}, marginal change was observed.

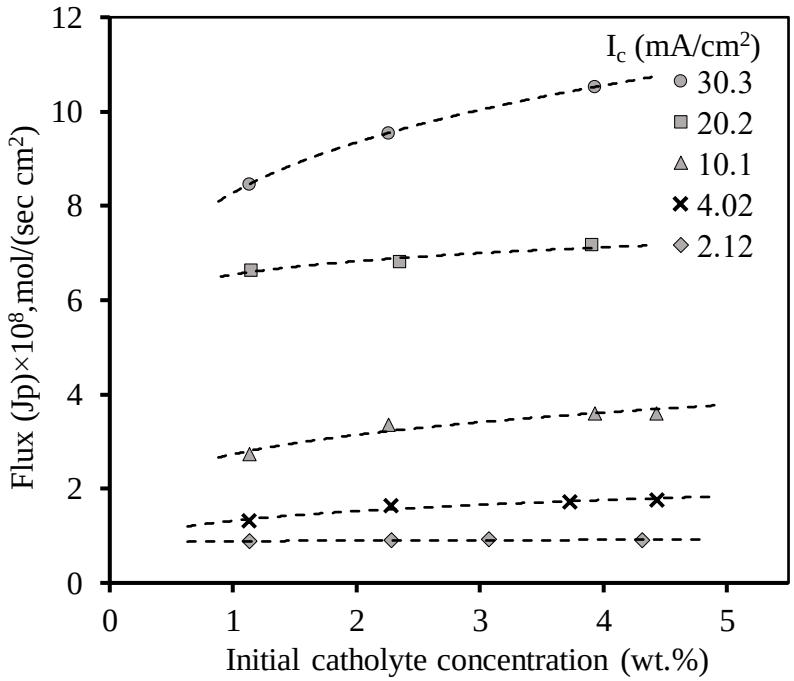


Fig. 4.2 Effect of initial catholyte concentration on molar flux

As the concentration of ions increase in the solution, it essentially provides the driving force to the movement of ions, and as a consequence molar flux increase. More the number of ions present in the solution, the higher become the flux obtained. However, it is worthwhile to note that in the present work, experiments were conducted in the lower range of initial concentration range up to 5 wt. % only. Thus, it may not be appropriate to assign any optimal initial catholyte concentration value or range. For that greater number of experiments is required to be performed at higher initial concentration. Nevertheless, on the basis of present experimental work 4.45 wt. % could be considered as the most suitable initial catholyte concentration for which higher molar flux was obtained.

4.3.2.2 Effect of initial catholyte concentration on current efficiency

Initial catholyte concentration has a considerable influence on the current efficiencies (CE). Fig. 4.3 presents the variation of current efficiency with respect to initial catholyte concentration at constant applied current density. An increasing trend was observed with an increase in initial catholyte concentration in the present work. However, beyond a certain range of initial catholyte concentration, a system might have reached a maximum current efficiency and thereafter it decreases to lower values (Luo et al. 2002).

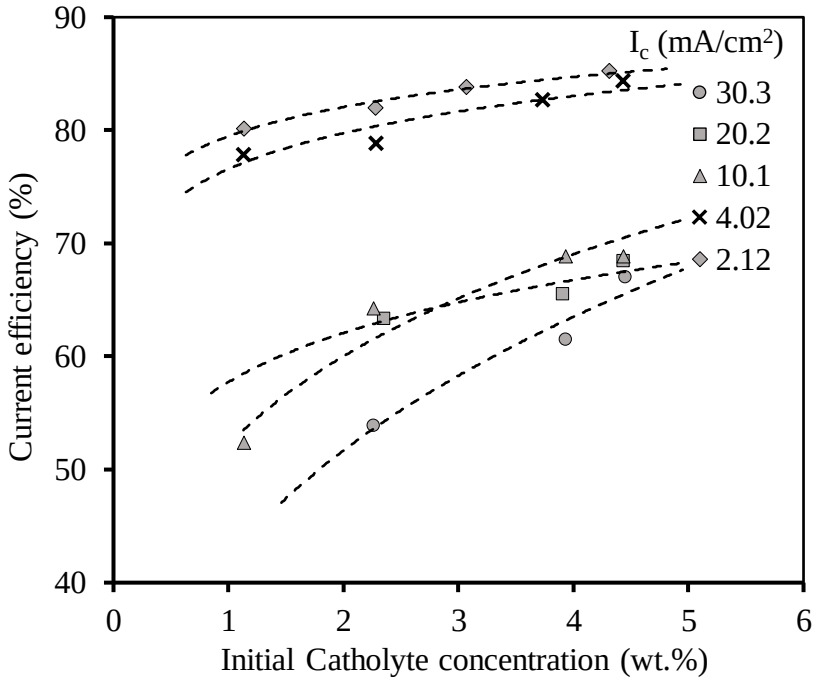


Fig. 4.3 Effect of initial catholyte concentration on current efficiency

A perusal of Fig. 4.3 indicates that for applied current densities 10, 20 and 30 mA cm^{-2}, the values of current efficiency increased from 64.27 to 68.86%, 63.35 to 69.78% and 53.86 to

67.02% respectively when initial catholyte concentration increased in the range from almost 2.2 to 4.5 wt. %. Even at low current densities, such as 2 and 4 mA cm^{-2}, current efficiency increased. Furthermore, the current efficiencies were observed to be 78.8 to 85.23% at lower I_c e.g. 2 to 4 mA cm^{-2}. However, current efficiency decreased when I_c increased from 10 to 30 mA cm^{-2} and was found out to be in the range of 50 to 70% only. Similar observations were reported by Luo et al. (2002) in the process of concentration of formic acid solution by electrodialysis (Luo et al. 2002). It is worthwhile to mention that the current efficiency increased with increasing solution concentration until the values reach maximum current efficiency. This underscores the importance of performing a greater number of experiments at higher concentration. Therefore, the determination of maximum current efficiency assumes significance, which unfortunately could not be carried out in the present experimental conditions as the feed solution was very dilute having low concentrations of sulfuric acid.

4.3.2.3 Effect of initial catholyte concentration on applied voltage

Initial catholyte concentration is a major influencing variable in the ED process. It has been observed that the membrane resistance is significantly lower than the resistance offered by dilute solution due to relatively high ionic concentration in the membrane (Strathmann 2004). At higher initial concentration, the number of ions present in the solution being higher, the increase in conductivity leads to the lower applied voltage (Chekioua and Delimi 2015). It was observed that an increase in initial catholyte concentration resulted in a reduction in external voltage required to maintain constant current density. The effect of initial catholyte concentration on applied voltage is presented in Fig. 4.4. A perusal of Fig. 4.4 indicates that at 1±0.15 wt. % C_{co}, the voltage required was 3 V for maintaining I_c 2.12 mA cm^{-2} while the same was 2.3 V at 4.3 wt. % C_{co}. Similarly, voltage decreased from 3.5 to 2.8 V and 7 to 3.5 V to maintain I_c 4.02 and 10.10 mA cm^{-2} respectively when C_{co} increased from 1±0.15 to 4.4±0.05 wt. %. Lower voltage variation from 2.3 V to 4.3 V was observed at higher C_{co} while the same was observed very high from 3 to 12 V at very low C_{co} 1±0.15 wt. % for the entire range of I_c. The voltage requirement was found to be very high i. e. 12 V when treated 1±0.15 wt. % solution.

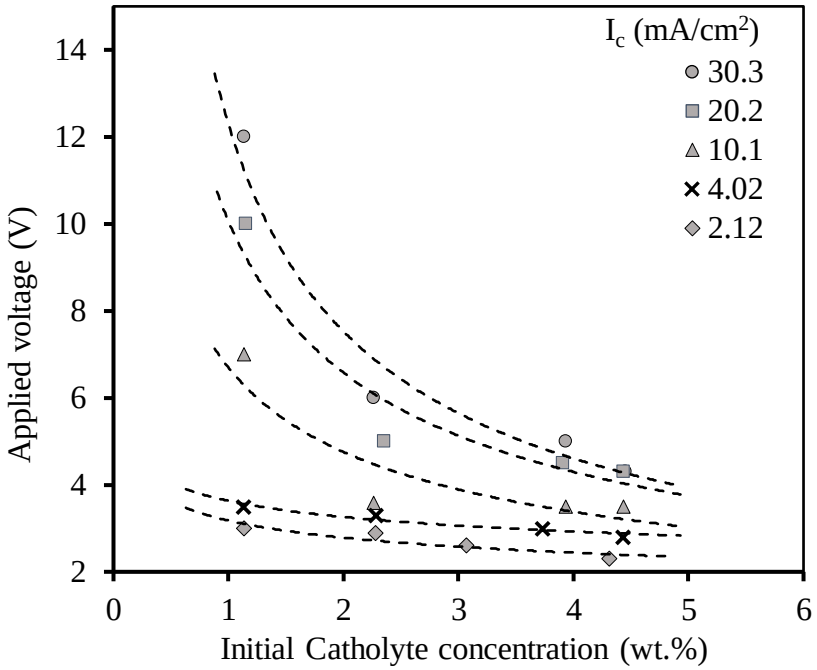


Fig. 4.4 Effect of initial catholyte concentration on applied voltage

These observations confirmed the presence of high electric resistance offered by a dilute solution. There is a need to increase the applied electric voltage gradually as catholyte concentration decreased with time during the experiment until it reached much less value like 0.5 wt. %. Thereafter even application of very high voltage was unable to maintain I_c and it showed a gradual drop thus indicating that further separation was uncontrollable. At this stage, it is appropriate to state that, with very low catholyte concentration having few sulfate ions present in the solution may lead to a high rate of water splitting and migration of H^+ and OH^- ions through the membrane which can damage the membrane.

In this section, the effect of the initial catholyte concentration on molar flux, applied voltage and current efficiency for Selemion AAV membrane has been discussed. A higher number of ions with higher current-carrying capacity and the most important is the conductivity of solution that increases with an increase in sulfuric acid concentration are accountable for higher molar flux, higher current efficiencies and lower applied voltage. A current density of 20 mA/cm^2 has been observed as a suitable value for further experimentation.

4.3.3 Effect of current density (I_C)

Current density is basically the number of ions crossing the membrane per unit area of the membrane, measured in mA/cm^2. A very high value of current density may become a reason for reaching the limiting current density as well as affect the performance of the electrode.

Electrodialytic separation of sulfuric acid was carried out in the range of current density of 2 to 50 mA/cm^2. When experiments were performed beyond 30 mA/cm^2 of current density, i. e. at 40 and 50 mA/cm^2, with sulfuric acid concentration in the range 1 to 5 wt. %, very high flux rates were observed but at the cost of the electrode. Based on the results obtained with the graphite electrode, experiments were performed in the range of current densities from 2 to 30 mA/cm^2.

Variation in current density affects the process performance in terms of flux, the extent of separation, current efficiency and applied voltage that are discussed in the following subsections.

4.3.3.1 Effect of current density on molar flux

The molar flux through the ion exchange membrane depends upon the current flowing between anode and cathode. Experiments were performed to observe the behavior of the process for different applied current densities.

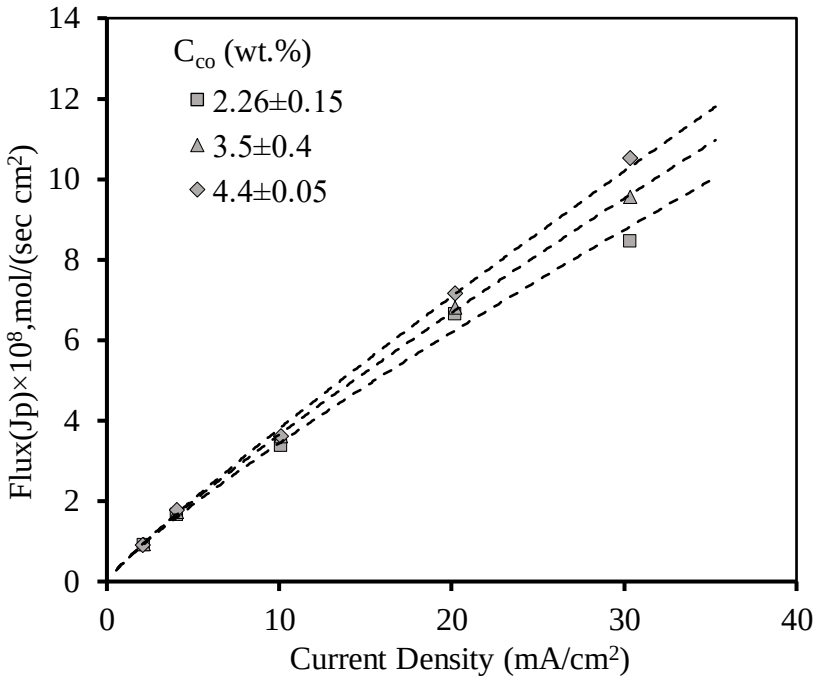


Fig. 4.5 Effect of current density on molar flux

Fig.4.5 presents the molar flux as a function of applied current density for three different catholyte concentrations viz. 2.26, 3.9 and 4.3 wt. %. Molar flux was found to increase almost linearly with applied current densities. It increased from 0.9×10^{-8} to 6.63×10^{-8}, 0.92×10^{-8} to 9.54×10^{-8} and 0.84×10^{-8} to 10.52×10^{-8} mol cm^{-2} s^{-1} for given values of catholyte initial concentrations when current density varied from 2 to 30 mA cm^{-2}.

Maximum flux was obtained at a current density of 30 mA cm^{-2} and 4.45 wt. % initial catholyte concentration. Fundamentally, the function of applied current density is to push the anions towards the anode. Higher the applied current density, the higher will be the applied force, resulting in enhanced flux. At higher current density, lesser time is required by the system to transport ions from catholyte to anolyte and higher flux is achieved. If the time required to transport the same number of ions from cathode to anode at higher current density is less, the process becomes faster. The data presented in Fig. 4.5 reveal that the rate of change of flux was more affected by applied current density than by initial catholyte concentrations.

4.3.3.2 Effect of current density on current efficiency

Current efficiency is basically the actual current utilization in the process for the movement of ions through the membrane and it is affected by several factors that are responsible for incomplete current utilization. Water splitting, hydronium ions migration, proton leakage can be considered as several such factors (Strathmann 2004). These factors must be taken into account as improper utilization of current contributes to the economy of the process.

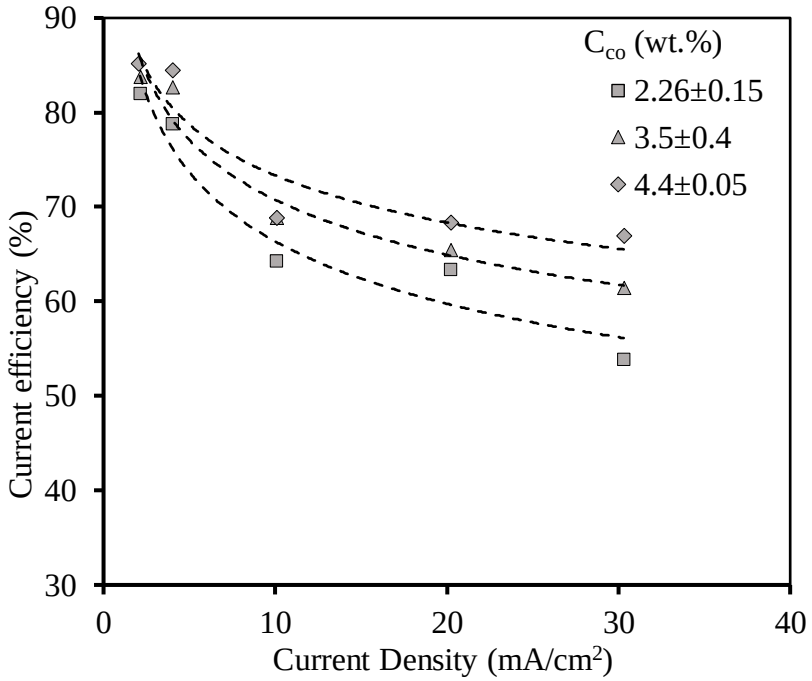


Fig. 4.6 Effect of current density on current efficiency

As in the present process, only sulfate ions migration is considered through the anion exchange membrane, the selectivity of the membrane might not contribute much. Furthermore, a low proton leakage Selemion AAV membrane is used in the present study

so minor leakage of the proton is unavoidable. Fig. 4.6 shows the current efficiency which was calculated from Eq. (3.2) given in materials and methods section 3.4.2 found decreasing with current density at constant C_{co}.

From Fig. 4.6 it is clear that current efficiency decreased with current density at a constant initial catholyte concentration. The present system was so dilute that, current efficiency was found to decrease beyond applied current density 2 mA cm^{-2}, presumably due to the onset of limiting current density (Luo et al. 2002; Akgemci et al. 2005). Thus, CE was found to decrease with applied current density for constant initial catholyte concentration. When C_{co} was 2.26 wt. %, efficiency decreased from 81.9 to 53.8%, and for C_{co} 3.9 wt. % it decreased from 83.8 to 61.4%. The main reason for achieving lower current efficiencies is the bubble formation on the surface of the membrane and the electrode as shown in Fig. 4.7, with little change in volume as well as the temperature of the solution, and high-water resistance at lower acid concentration.

Fig. 4.7 Formation of bubbles on the surface of the electrode

During an electrodialytic separation of sulfuric acid from its dilute solution at constant current density, catholyte gets depleted in sulfuric acid concentration with the movement of ions through the membrane with time. Very dilute catholyte solution provided very high electric resistance and may lead to reduced utilization of actual current supplied. Under this condition, if the current density is increased further, bubble formation might occur on the

surface of the membrane with a change in volume as well as the temperature of the solution. These additional effects of increasing current density are responsible for obtaining lower values of current efficiency. Applied current density is not a certain value and it can change with the working system and the properties of the membranes (Luo et al. 2002). Best results were observed for lower I_c and higher initial catholyte concentrations for the present process. Higher efficiencies were obtained at lower current density values of 2 to 4 mA cm^{-2} but at a high initial catholyte concentration of 4.45 wt. % and with corresponding minimum molar flux. So, for the present process, 20 to 30 mA cm^{-2} current density can be suggested as the appropriate range where the molar flux is reasonably higher and efficiencies are in the range 60 to 70%.

4.3.3.3 Effect of current density on applied voltage

An electrical potential gradient that is accountable for the migration of ions is established by applying a voltage difference between two electrodes dipping into an electrolyte solution. Cations migrate towards the negatively charged cathode and anions towards the positively charged anode (Strathmann 2004). These migrated ions carry current with them and when the current is measured per unit area of the membrane defines current density (I_c). Higher current densities are maintained by applying a higher potential difference causing migration of the greater number of ions from catholyte to anolyte and the same is observed with the present system. A range of applied voltage required for maintaining various current densities for different constant initial catholyte concentration was investigated.

As shown in Fig. 4.8, when experiments were completed at constant C_{co} in the range of 2 to 5 wt. %, the applied voltage was found to increase with current density. Moreover, at lower C_{co} 2.26 ± 0.15 wt. %, there was an increase in applied voltage from 2.9 to 6 V with current density ranging from 2.02 to 30.3 mA cm^{-2}. A similar trend was observed in the case of C_{co} 3.5±0.4 wt. % and 4.4±0.05 wt. % where voltage variation was from 2.6 to 5V and 3 to 4.3 V. These data show that lower applied voltage is required to maintain lower current densities and the vice versa for the same initial catholyte concentration (Baltazar et al. 1992).

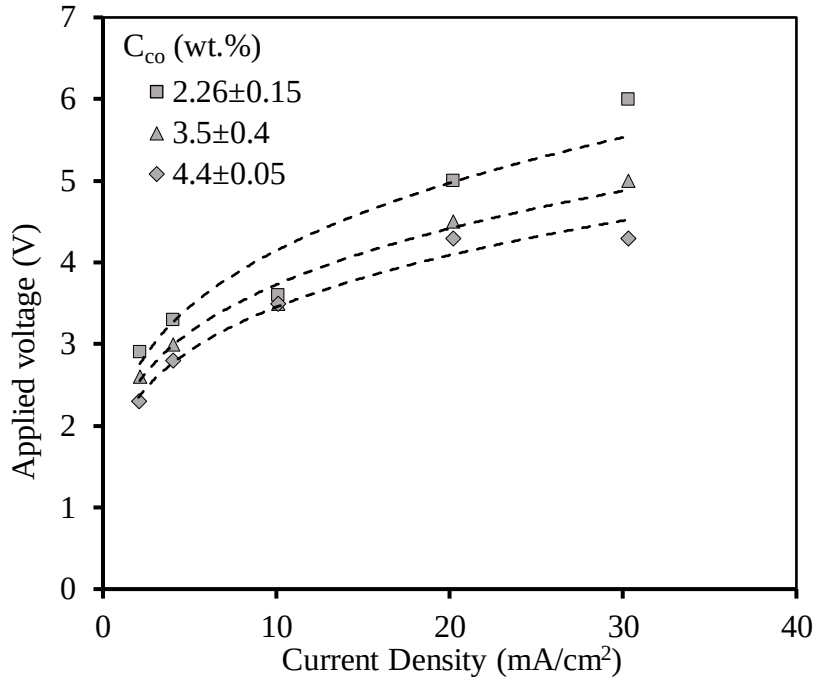


Fig. 4.8 Effect of current density on applied voltage

At constant Cco, the current efficiency was observed to be high at lower I_c (Baltazar et al. 1992; Luo et al. 2002; Akgemci et al. 2005) as shown in Fig. 4.3. When I_c was kept in a lower range 2 to 4 mA cm^{-2}, efficiencies were estimated to be higher and in the range of 78.8 to 85.23%. When experiments were carried out at lower I_c, no negative effects such as bubble formation at the surface of the electrode, volume change or water splitting were observed. As a result, the current efficiency was higher in all cases at lower I_c. It is therefore evident that lower I_c gives higher efficiencies, and for maintaining such lower I_c, the applied voltage required should also be lower. So, the operating cost of the process might also be lower when operated at lower current densities. Taken together these observations point out that the ED used in the work was a less energy-intensive process for separation of sulfuric acid from its dilute solution. But interestingly, the molar flux calculated using Eq. (3.1) given in materials and methods section 3.4.1 is very low at lower applied I_c as shown in Fig. 4.5, and so appropriate values of all these variables must be selected. The recommended value of the current density for the present process is 20 mA cm^{-2} with a voltage range from 2 to 6 V.

4.3.4 Effect of catholyte and anolyte initial concentration difference

The effect of the initial concentration difference of catholyte and anolyte on the current efficiency is presented in Fig. 4.9. A perusal of Fig. 4.9 implies that when the process is

operated using equal catholyte and anolyte initial concentration (C_{co} = C_{ao}), the CE was reported to be very high, even more than 100% for some cases (Luo et al. 2002).

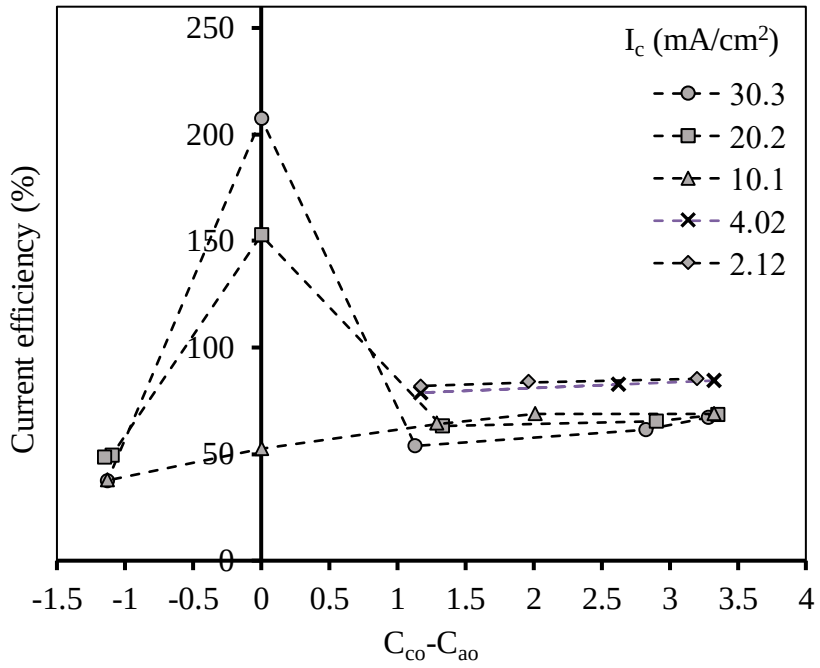


Fig. 4.9 Effect of catholyte and anolyte concentration difference on current efficiency

When the values of applied current density were 20 and 30 mA cm^{-2}, CE was estimated to be 152.7% and 207.5% respectively. Due to identical anolyte and catholyte initial concentrations at the beginning of the process, no membrane potential gradient could be generated. In such a case in the absence of current and diffusive resistances offered by solution as well as membrane could be well considered to be the same on both the sides. This could be the reason for obtaining maximum CE as well as flux for this case. Even for the studied dilute solution with catholyte initial concentration about 1±0.1 wt. %, when experiments were performed at higher applied current density viz. 20 and 30 mA cm^{-2}, it was observed that the movement of ions was very fast. Although maximum molar flux was obtained, the experiment could not be carried out for a longer time. CE suddenly dropped thereafter but once again gradually increased for positive concentration difference. When experiments were carried out after maintaining positive catholyte to anolyte initial concentration difference (C_{co}>C_{ao}), CE was found to increase for almost all cases. This has already been discussed in section 3.2 in detail. If special case (C_{co}= C_{ao}) data were to be ignored, overall it was found to be an increasing trend of CE for C_{co}>C_{ao}. A reverse trend was observed for negative catholyte to anolyte initial concentration difference (C_{co}< C_{ao}).

CE was reported to be 37.3%, 49.3% and 37.6% for current densities of 30, 20 and 10 mA cm^{-2} respectively. CE with a negative concentration difference was even less than that with a positive concentration difference. When the anolyte concentration was more than catholyte concentration, efficiencies were found out to be very less. This proves that there is a definite effect of anolyte initial concentration on current efficiency. When the catholyte initial concentration was increased, CE increased as well, but it subsequently decreased with an increase in anolyte initial concentration. This may be due to back diffusion of ions from anolyte to catholyte restricting the movement of ions in the opposite direction of concentration gradient i. e. from catholyte to anolyte, and ultimately it requires more applied current to move and hence lesser CE. These observations are in good agreement with those reported by Jaroszek et al. (2017) in the production of sulfuric acid using EED (Jaroszek et al. 2017) and Luo et al. (2002) in the electrodialysis of formic acid solution (Luo et al. 2002).

4.3.5 Extent of sulfuric acid separation (%)

Separation/movement of sulfuric acid through the membrane depends on the feed concentration, process variables, membrane properties and characteristics. With a single type of AEM, flux is mostly influenced by the current density.

Table 4.3 Sulfuric acid separation (% separation) obtained in terms of wt. % reduction in catholyte concentration.

Sr. No.	Initial catholyte concentration (wt. %)	% Separation obtained at various values of Current density				
		2.12 (mA cm^{-2})	4.02 (mA cm^{-2})	10.1 (mA cm^{-2})	20.2 (mA cm^{-2})	30.3 (mA cm^{-2})
1	1±0.15	19	36	50	99	99
2	2.26±0.15	10	18	31	59	78
3	3.5±0.4	8	12	23	53	51
4	4.4±0.05	5	10	17	34	49

It has been discussed in the previous section 4.3.3.1 that the increase in current density results in the increase in the molar flux due to higher applied voltage. It is apparent that applied voltage forces the sulfate ions to migrate from catholyte to anolyte. This in a given time extent, the separation in terms of wt. % reduction in catholyte sulfuric acid concentration is obtained higher for higher I_c. In other words, the treatment or separation

rate increases with an increase in the current density (Chekioua and Delimi 2015). A series of experiments were performed at various current densities and percent reduction in catholyte sulfuric acid concentration was calculated using Eq. (3.3) and the data are presented in Table 4.3. At C_{co} 4.4±0.05 wt. %, separation obtained was 5 to 49% with corresponding current density from 2.12 to 30.3 mA cm^{-2} whereas it was 19 to 99% in case of C_{co} 1±0.15 wt. %. These observations support the possibility of complete removal of acid contents from catholyte (<0.01 wt. %) using ED. An increase in current density in the given range resulted in improved separation. Furthermore, the current efficiency of anion transport (HSO_4^-, SO_4^{2-}) is independent of the kind of metal cation present on the cathode side of the membrane. In addition, the permeabilities of cations from the cathode to anode side of AAV in the electrodialytic and diffusive processes are similar despite the presence of the external electric field acting against the concentration force. Therefore, separation of sulfuric acid from a solution generated from metal pickling units, containing metal cations such as Mg^{2+}, Zn^{2+}, Na^+ (Koter et al. 2014) treated this way can generate catholyte with traces of sulfuric acid. Metal-free acid can be obtained as anolyte that can be discharged at a minimal cost of acid treatment or neutralization.

The separation of sulfuric acid was also carried out in presence of other metal impurities like sodium and copper. Few experiments were also performed with mixture of hydrochloric acid and sulfuric acid. When performance of ED was carried out using sulfuric acid solution as anolyte and sodium sulfate solution as catholyte, sodium was found lesser in anolyte than catholyte. In presence of copper sulfate solution as catholyte, the copper was found deposited on the surface of graphite cathode as thin layer under electrodialytic conditions. On the basis of metal activity series, the more reactive metals such as Fe, Mg, Na, Zn etc. remains in the catholyte and comparatively pure sulfuric acid solution can be obtained as anolyte. Since anion exchange membrane was used only in the present study, the separation of sulfuric acid from mixture of sulfuric acid and hydrochloric acid was found difficult. Rather, during electrodialytic separation of acid mixture using Selemion AAV membrane the chloride ions were transferred more to anolyte compared to sulfate ions.

4.3.6 Performance of AMI 7001S membrane

AMI Membrane is an anion exchange membrane procured from Membrane International Inc., USA. It has a thickness of about 0.45 mm and an ion exchange capacity of about 1.3 meg/q as shown in Table 3.2 in chapter 3. The thickness of the membrane is more as

compared to other membranes used in the present study. AMI membrane was soaked in a feed solution for 24 hours before use. When an experiment was performed with 5 wt. % of anolyte and catholyte solution using AMI membrane, no change in concentration of both the compartment could be observed. Experiments conducted with even higher acid concentrations did not perform well and flux rate obtained was almost zero. These results might be due to the thickness of the membrane which was even doubled in size when soaked in the feed solution. The present process is also a batch process having no additional driving force like pressure or convection might also be a reason for the poor performance of the membrane. This particular membrane was not used for further experimentation in the cascaded ED process.

4.4 Cascaded electrodialysis system

Electrodialysis cell is a key component in an electrodialytic unit that can be operated in different modes such as batch type or continuous. In many cases, the desired concentration of the solution cannot be achieved in a single pass through ED cells and therefore two or more cells can be placed in series (Strathmann 2004). A cascaded ED system constituted of six electrodialyzers was designed to increase the concentration of dilute sulfuric acid. Commercially available graphite sheets were used as electrodes as they could be considered a low-cost electrode with better corrosion resistance than SS 316L. The aim of this work is to increase the acid concentration by 5 wt. % per stage.

4.4.1 Performance of different membranes

Sulfuric acid enrichment by ED is affected by a number of factors wherein the type of membrane used plays a key role. Hence, the performance of the cascaded ED process was analysed in terms of its ability to enrich acid concentration, current efficiency and voltage requirements using all the three membranes. Experiments were performed at a constant current density of 20 mA/cm^2 using three different types of AEMs namely Selemion AAV, Selemion AMV and IPA. Stage-wise concentration enrichment data along with voltage requirements for different AEMs are shown in Table 4.4.

Table 4.4 Stage wise catholyte concentration reduction and anolyte concentration enrichment with time and applied voltage with Selemion AAV, Selemion AMV and IPA membrane at a constant current density of 20 mA/cm^2 and graphite electrode.

Stage No.	Applied voltage (volt)	Time (min.)	Anolyte concentration (wt. %)		Catholyte concentration (wt. %)	
	V	t	Initial (C_{ao})	Final (C_{af})	Initial (C_{co})	Final (C_{cf})
Selemion AAV						
1	4.4-10	660	5.15	9.98	5.15	0.37
2	4.3-4.5	660	10.29	14.95	10.29	5.64
3	4.2-4.3	660	15.19	19.85	15.19	10.54
4	3.9-4.0	660	20.58	25.23	20.58	15.93
5	3.8-3.9	660	25.48	26.95	25.48	24.01
6	3.7-3.8	660	29.40	31.38	29.40	28.2
Selemion AMV						
1	4.3-9	600	5.15	10.05	5.15	0.25
2	4.2	600	10.05	15.19	10.05	4.90
3	4.1	600	15.19	20.09	15.19	10.29
4	4	600	20.58	25.48	20.58	15.68
5	3.9	600	25.48	27.44	25.48	24.01
6	3.8	600	29.40	30.87	29.40	28.5
IPA (Indigenous)						
1	4.3 - 10	660	4.90	9.56	4.90	0.25
2	4.2	840	10.29	15.44	10.29	5.15
3	4.1	840	15.19	20.09	15.19	10.05
4	4.0	840	20.58	25.48	20.58	15.44
5	3.9	840	25.48	27.93	25.48	23.03
6	3.8	840	29.40	31.85	29.40	27.93

4.4.1.1 Stage-wise concentration enrichment

Since AEMs are made of polymeric materials, their swelling, as well as proton leakage characteristic, affects the performance of the separation process by ED. Sulfuric acid recovery by ED cannot be developed on an industrial scale because of the proton leakage of polymeric anion exchange membranes which has been found up to now.

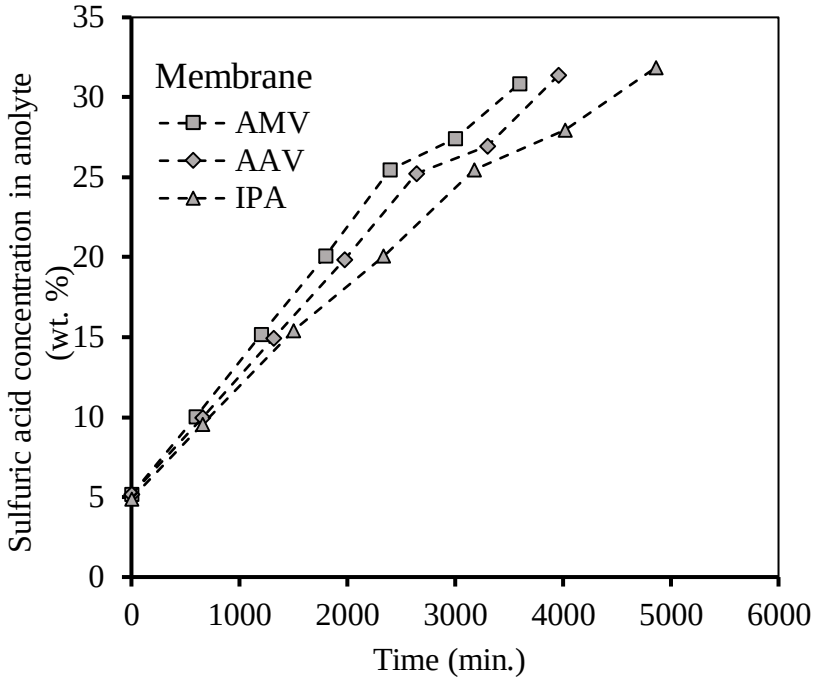


Fig. 4.10 Sulfuric acid concentration enrichment with time

Generally, the acid concentration reaches a limiting value at which the current efficiency falls to zero (Cherif et al. 1988). V Baltazar et al. (1992) studied proton leakage through different AEMs, CEMs and BPMs and showed that the characteristic of the ion exchange membrane used plays an important role in the recovery of acid (Baltazar et al. 1992). Water present in AEM acts as an excellent mediating agent for the proton leakage (Lorrain et al. 1997). Proton leakage is a major problem associated with most commercial anion-exchange membranes, which makes them unsuitable to use to recover sulfuric acid (Cherif et al. 1988). Three different AEMs tested under present experimental conditions and results obtained are shown in Fig. 4.10 and Fig. 4.11.

The concentration of sulfuric acid was found to increase to the tune of 5 wt. % in stages 1 to 4 as shown in Table 4.4 with all the three membranes. Selemion AMV has been reported as a standard anion exchange membrane and is used extensively in various ED applications. When it was tested under present experimental conditions, it could enrich sulfuric acid concentration up to 25.48 wt. % in approximately 2400 minutes in stages 1 to 4 as shown in Fig. 4.10. However, the results obtained in stages 5 and 6 were not satisfactory. Similar observations have been recorded with the other two membranes. Selemion AAV could increase acid concentration up to 25.23 wt. % in approximately 2640 minutes whereas IPA increased up to 25.48 wt. % in approximately 3180 minutes. Starting with an initial concentration of 29.4 wt. %, after the completion of stage 6, the sulfuric acid concentration

was reported to be 31.38, 30.87 and 31.85 wt. % in 660, 600 and 840 minutes by Selemion AAV, Selemion AMV and IPA membrane respectively. The anolyte concentration increased about 5 wt. % each in stages 1 to 4 in order AMV>AAV>IPA, but beyond stage 4 the results did not follow the same trend as highlighted by the dotted circle in Fig. 4.11.

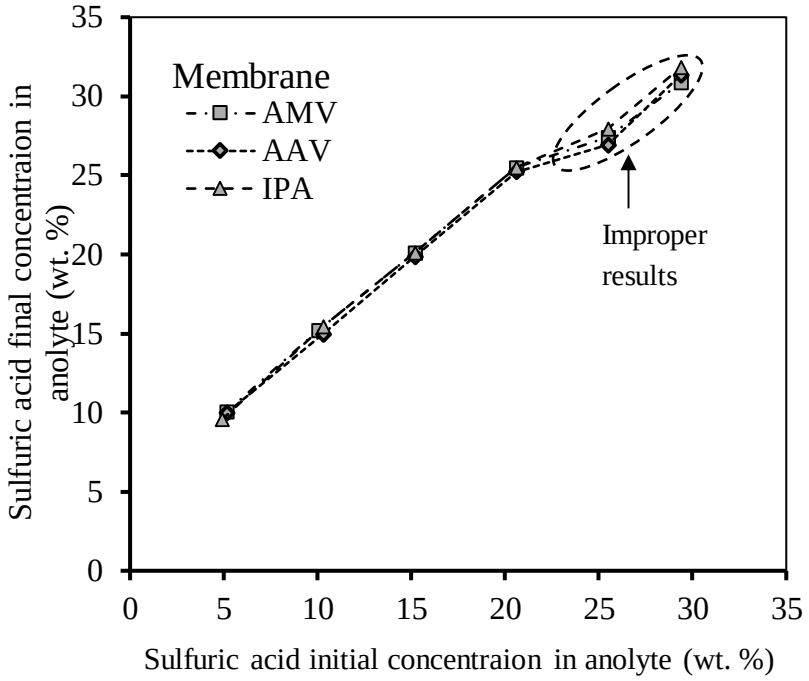


Fig. 4.11 Stage wise initial and final anolyte concentration

Low proton leakage membranes such as Selemion AAV has been reported to be the best candidate for the concentration of sulfuric acid. Selemion AAV membrane has been reported as more suitable amongst five different types of membranes to concentrate sulfuric acid up to 3.5 mol/l (Jaroszek et al. 2017). Selemion AAV has already been proven as a low proton leakage membrane and used in ED for the acid enrichment process. In comparison with Selemion AAV membrane, the acid enrichment ability of Selemion AMV membrane was observed higher in the present study. Though IPA membrane could enrich sulfuric acid little lower than the other two membranes, its performance was observed equivalent to the low proton leakage membrane. The fluxes of sulfuric acid were observed to be the highest for AMV membrane and smallest for IPA membrane. This could be linked to ion exchange capacity and thickness of the membrane and in fact the length of the diffusion path which was the highest for IPA membrane. These observations are in good agreement with the findings reported by Jaroszek et al. (2017) for process with the recirculation of solution

(Jaroszek et al. 2017). The performance and results obtained with IPA membrane are discussed in detail in the following section.

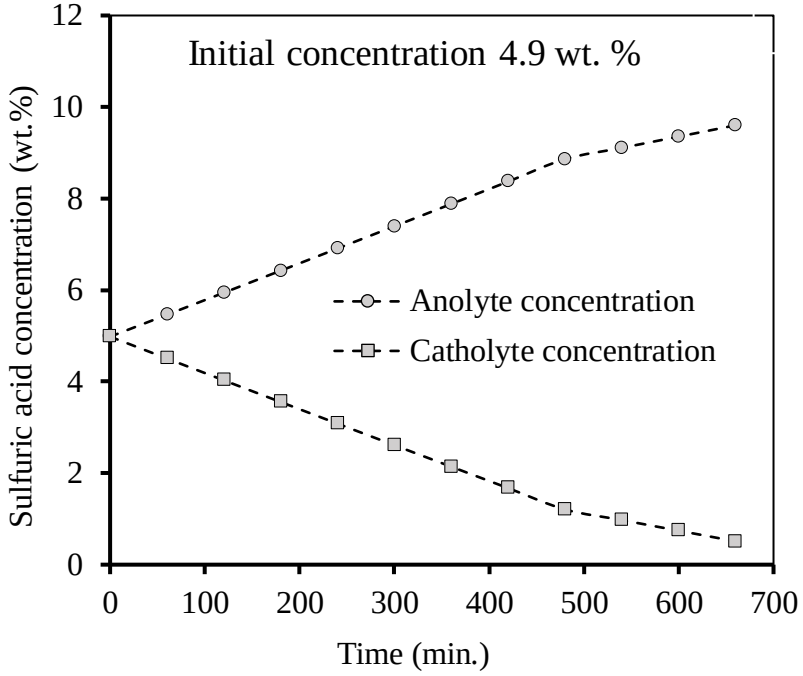


Fig. 4.12 Stage wise sulfuric acid concentration enrichment at initial concentration of 4.9 wt. % and a constant current density of 20 mA/cm^2 and IPA anion exchange membrane

Results obtained during stage-wise sulfuric acid concentration using the indigenous IPA membrane are shown graphically in Fig. 4.12. As shown in Fig. 4.12, the first stage took almost 660 minutes to reach 9.56 wt. % anolyte concentration from an initial concentration of 4.9 wt. % with a simultaneous reduction in catholyte concentration to 0.25 wt. %. Similarly, consecutive stages 2, 3 and 4 took almost 840 minutes for each 5 wt. % concentration enrichment. Stages 5 and 6 as could not produce satisfactory results. Results obtained with stage 5 are shown in Fig. 4.13. These observations are in good agreement with the observations reported by Yongtao et al. in 2015 in production of sulfuric acid by liquid absorption and oxidation of low concentration SO_2 in aqueous solutions as well as electrodialysis enrichment in the same reactor (Yongtao et al. 2015).

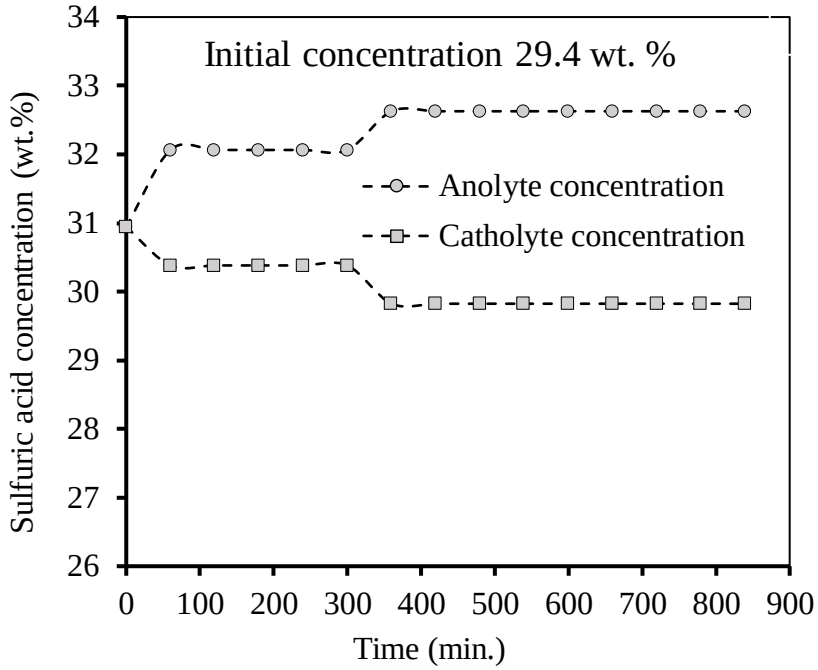


Fig. 4.13 Stage wise sulfuric acid concentration enrichment at an initial concentration of 29.4 wt. % and a constant current density of 20 mA/cm^2 and IPA anion exchange membrane

Fig. 4.12 represents how the concentration gradient (C_{at}-C_{ct}) changed during the process of transfer of sulfate ions from catholyte to anolyte. The concentration gradient was obviously zero at t = 0 min. because of the same initial catholyte and anolyte concentration. Under the influence of the applied electric field, the transfer of sulfate ions towards the anodic compartment resulted in the enrichment of the sulfuric acid concentration leading to the simultaneous development of concentration gradient. It has been reported in the literature that the back-diffusion results from concentration gradient across the IEM and increases with an increase in the concentration ratio between the streams separated by IEM (Tanaka 2003; Jaroszek et al. 2017). Apart from this, concentration polarization (CP) is an inherent, inevitable and fundamentally important phenomena in electromembrane processes (Tanaka 2003; Le 2012; La Cerva et al. 2018). In the case of ED, the effect of CP in the liquid film formed at the upstream membrane is to deplete ions in the boundary layer as ions are extracted through the membrane faster than they arrive at the interface from the bulk solution. Therefore, ionic concentration (C_{SO4}^{-2}) becomes a lower interface than that in the bulk solution. The depletion of the permeating ion increases the electrical resistance (Strathmann 2004). On the other hand, the sulfate ions concentration (C_{SO4}^{-2}) is greater in the boundary layer formed at the downstream side of the membrane surface. As reported in

the literature, with a high linear velocity of catholyte and anolyte solutions, a turbulent flow inside the chamber of ED renders the impact of CP adjacent to the IEM negligible (Jaroszek et al. 2017) and hence the effect of CP can be neglected. The same becomes appreciable in batch ED where the fluid is stirred manually and hence it is essential to consider it. Along with this phenomenon, acid back diffusion and the proton leakage characteristic of the membrane is also responsible for the observed behavior of the enrichment process.

4.4.1.2 Effect of acid enrichment on current efficiency

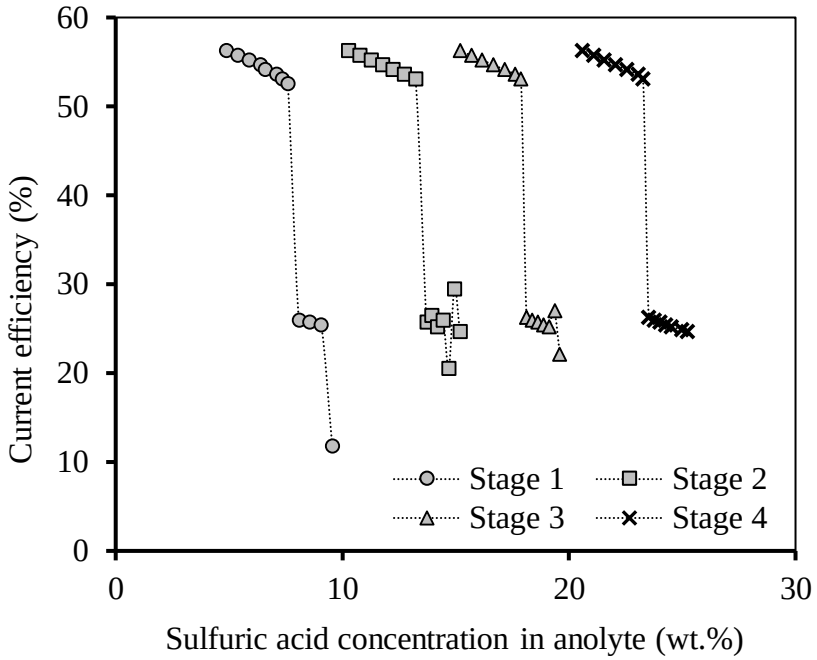


Fig. 4.14 Effect of sulfuric acid enrichment on current efficiency of stages 1 to 4 performed at a current density of 20 mA/cm^2 and IPA anion exchange membrane

In the ED process particularly, there are many factors affecting current efficiency such as catholyte concentration, current density, water resistance, etc. The effect of these factors has already been discussed in previous sections (Section 4.2.2 and 4.2.3). When it comes to acid enrichment by a membrane, acid back diffusion due to concentration gradient i. e. increase in anolyte concentration greater than catholyte concentration is also one of the factors affecting CE. Effect of the same on the performance of IPA membrane has been discussed in the following section.

Fig. 4.14 represent the effect of the increase of sulfuric concentration in anolyte on current efficiency for stage 1. Initially, high CE in the range of 50 to 60% was observed, then after CE decreased rapidly with the decrease in sulfuric acid concentration in catholyte less than

1 wt. %. The lowest value of CE of 10% was observed with stage 1. The corresponding increase in sulfuric acid concentration in anolyte more than 8 wt. % led to the large concentration gradient and back diffusion (Luo et al. 2002; Jaroszek et al. 2017). As discussed in previous sections, this might be the reason for observing a rapid decrease in CE. Lower current densities were observed for each stage after generation of more than 7 wt. % concentration gradient. A similar trend was observed with all other stages of the cascaded ED process with IPA membrane. In previous sections (5.3.4), the effect of anolyte and catholyte concentration difference on CE has been reported for dilute sulfuric acid and CE values were found below 50% for the case $C_{ao}>C_{co}$ represented in Fig. 4.9. Additionally, it has been reported that in the acid enrichment process, the acid concentration reaches a limiting value at which the current efficiency falls to zero (Cherif et al. 1988). Similar observations were reported during acid enrichment using stages 5 and 6 where current efficiencies were observed about 60% initially and then fallen to zero.

Sulfuric acid is very complicated system. The conductivity of the sulfuric acid solution plays a major role in the electrodialytic movement of sulfate ions through the membrane. As reported in literature, the conductivity of sulfuric acid solution increases up to certain value and then decreases with acid concentration (Darling 1964). Thus, the concentrate resulted in an increase of the voltage for the same current density. This may cause an overall current efficiency decrease (Luo et al. 2002). This behaviour of sulfuric acid might be one of the possible reasons and responsible for achieving lower values of current efficiency and limiting the enrichment of sulfuric acid beyond 28 wt. % concentration.

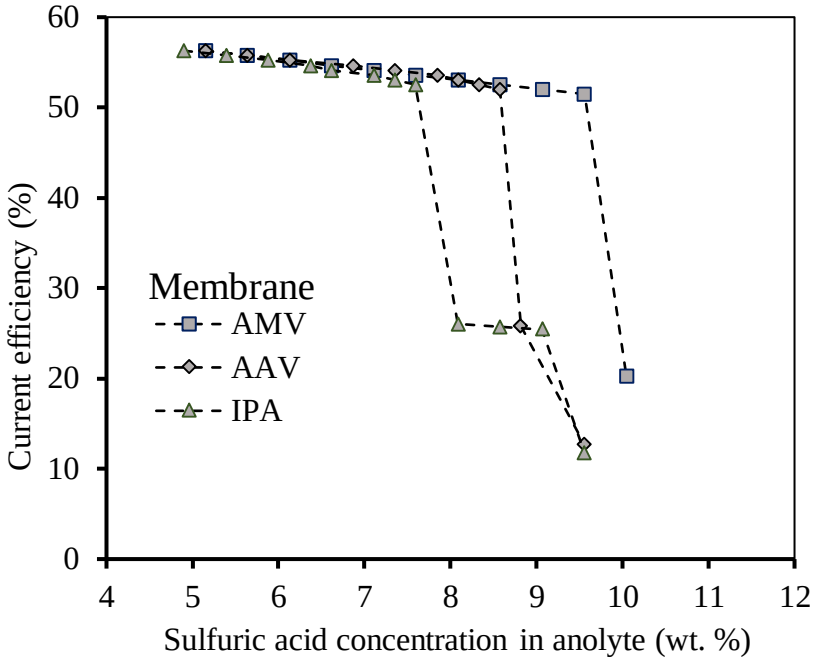


Fig. 4.15 Effect of sulfuric acid concentration enrichment on current efficiency for stage 1 with different membranes

Fig. 4.15 represents the effect of the increase of sulfuric concentration in anolyte on the current efficiency for stage 1 with all the three AEMs. Initially, high CE in the range of 50 to 60% was observed, followed by a sudden decrease in CE beyond a certain value of concentration gradient. For example, when catholyte concentration was reduced to less than 1 wt. % and the concentration gradient reached about 9 wt. %, CE decreased from 52 to 20 % with the Selemion AMV membrane. The same was observed with the Selemion AAV and IPA membrane when the gradient exceeded the value of about 8 wt. % and 7 wt. % respectively. A similar trend was observed with all other stages of the cascaded ED process and with all the three membranes. Minimum values of CE of 10% were observed with the Selemion AAV and IPA membrane in comparison with Selemion AMV membrane. Overall efficiencies were observed higher with AMV membrane and in order AMV>AAV>IPA.

4.4.1.3 Voltage requirements

Fig. 4.16 shows the voltage varied with time for stages 1 to 6 to maintain the current density at a constant value of 20 mA/cm^2 during sulfuric acid enrichment process.

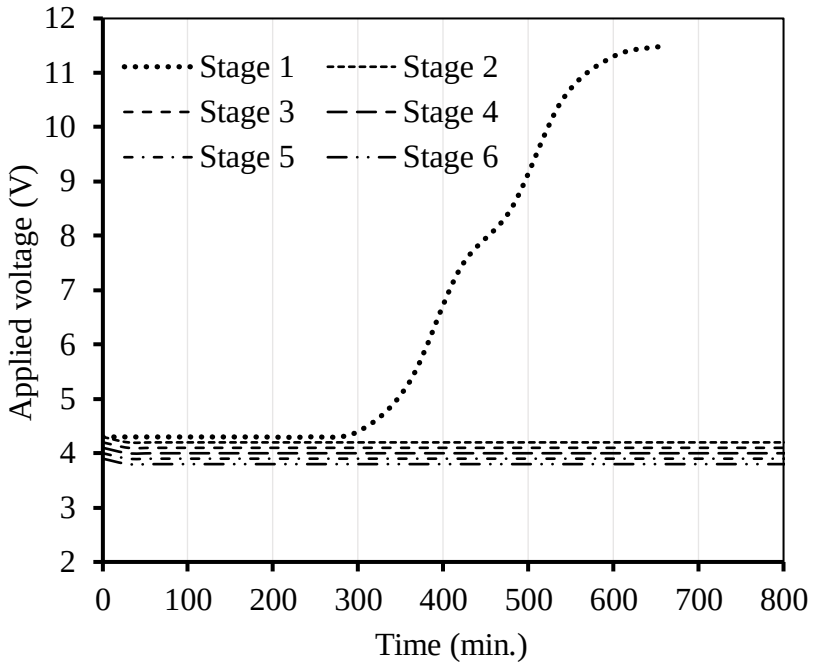


Fig. 4.16 Variation in voltage during acid enrichment in stages 1 to 6 with IPA membrane

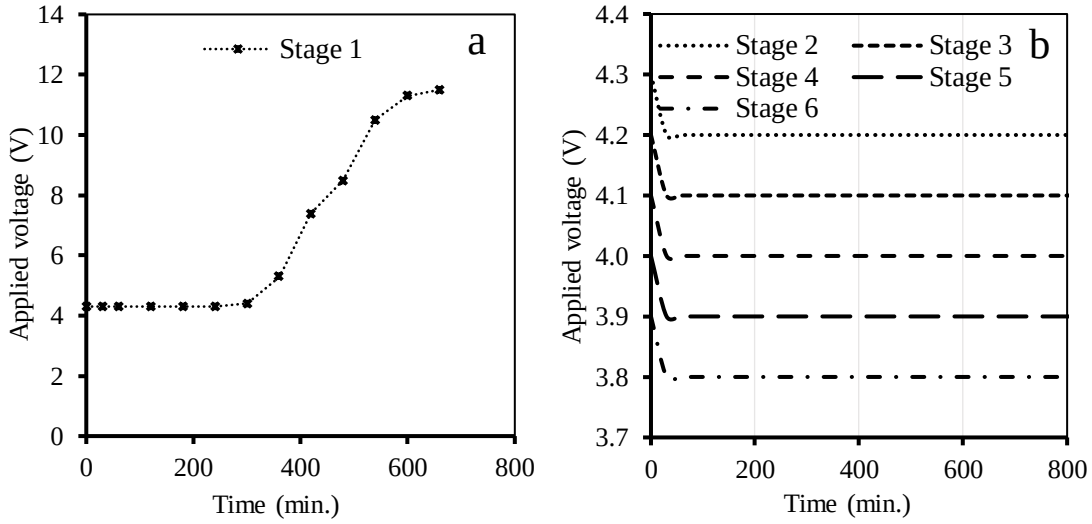


Fig. 4.17 Variation in voltage during acid enrichment in (a) stage 1 and (b) stages 2 to 6 with IPA membrane

At the beginning of the experiment, the applied voltage was observed a little higher for about 30 minutes and then it decreased to a lower value. Zouhri (2013) reported similar observations in the generation of sulfuric acid and sodium hydroxide from the sodium sulphate salt by electro-electrodialysis (Zouhri 2013). As shown in Fig. 4.17 (b), applied voltage decreased by 0.1 V for each stage of ED and then it was observed almost constant except for stage 1. This period may be called as an initial adjustment period.

Voltage requirements have to be set initially to maintain the current density at a constant value and it is mainly a function of initial acid concentration and current density. As represented in Fig. 4.17 (a), for stage 1, when initial catholyte and anolyte concentration was 4.90 wt. %, the initial applied voltage was only 4.4 V, which increased gradually with the decrease in catholyte concentration. With the progress of the enrichment, an increase in concentration gradient i.e. increase in back diffusion increased resistance to ion transfer from catholyte. Furthermore, the catholyte was diluted to 0.25 wt. % concentration and had a conductivity of just 12 mS. So, the resistance provided by water also increased the demand for the external force for the ion transfer. Therefore, the applied voltage was needed to be increased with time to maintain constant current density throughout the process. An applied voltage was increased from 4.3 to 10 V with dilution in catholyte concentration. The combined effect of back diffusion, concentration polarization and solution conductivity increased the demand for applied voltage with the process in stage 1. Then after in every stage, there was a decrease in catholyte concentration by 5 wt. %, with the concentration varying in the range of 10 to 30 wt. %. Since a higher concentration solution was always present in cathode and anode compartment in all the stages except stage 1, the voltage required then varied in the range 3.8 to 4.3 V and that difference was not very significant as shown in Fig. 4.17 (b). It can be concluded from these observations that the higher concentration of solution does not have a great effect on the applied voltage of the cell for the studied ED process. For stages 5 and 6, even a supply of higher voltage for a longer time could not increase the anolyte concentration much. Similar trend was observed with the Selemion AAV and Selemion AMV membranes. On the basis of experimental results given in Table 4.4, it is clear that the voltage requirements are almost the same for all the membranes to enrich sulfuric acid concentration under present experimental conditions. Inspite of having the same voltage demands with all the membranes, energy consumptions differed due to different time consumptions.

4.5 Energy and cost considerations

4.5.1 Energy consumption in electrodialysis

Energy consumed to perform the separation is the key factor determining the overall efficiency of an ED process. The energy consumed by the process depends on the cell voltage that is affected by the factors such as solution resistance and current density. At a constant current density of 20.2 mA cm^{-2}, the energy consumed during the acid enrichment

process was calculated using Eq. (3.4) in kJ/l. Energy consumed by different membranes to enrich sulfuric acid concentration stage-wise is shown in Fig. 4.18.

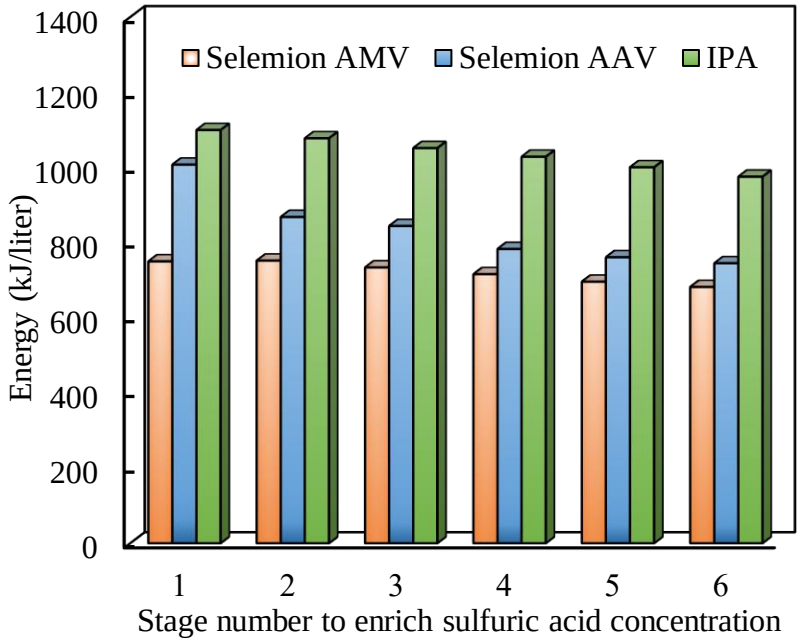


Fig. 4.18 Stage-wise energy consumed by different membranes to enrich sulfuric acid concentration

As shown in Fig. 4.18 energy estimated was found to be higher for concentration enrichment from 5 to 10 wt. % in stage 1. Gradually it was found to decrease with an increase in initial catholyte concentration. Since the decrement is not significant, it can be said that the energy required for each 5 wt. % concentration increment is almost constant. A similar trend was observed with all the AEMs used in the present study and energy requirements are found minimum with Selemion AMV membrane in order IPA>AAV>AMV as shown in Fig. 4.19. The overall performance of all the membranes observed during the acid enrichment process by electrodialysis is summarized in Table 4.5. Under present experimental conditions, the ability of the Selemion AMV membrane was observed to be higher compared to the other two membranes to enrich acidic solution. Voltage and time requirements and consequently energies consumed in all the stages during the process were also observed to be lower with the Selemion AMV membrane and in order AMV<AAV<IPA as shown in Table 4.5.

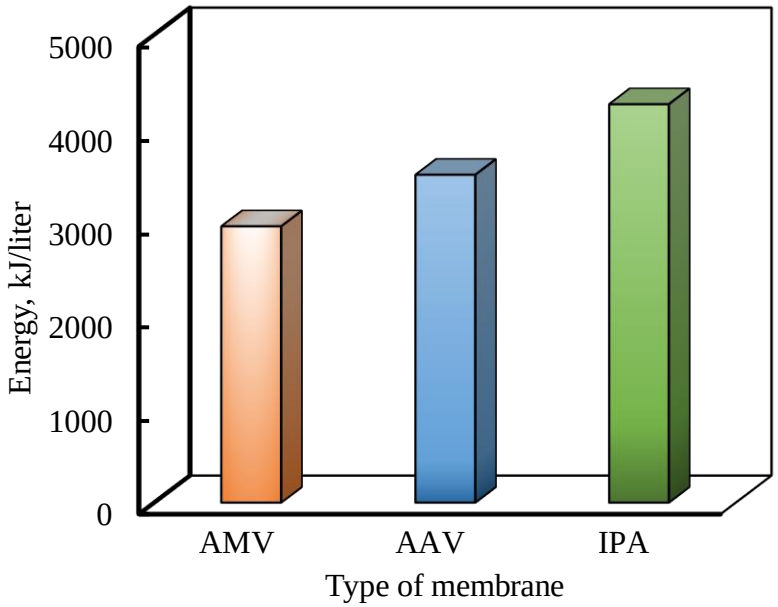


Fig. 4.19 Overall energy consumed by different membranes in stages 1 to 4 to enrich sulfuric acid concentration from 5 to 25 wt. %

Table 4.5 Overall membrane performance to enrich sulfuric acid concentration by cascaded ED process

Sr. No.	Characteristics	Membrane order
1	Ability to concentrate acid	AMV>AAV>IPA
2	Current efficiency	AMV>AAV>IPA
3	Voltage requirements	AAV≈AMV≈IPA
4	Time requirements	AMV<AAV<IPA
5	Energy requirements	AMV<AAV<IPA

The fluxes of sulfuric acid were observed largest for AMV membrane and smallest for IPA membrane. Current efficiencies were varied in the range of 50 to 60% initially and then decreased to lower values with all the three membranes and observed higher in order AMV>AAV>IPA. Major differences were observed in the performance of the Selemion AMV membrane with the other two AEMs, but IPA membrane performed equivalent to Selemion AAV, a low proton leakage membrane to enrich sulfuric acid concentration.

4.5.2 Electrodialysis-Evaporation integrated process

Cascaded ED system suggested in the present work was found capable of enriching sulfuric acid concentration stage-wise up to about 28 wt. % effectively with all the three membranes with almost the same applied voltage but different time and energy consumption. On the other hand, evaporation as the conventional process has been reported as a highly energy intensive process to enrich the solution concentration. In order to compare the performance of electrodialysis with evaporation on the basis of energy consumption, the thermal energy required for the same by EV was estimated using Eq. (3.5) given in materials and methods section 3.4.4. A close inspection of Fig. 4.20 indicates that a decreased trend in energy consumption was observed in stages 1 to 6 for both the processes. Thermal energy increased with a decrease in sulfuric acid concentration i. e. increase in water content. Evaporation needs a higher quantity of steam to evaporate a large quantity of water.

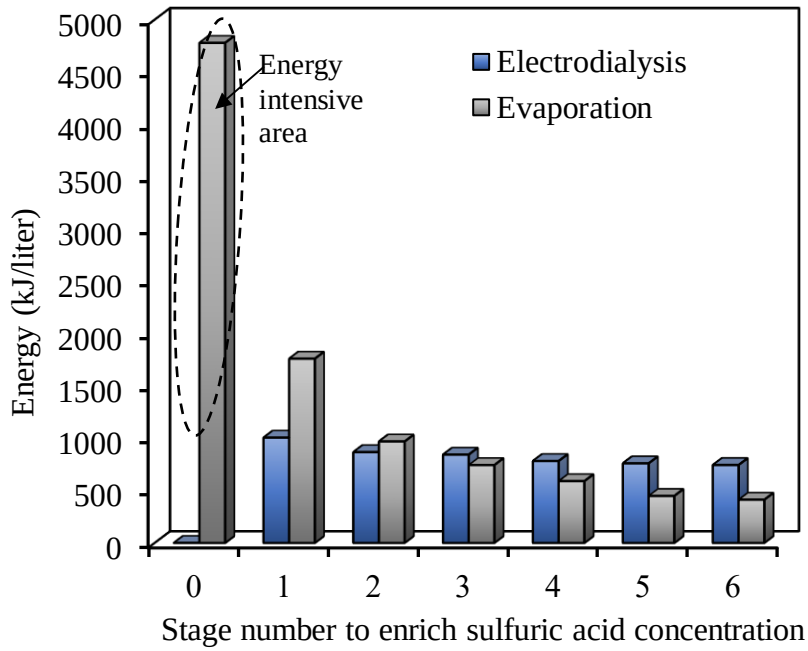


Fig. 4.20 Comparison in energies consumed by electrodialysis (Selemion AAV membrane) and evaporation

When calculated thermal energies, it was observed that when sulfuric acid is very dilute and has a concentration of about 1 wt. %, the energy required to enrich it up to 5 wt. % is too high for EV than ED as shown in Fig. 4.20. This area is represented by dotted lines in Fig. 4.20 as an energy intensive area that generates the possibilities of process integration of ED and EV. So, further experiments were performed to enrich sulfuric acid concentration using 4 stages, each stage increment by 1 wt. % with the Selemion AAV membrane.

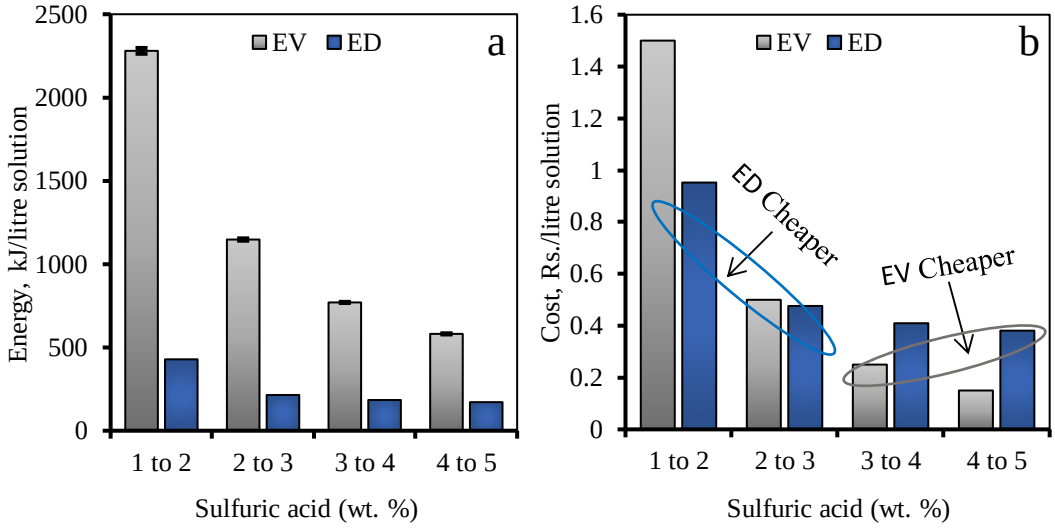


Fig. 4.21 Energy requirements (a) and estimated cost (b) to increase each 1 wt. % anolyte concentration

The electrical energy (kJ/l) required for the concentration enhancement of sulfuric acid by ED was estimated at a current density of 20.2 mA cm^{-2} using Eq. (3.4). For an increase in anolyte concentration from 1 to 2 wt. % the energy consumption was estimated to be 428 kJ/l. This corresponds to the transfer of 0.1 mole of sulfate ions from the feed solution (Masigol et al. 2012; Parsa et al. 2015). The thermal energy required for the same by EV was also estimated to be 2280 kJ/l using Eq. (3.5). It implies that ED has almost five-fold less energy expenditure than EV as shown in Fig. 4.21 (a). The same was also observed when concentration rose from 2 to 3 wt. %. This distinction between energies by ED and EV reduced as concentration increased.

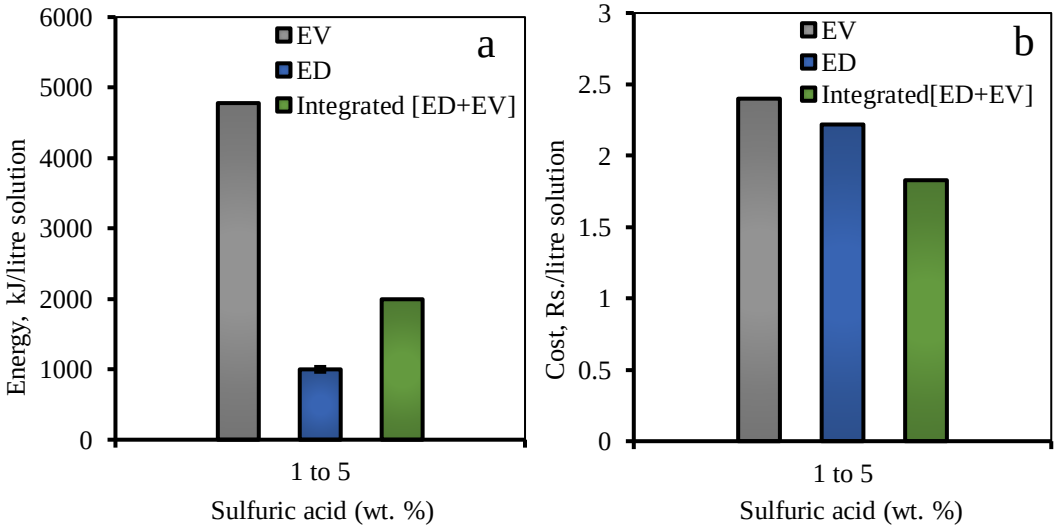


Fig. 4.22 Energy requirements (a) and estimated cost (b) to increase 1 to 5 wt. % anolyte concentration

Cumulative energy required to elevate anolyte concentration from 1 to 5 wt. % is represented graphically in Fig. 4.22 (a) and estimated to be only 998 kJ/l when compared with the 4800 kJ/l calculated by EV. This value turns out to be nearly 4.8 times lesser than EV. EV has been reported to be a tremendously expensive process because of the high amount of steam requirements (Kalogirou 2005; K et al. 2014), and other auxiliary equipment requirements such as preheater, condenser, SO_3 mist eliminator, etc.

In the present work, EV cost was approximated assuming 70% evaporator efficiency with 1.8 Rs. /kg saturated steam cost whereas for ED it was estimated in terms of kWh available at a rate of Rs. 8/unit according to the prevailing rate in India. Fig. 4.21 (b) represents that the cost required by ED is Rs. 0.9 /liter solution while the same by EV is Rs. 1.5/ liter solution to elevate concentration from 1 to 2 wt. %. The cost incurred in the ED was almost similar to that by EV for 2 to 3 wt. % increment but thereafter it exceeded that of EV for further acid strength enhancement. As shown in Fig. 4.21 (b), ED was found to be cheaper for stages 1 and 2 and then for stages 3 and 4 EV was observed to be cheaper providing an option for process integration. Membrane separation methods have shown great potential for replacing or complementing traditional technologies (Zhang et al. 2011; K et al. 2014; McGovern et al. 2014) and ED-EV integration was reported to be comparatively cheaper (Rockstraw et al. 1990). From these observations, it can be inferred that dilute sulfuric acid should be concentrated first using ED and then further concentration can be done by EV. The present work proposes the integration of ED and EV to reduce the load of either EV or ED alone for the concentration of acid. A proposed integrated process is shown in Fig. 4.23.

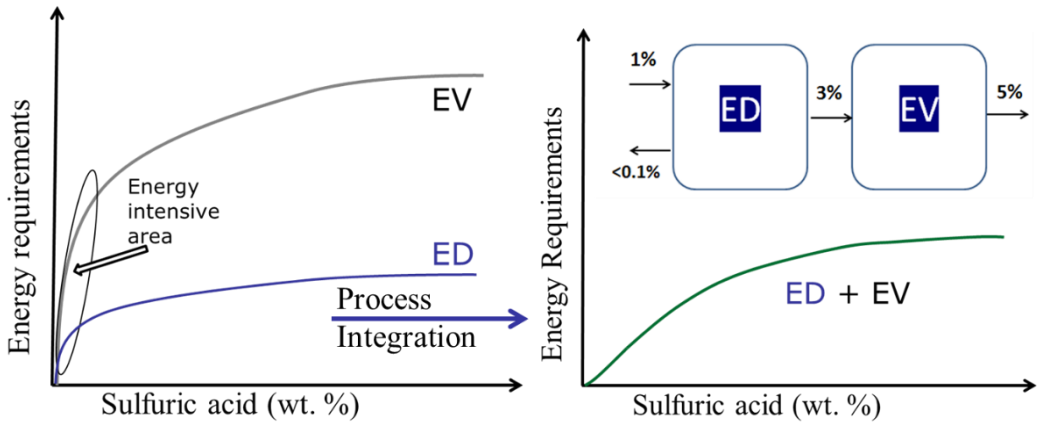


Fig. 4.23 Graphical representation of electrodialysis and evaporation integrated process

Fig. 4.22 represents the energy and cost requirements for the integrated process of ED and EV. When integration was carried out, the energy required to raise the sulfuric acid concentration from 1 to 5 wt. % was found to be 1994 kJ/liter and cost for the same was envisioned to be 1.83 Rs. /liter against 2.2 Rs. /liter for ED and 2.4 Rs. /liter for EV respectively. Estimation of cost requirement of an integrated process was approximated to be 21% and 24% cheaper than either ED or EV alone respectively. This concludes that the integrated process is more economical and may lead to profit when designed and operated on a large scale particularly for a dilute acidic solution. The cost of electrodialytic separation for concentration enhancement may even be lower if other alternate sources of electricity are available such as solar energy, wind energy or if sources are generated for supplying energy at a lower rate.

4.5.3 Approximate economic analysis

ED has been reported to be a technically viable process for effective acid recovery and producing a more concentrated product than in the feed, capable of delivering a cleaner acid product than evaporation (Baltazar et al. 1992). The use of ED to produce purified water and a concentrated solution from an aqueous stream up to some intermediate level has been evaluated as an economical pre-treatment process to the further purification step in an integrated electrodialysis-evaporation process for the treatment of aqueous process streams containing electrolytes (Rockstraw et al. 1990). ED was reported not only to be feasible and cheaper (Urano et al. 1984) for acidic wastewater regeneration, but also profitable in terms of acid recovery from wastewater (Kroupa et al. 2015). Energy consumption and investment costs e.g., membranes used, feed flow velocity and pressure drop of the feed solution in the cell affect the most the operation cost of ED (Baker 2004; Regel-Rosocka 2010). This particular section presents an economic evaluation on the separation of sulfuric acid from model spent liquor using the ED process operated batch-wise and for cascaded ED process operated in 6 stages.

Membrane properties and feed solution composition are the key components in determining the performance of ion-exchange membrane separation processes. In addition, equipment design parameters such as the stack (ED cell) construction, the feed flow velocities and mode of operation are the other parameters to be considered (Strathmann 2004). The ED cell is a key component in the ED unit. Various modes of operation such as batch type or continuous are possible. These parameters affect the investment as well as the operating cost of the

process. The voltage requirements depend upon the mode of operation used. The actual voltage drop and hence the energy consumed is higher in the batch process since the concentration of the ions in solutions adjacent to the membrane surfaces are significantly lower than the bulk solution values. The actual voltage drop in batch process may be larger than the same in the absence of polarization as in case with the ED processes with the circulation of solution (Baker 2004). In commercial ED plants, concentration polarization is controlled by circulating the solution through the stack at a high rate. The circulation pumps consume approximately one-quarter to one-half of the total power.

In the present work, the ED process is operated completely in a batch mode without the use of any moving element. No pump for solution circulation is used in the system studied and hence pumping energies required are zero that may reduce the operating cost of the system. Under these conditions, the operating cost of the process is due to the electrical energies consumed to move the ions from catholyte to anolyte. The energy consumed by the process depends on the cell voltage that in affected by factors such as solution concentration, current density (Baker 2004) and type of transported ions (Wiśniewski and Wiśniewska 1997). Since the cascaded ED process in the present study, is operated at a constant current density with a single type of ions, energy consumption depends upon the concentration of the solution. Time and voltage requirements to increase the sulfuric acid concentration are found different with different membranes and hence different power consumption and cost of the process. It has also been reported in the literature that the cost of electrodes may significantly affect the costing of the system. The use of platinum coated titanium in ED system for in-home water desalination contributed more than 90% of the component cost (Nayar et al. 2015). Though effective, the use of costly electrodes may not be economically viable at large scale due to their significant cost contribution. Considering this point additionally, graphite has been used in the present study. Overall, the present work is aimed in making economical ED system by using low-cost electrodes, an acrylic ED module and an IPA anion exchange membrane with no moving elements present in the system.

The fixed cost for a single batch ED process includes the cost of ED module, anion exchange membrane, electrodes, stirrer and miscellaneous cost. The fixed cost for the construction of one laboratory-scale ED module was estimated to be 7400/- Rs. as represented in Table 4.6.

Table 4.6 Cost of various components of ED process used in the present study.

Sr. No.	Component	Approximate cost (Rs.)
1	Module (acrylic) including making charges (lab scale, Capacity 550 ml)	3500/-
2	Electrode (Graphite)	600/-
3	Stirrer	300/-
4	Membrane (IPA)	2000/-
5	Miscellaneous	1000/-
	Total	7400/-

In the present work, the preliminary cost analysis was carried out on the basis of power consumption (P_w) which was calculated using Eq. (4.1).

$$P_w = \frac{V\ I\ watt}{V_l\ ml}\left(\frac{1000\ ml}{1000\ watt}\right) \quad kW/l \qquad (4.1)$$

The power requirements calculated in kW/l is then multiplied by the actual time consumed and unit cost of power that were considered to be Rs. 8.0 per 1 kWh in Gujarat at the prevailing time. As discussed in sections 4.5.2, the cost of treatment per liter of anolyte solution was about Rs. 2.4 and Rs. 2.2 by evaporation and electrodialysis respectively. When carried out the integration of ED and EV, the cost reduced to Rs. 1.83/liter. It can be concluded from the results of the cost analysis that the electrodialysis is cost-effective membrane separation process and cheap compared to evaporation for concentration enhancement of dilute sulfuric acid from 1 to 5 wt. %. Cascaded ED process took almost 67 hours to concentrate acid from 5 to 25 wt. % in stages 1 to 4 for which operating cost was estimated to be approximately 9.5 Rs. /liter. The cost estimated for each stage in the cascaded ED process was approximately 2.5 Rs. /liter per stage. Graphite electrodes had to be replaced after complete 1 cycle of cascaded ED process and after about 80 hours of continuous operation. Treatment of a limited quantity of dilute spent acidic liquor by ED is technically feasible and economically viable option. Sulfuric acid concentration enhancement by cascaded electrodialysis process is expensive. ED can be a more cost-effective option if other cheaper means of electricity generation are available (wind energy, solar energy). In addition to this, there might be some error in the cost consideration because we have not considered here the cost of pretreatment of the spent acidic solution and other associated cost and hence

the actual cost of treatment might be different from the estimated cost. Scale up of the studied process is possible with the membrane available in its largest size. On the basis of the maximum size of the IPA membrane (80 cm × 40 cm) available, the ED module can be scaled up (80 cm × 40 cm × 4.5 cm) to treat the spent liquor of 20 litre in a single module. Costing of the scaled-up process requires the exact knowledge of the relations between process variables and performance parameters with large size membranes and electrodes and it is quite difficult task in the absence of the experimental data.

4.6 Application of Nernst-Planck equation

Molar flux across the ion exchange membrane is an important index of electrodialytic separation. Although the Selemion AAV membrane used in the present study was a low proton leakage anion exchange membrane, minor leakage of the proton was unavoidable. Ideally, at the catholyte-membrane interface, the bisulfate ion HSO_4^- dissociates into sulfate ion which crosses the membrane and a proton remain in the cathode compartment. The present process being a batch one, catholyte and anolyte concentration, along with molar flux varied with passage of time.

In the electrodialysis process the total flux is the contribution of three different types of fluxes represented by Eq. (4.2). Assuming unidirectional flow,

1 Flux due to motion/velocity of fluids { J_u }

2 Flux due to natural diffusion based on concentration gradient { J_D }

3 Flux due to migration of ions based on membrane electric potential based on concentration gradient { $J_{\emptyset}$ }

4 Flux due to applied electric potential { $J_{\emptyset a}$ }

$$J_{total} = J_u + J_D + J_\theta + J_{\theta a} \qquad (4.2)$$

In the present system, the flux of sulfate ions is only studied and all the terminologies are used for the molar flux of sulfate ions only. In the given process, the velocity component is zero; i. e. flux contribution due to the motion of the fluid is zero, represented by Eq. (4.3)

$$J_u = 0 \qquad (4.3)$$

Based on velocity component zero, Eq. (4.2) reduces to,

$$J_{total} = J_D + J_\theta + J_{\theta a} \qquad (4.4)$$

The magnitude of various fluxes (J_D, J_θ and $J_{\theta a} = J_{p1}$) as estimated following equations in the Materials and Methods section 3.4 are presented in Table 4.7. Fluxes were calculated both in the presence and in absence of current ($I_c = 0$) as the membrane potential was generated on the bases of catholyte and anolyte concentration gradient. When no current was supplied to the system, potential developed across the membrane was calculated and shown as V_m. As Nernst membrane potential V_m is a function of concentration ratio, all V_m values are zero when anolyte and catholyte initial concentrations are same. All flux values were calculated based on the average values of V_m generated naturally during each 30 min period of total experimental run as shown in Table 4.7. Data indicate that the contribution of diffusive flux (J_D), as well as membrane potential based flux ($J_Ø$), was very less as against practical flux either in presence of applied electric current or even in its absence. It is evident from Eq. (4.5), that, when $J_u = 0$, the contribution of J_D and $J_Ø$ in the total flux is negligible. Thus, the total flux (J_{total}) is mainly the contribution of flux ($J_{Øa}$) due to the applied electric field only. Therefore, under the influence of an electric field, Eq. (4.4) can be approximated as

$$J_{total} = J_{\theta a} \qquad (4.5)$$

Practical flux values were found out to be much larger than all other flux values. Experimental flux (J_p) is influenced by the applied current, whereas J_D and $J_Ø$ values have a major influence of concentration gradient and membrane potential generated based on initial catholyte and anolyte concentration difference respectively. Flux could be positive or negative depending on ionic movements from catholyte to anolyte or the vice versa based on V_m generated as well as a concentration gradient. In the present study, all the practical flux values were positive as the ionic movement was from catholyte to anolyte, implying that there was a definite effect of applied current on flux, as a result of which, ions could move against the concentration gradient. Even it was observed that the flux had increased with applied current as well as initial concentration, with the minor effect of anolyte concentration. This shows that when applied voltage and current values are very high for such type of dilute solution system, flux is influenced mainly by initial concentration, applied voltage and current only. However, the influence of anolyte concentration was observed to be marginal barring a few special cases where V_m was zero.

It was observed that the total flux was not only the contribution of diffusive and electrochemical flux, but there was a definite effect of applied current density on it as well. According to the Nernst-Planck equation, when there is no concentration difference, no membrane potential gradient is generated: V_m=0. Hence, net fluxes are also considered zero. As applied current density was increased by applying external driving force i.e. applied voltage, there was an increase in molar flux for the same concentration values of anolyte and catholyte. Therefore, the effect of applied current density must be taken into account.

Table 4.7 Various fluxes through an anion exchange membrane under electrodialysis process

Exp. Run. No.	I_c (mA/cm^2)	C_{co} (wt. %)	C_{ao} (wt. %)	C_{at} (wt. %)	V_m (mV)	$J_D \times 10^8$ (mol/cm^2 s) [in absence of current]	$J_\theta \times 10^8$ (mol/cm^2 s) [in absence of current]	$J_p \times 10^8$ (mol/cm^2 s)	$J_{m1} \times 10^8$ (mol/cm^2 s)	SSD
1	30.3	1.13	1.13	2.26	0.000	0.000	0.000	32.585	--	--
2	30.3	2.26	1.13	2.89	-8.899	0.525	0.008	8.459	9.223	0.587
3	30.3	4.45	1.17	3.36	-17.152	1.523	0.031	10.525	8.845	0.460
4	30.3	3.93	1.11	3.20	-15.556	1.281	0.025	9.543	9.727	0.033
5	30.3	2.26	3.39	4.61	5.206	-0.525	-0.005	5.863	--	--
6	20.2	4.43	1.08	2.57	-18.122	1.555	0.033	7.161	6.983	0.103
7	20.2	4.52	5.88	7.40	3.377	-0.631	-0.006	7.305	--	--
8	20.2	3.91	1.11	2.32	-16.167	1.300	0.026	6.810	6.856	0.002
9	20.2	2.26	3.36	4.65	5.092	-0.511	-0.005	5.163	--	--
10	20.2	2.26	3.41	4.68	5.281	-0.534	-0.005	5.086	--	--
11	20.2	2.35	1.02	2.40	-10.716	0.617	0.010	6.632	6.384	0.061
12	20.2	1.15	1.15	2.29	0.000	0.000	0.000	15.990	--	--
13	10.1	2.26	0.97	1.67	-10.860	0.599	0.010	3.364	3.297	0.004
14	10.1	1.13	1.13	2.29	0.000	0.000	0.000	2.739	--	--
15	10.1	4.43	1.11	1.86	-17.770	1.541	0.032	3.605	3.915	0.097
16	10.1	3.93	1.92	2.82	-9.197	0.933	0.015	3.806	0.233	0.001
17	4.0	2.28	1.11	1.52	-9.242	0.543	0.009	1.642	1.301	0.116
18	4.0	3.73	3.34	3.77	-1.418	0.181	0.002	1.722	1.755	0.001
19	4.0	4.43	1.11	1.40	-17.770	1.541	0.032	1.760	1.5174	0.059
20	2.1	3.07	1.11	1.34	-13.061	0.910	0.016	0.921	0.891	0.001
21	2.1	2.28	1.11	1.33	-9.242	0.543	0.009	0.901	0.616	0.081
22	2.0	4.31	1.11	1.35	-17.417	1.486	0.030	0.901	0.9010	0.000

Considering this effect, Eq. (4.7) was proposed to calculate molar flux. All the constants and coefficients of Eq. (4.7) were calculated using SOLVER analysis tool in excel.

$$J_{m1} = f(I_c, C_{co}) \qquad (4.6)$$

$$J_{m1} = A + aI_c^b + cC_{co}^d \qquad (4.7)$$

Table 4.7 also includes the flux values calculated based on model Eq. (4.7) developed. The proposed equation is applicable to the system where catholyte to anolyte initial concentration difference is positive and when $C_{co} \neq C_{ao}$. Diffusion flux was assumed to be negligible in flux calculation as their effect was very less in the presence of higher applied currents.

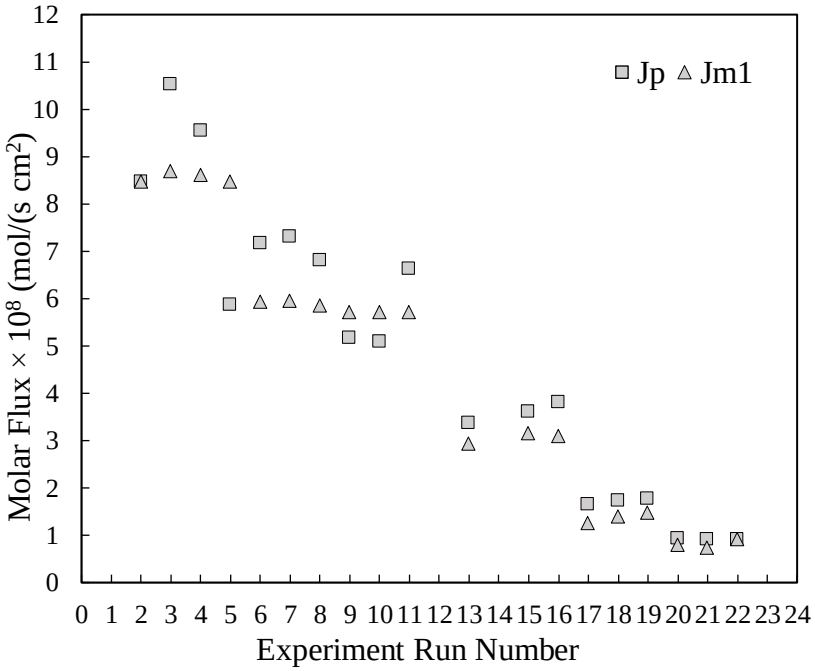


Fig. 4.24 Variation between experimental molar flux and flux calculated using model equation (J_{m1}).

The values of the constants and the coefficients of Eq. (4.7) were calculated for given conditions. The value of constant A was found to be 0.064, while the values of other coefficients such as a, b, c and d were calculated to be 0.285, 0.988, 0.009 and 2.397 respectively. Model-based calculated flux values were compared with practical flux and they were matching with minor deviations as shown in Fig. 4.24. Better results are obtained at lower values of current densities. Though the experiments were performed in particular range of process variables, they were performed at different set of conditions that may not generate any trendline and hence are shown by point in Fig. 4.24, 4.25 and 4.26.

Eq. (4.7) relates molar flux with the current density and initial catholyte concentration and it was used for the experimental data obtained from the batch ED analysis. Still, an extensive error between experimental and modeling result data was noted. Baltazar et al. (1992) reported that there is a linear relationship between product acid concentration and current density. They performed experiments under conditions of constant current density and variable voltage to recover sulfuric acid (Baltazar et al. 1992). In the present study, the cascaded ED process was operated at constant current densities, variable voltage and different acid concentrations. It has also been reported that the anolyte concentration affects the performance of the process as described in detail in section 4.3.4 and 4.4.1.2.

Therefore, the next approach was to develop an equation relating molar flux with initial catholyte concentration, initial anolyte concentration and current density with the additional experimental results generated from the cascaded ED process. Eq. (4.8) represents the flux as a function of initial catholyte and anolyte concentration, and current density.

$$J_{m2} = f(I_c, C_{co}, C_{ao}) \qquad (4.8)$$

Table 4.8 Experimental and predicted molar flux through an anion exchange membrane under electrodialysis process.

Exp. Run No.	I_c (mA/cm^2)	C_{co} (wt. %)	C_{ao} (wt. %)	J_p	J_{m2}	SSD
1	30.30	2.26	1.13	8.46	9.17	0.5141
2	30.30	3.93	1.10	9.54	9.69	0.0233
3	30.30	4.45	1.17	10.52	9.86	0.4271
4	20.20	2.35	1.02	6.63	6.03	0.3486
5	20.20	3.91	1.01	6.81	6.53	0.0764
6	20.20	4.43	1.08	7.16	6.70	0.2048
7	20.20	5.16	5.15	5.22	5.37	0.0255
8	20.20	10.30	10.29	5.08	5.37	0.0868
9	20.20	15.20	15.19	5.08	5.37	0.0868
10	20.20	20.60	20.58	5.08	5.37	0.0891
11	10.10	2.26	0.97	3.36	3.10	0.0651
12	10.10	3.93	1.92	3.60	3.23	0.1365
13	10.10	4.43	1.11	3.60	3.74	0.0216
14	4.02	2.28	1.11	1.64	1.46	0.0294
15	4.02	3.73	1.11	1.72	1.89	0.0307
16	4.02	4.30	1.11	1.76	2.11	0.1259
17	2.12	2.28	1.11	0.90	1.03	0.0172
18	2.12	3.07	1.11	0.92	1.21	0.0894
19	2.04	4.31	1.11	0.90	1.66	0.5835

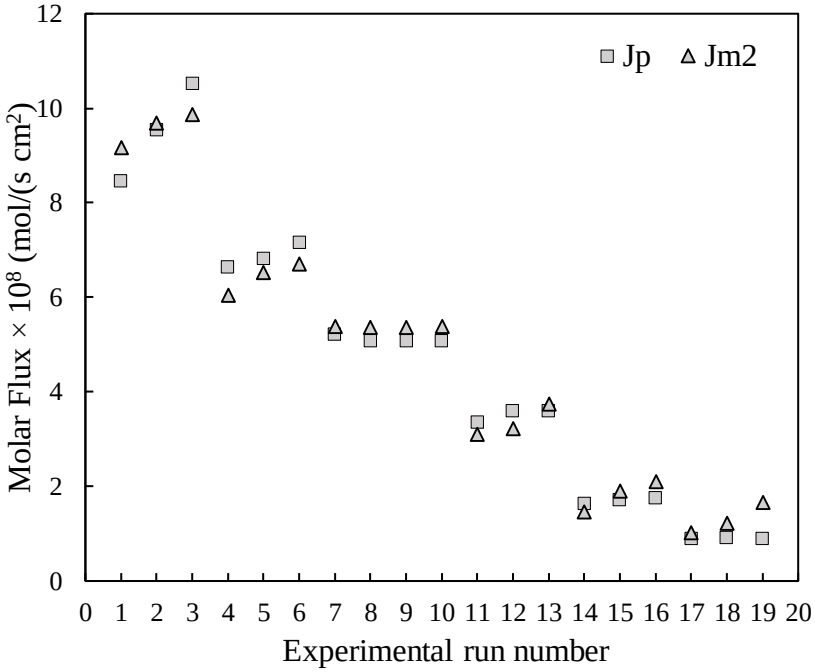


Fig. 4.25 Variation between experimental molar flux and flux calculated using model equation (J_{m2}).

Better results were obtained using the second approach as shown in Fig. 4.25. The predicted values of molar flux are in good agreement with the practical molar flux and errors are minimum compared to the first approach as shown in Table 4.8. Once estimated the molar flux based on an equation developed, it helps to calculate the approximate time required for given separation at selected values of acid concentration and current density. Additionally, an attempt was also made to relate the same variables with the voltage requirements and values predicted from developed Eq. (4.9) were compared with the experimental values.

$$V_m = f(I_c, C_{co}, C_{ao}) \qquad (4.9)$$

A good match was observed between experimental (V_p) and predicated (V_m) values of applied voltage as shown in Table 4.9 and Fig. 4.26. Using given values of current density, catholyte and anolyte initial concentrations, the developed equation helps to calculate voltage requirements. Eq. (4.8) and (4.9) predicts the values of molar flux and voltage requirements respectively, that ultimately helps to calculate time requirements and power consumption for the desired separation. All the equations were developed using MATLAB programming (MATLAB R2018a, version 2018 in a symbolic mathematics tool box) and values of constants and coefficients are represented in Appendices.

Table 4.9 Actual and predicted applied voltage requirements under electrodialysis process.

Exp. Run No	I_c (mA/cm^2)	C_{co} (wt. %)	C_{ao} (wt. %)	V_p	V_m	SSD
1	30.30	2.26	1.13	6.00	5.56	0.1928
2	30.30	3.93	1.10	5.00	5.01	0.0003
3	20.20	2.35	1.02	5.00	4.86	0.0189
4	20.20	3.91	1.01	4.50	4.34	0.0229
5	20.20	5.16	5.15	4.40	4.47	0.0063
6	20.20	4.95	4.90	4.40	4.49	0.0100
7	30.30	4.45	1.17	4.30	4.86	0.3155
8	20.20	4.43	1.08	4.30	4.19	0.0116
9	20.20	10.30	10.29	4.30	4.16	0.0175
11	20.20	20.60	20.58	4.00	3.91	0.0074
10	20.20	15.20	15.19	4.10	4.01	0.0066
12	20.20	25.50	25.48	3.80	3.84	0.0021
13	20.20	29.45	29.40	3.70	3.80	0.0104
14	10.10	2.26	0.97	3.60	4.04	0.1955
15	10.10	3.93	1.92	3.50	3.63	0.0190
16	10.10	4.43	1.11	3.50	3.34	0.0226
17	4.02	2.28	1.11	3.30	3.29	0.0000
18	4.02	3.73	1.11	3.00	2.82	0.0294
19	2.12	2.28	1.11	2.90	2.95	0.0030
20	4.02	4.30	1.11	2.80	2.64	0.0238
21	2.12	3.07	1.11	2.60	2.69	0.0085
22	2.04	4.31	1.11	2.30	2.28	0.0004

The proposed empirical equation of applied voltage used in the present work was validated by estimating the voltage values using model equation and comparing it with the actual value of voltage required for particular case given in the research paper. The predicted and actual values of applied voltages are given in Table given below. Predicted voltage values match closely with the actual voltage values. The voltage required was in the range from 4.8-5.5 V at 32.50 mA/cm^2 current density and 5 wt. % of initial catholyte and anolyte concentration (Cifuentes et al. 2002) and the same was estimated to be 5.32 V from model equation. Similarly estimated value of voltage was 4.55 V from model equation and required voltage at 8.33 mA/cm^2 current density and 10 wt. % initial catholyte and anolyte concentration was 5 V (Zouhri 2013).

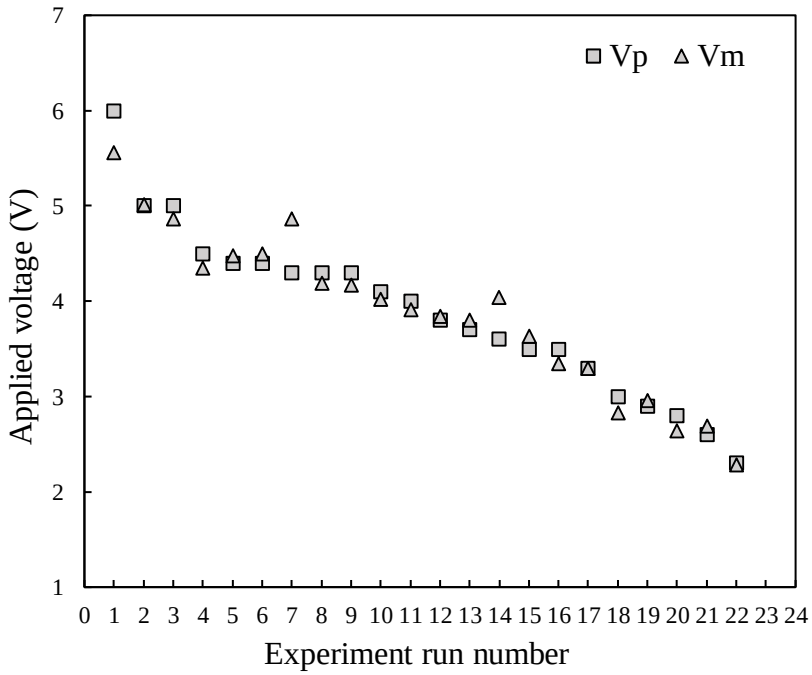


Fig. 4.26 Variation between experimental values of applied voltage and voltage calculated using model equation

4.7 Membrane characterization

4.7.1 FTIR analysis

Interpretation of the FTIR spectrum can be of great help in determining the presence of functional groups in the ion-exchange membrane specimen (Le 2013). A close inspection of the FTIR spectra of the pristine and used membranes as presented in Fig. 4.27 indicates the presence of a number of sharp, medium and broad peaks in the entire range of 400-4000 cm^{-1}. Principal band assignments of FTIR spectra over wave number 4000-400 cm^{-1} are presented in Table 4.10.

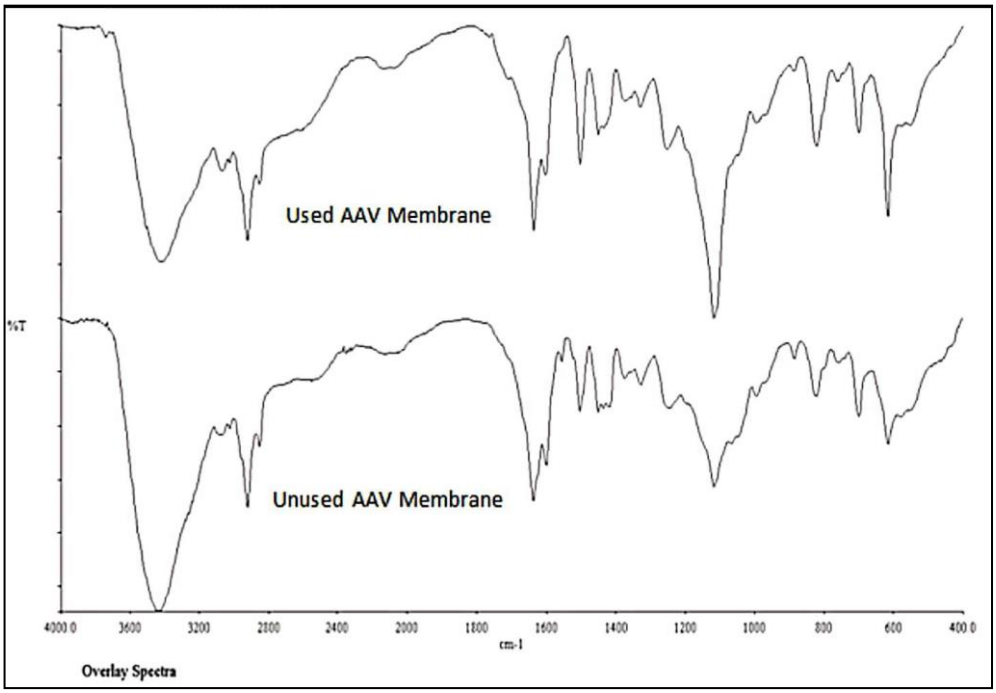


Fig. 4.27 FTIR spectra of Selemion AAV membrane used in the present study

Table 4.10 Principal band assignments of FTIR spectra over wave number 4000-400 cm^{-1} for Selemion AAV membrane.

Wave numbers (cm^{-1})	Band assignment
3025.78; 3071.83	C = C stretching vibration
1452.62; 1436.01	Skeletal in plane stretching vibration C = C
2925 –2854	Stretching vibration of $–CH_2$ group
1328.76; 968.07	Bending vibration of CH_3 group in aliphatic chain
3441	Stretching vibration of O – H
1117.48	Stretching vibration of C – N vibration of quaternary ammonium group.
1068	C –H bending vibration

The AAV ion exchange membrane is fabricated by copolymerization of styrene, chloromethyl styrene and divinyl-benzene followed by subsequent incorporation of quaternary ammonium group as an ion-exchange functional group. The peaks at 3025.78 cm^{-1} and 3071.83 cm^{-1} are associated with the stretching vibration of C = C groups of aromatic hydrocarbons which corroborates the grafting of styrene in the anion exchange membrane. Two distinctly characteristic broad absorption band one at 3441 cm^{-1} and the other at 1117.48 cm^{-1} represent the stretching vibration of O – H of water molecules and C–N bond of the quaternary ammonium group respectively. The observations indicate that

quaternary ammonium group has been adequately incorporated into the AAV anion exchange membrane. A couple of bands at 701.45 and 761.12 cm^{-1} can be ascribed to the aromatic C − H deformation of mono-substituted benzene ring of grafted polystyrene of the AAV membrane. The band at 825 cm^{-1} is due to di-substituted benzene ring of divinyl benzene cross link of the membrane. It was observed from the spectral analysis that quaternization of the IR bands of aromatic ring C = C and aromatic ring backbone –CH– bending vibration were shifted to a relatively lower frequency. Broadening and shifting of certain bands might have occurred as a result of quaternization and copolymerization reaction and introduction of ion exchange groups thereby making them inadequate for precise quantitative determinations. Additionally, a lower wave number represents the increase in the bond length, and this might be a result of the electrostatic interaction between the functional groups present in the anion exchange membrane.

Table 4.11 Principal band assignments of FTIR spectra over wave number 4000-400 cm^{-1} for Selemion AMV membrane.

Wave numbers (cm^{-1})	Band assignment
3422.80	Stretching vibration of O – H
3021.81	C-H Stretching (Alkene)
2959.01;2923.63; 2853.48	C-H Stretching (Alkane)
1631.50; 1615.83	C- C Multiple Bond Stretching (Alkene)
1511.62	N-H Bending Vibrations (Secondary Amides)
1486.92; 1477.98	C-H Bending (Alkane) $–CH_2-$
1427.84;1381.88	Aromatic compound C=C stretching
1243.65; 1198.97	C-O carboxylic acid
1099.84	O-H Bending and C-O stretching vibrations (Primary alcohols)
1021.20	Stretching Ether C-O

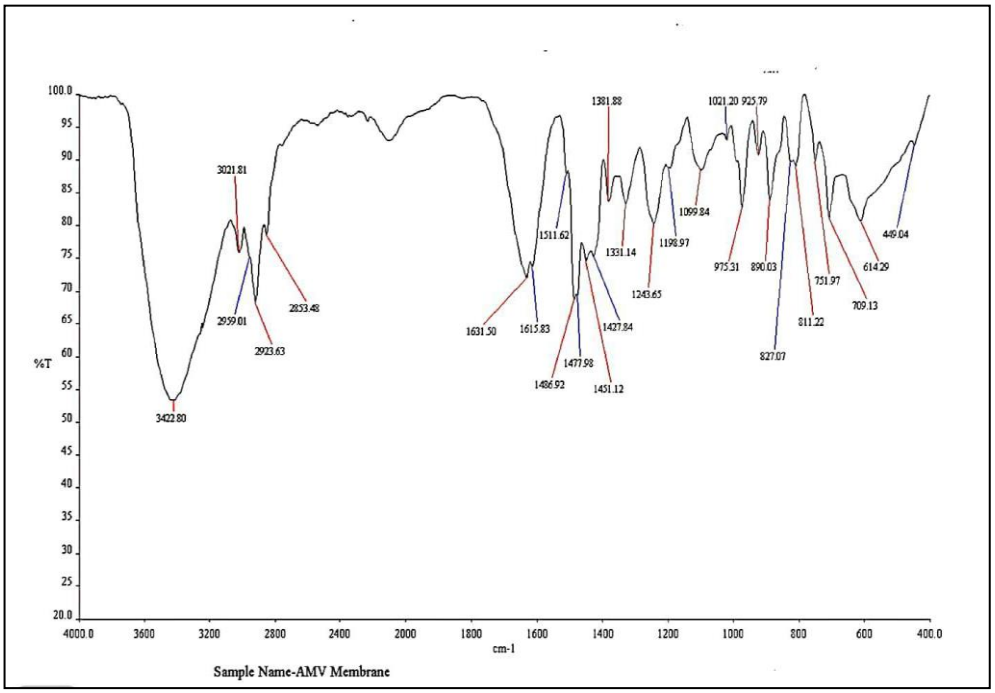


Fig. 4.28 FTIR spectra of Selemion AMV membrane used in present study

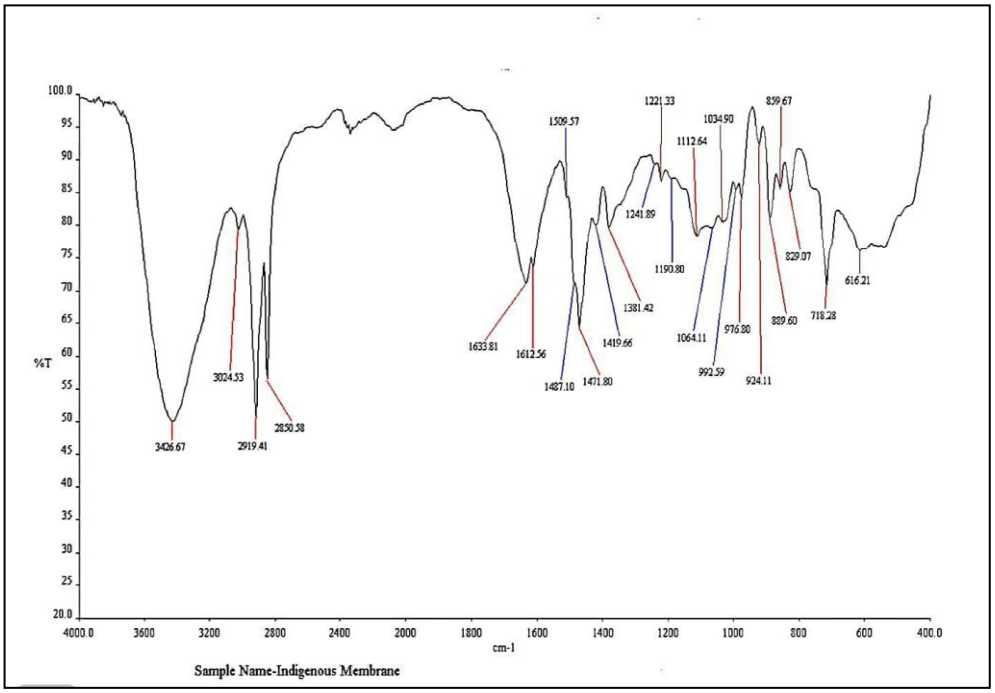


Fig. 4.29 FTIR spectra of IPA membrane used in present study

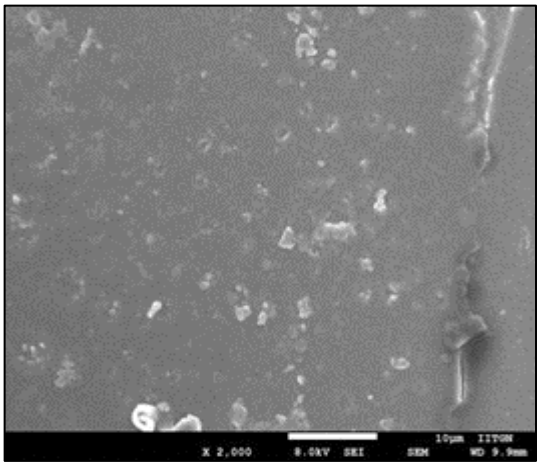
Table 4.12 Principal band assignments of FTIR spectra over wave number 4000-400 cm^{-1} for IPA membrane.

Wave numbers (cm^{-1})	Band assignment
3426.67	O-H stretching Vibrations (Alcohol & phenols)
3024.53	C-H stretching (alkene) vinyl
2919.41; 2850.58	C-H stretching (alkane)
1633.81; 1612.56	N-H Amines Primary
1509.57	C=C stretching Aromatic
1487.10	N-O asymmetric stretching vibrations presence of nitro compound
1471.80	C-H Stretching (Alkenes)
1419.66	C=O Carboxylic acid
1381.42	C-H deformation
1241.89; 1221.33	C-N Aromatic Amine
1190.80	$-CH_2X$ stretching vibrations presence of alkyl halide
1112.64; 1064.11	C-O Primary, Secondary alcohol
1034.90	C-O ether

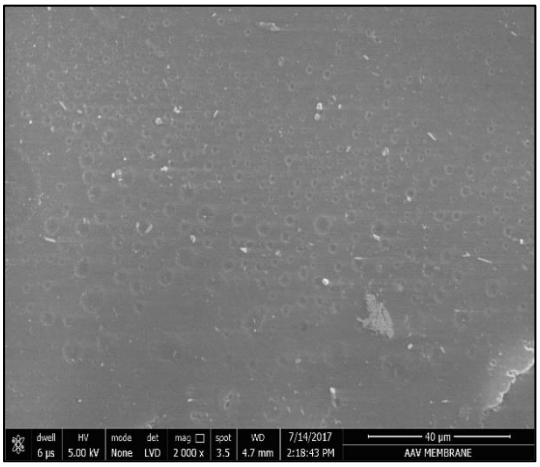
Band assignments of FTIR spectra over wave number 4000-400 cm^{-1} are presented in Table 4.11 and 4.12. The Selemion AMV ion exchange membrane is fabricated by copolymerization of styrene, and butadiene and Indigenous IPA ion exchange membrane is fabricated by copolymerization of styrene and divinyl benzene. The peaks at 3025.78 cm^{-1} and 3071.83 cm^{-1} are associated with the aromatic benzene system (C-H str.) which belongs to styrene. Strong absorption of C=C str appears around 1600 cm^{-1}. Aliphatic system (C-H str) appears below 3000 cm^{-1}, 2800-2980 cm^{-1}. Alkane system C-H bending shows broad peaks 1480-1450 cm^{-1}. Distinctly characteristic broad absorption band (O-H str) around 3400 cm^{-1} and the (C-O str) at 1100 cm^{-1}. In finger print zone, it is difficult to assign bands due to overlapping and broadening of multiple bands. However, these bending absorptions are according to presence of aromatic and aliphatic system.

4.7.2 SEM analysis

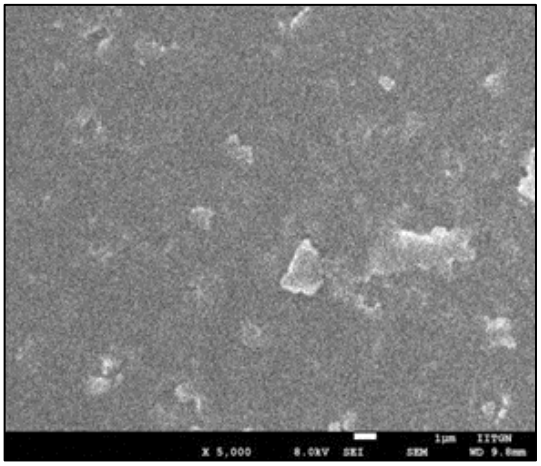
The surface topography of the pristine and used AAV membrane from the present study of electrodialysis of dilute sulfuric acid was investigated following scanning electron microscopy (SEM). Fig. 4.30 represents the SEM micrograms of the membrane specimens at different magnifications.



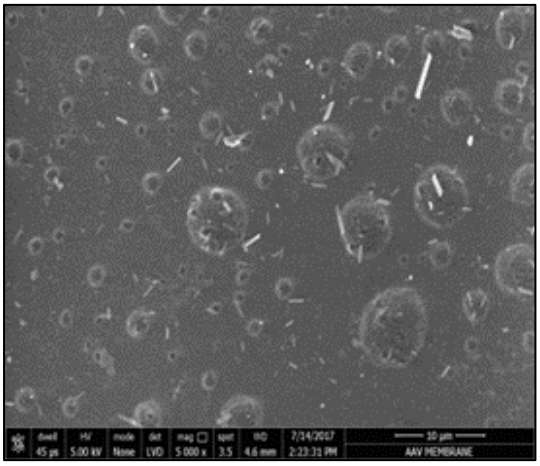
Pristine membrane (Top surface, Magnification 2000 ×)



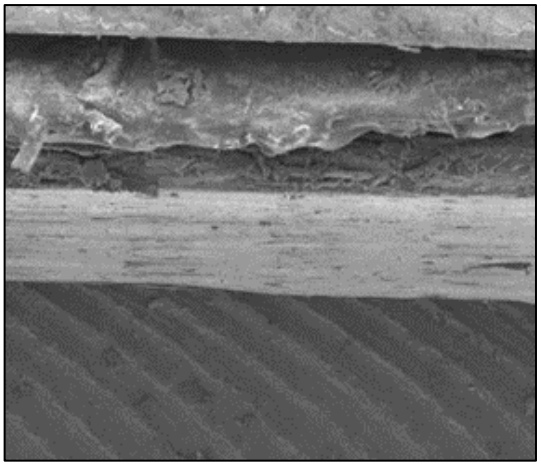
Used membrane (Top surface, Magnification 2000 ×)



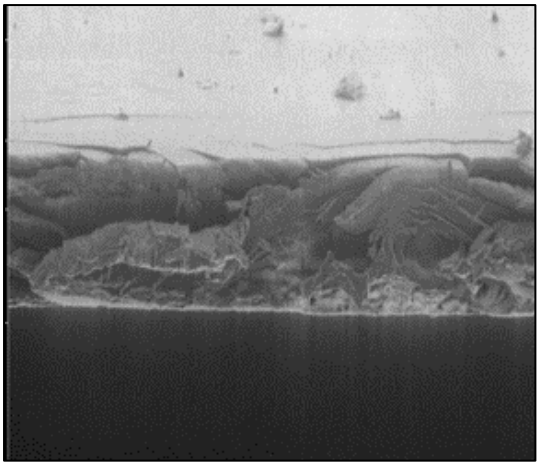
Pristine membrane (Top surface, Magnification 5000 ×)



Used membrane (Top surface, Magnification 5000×)



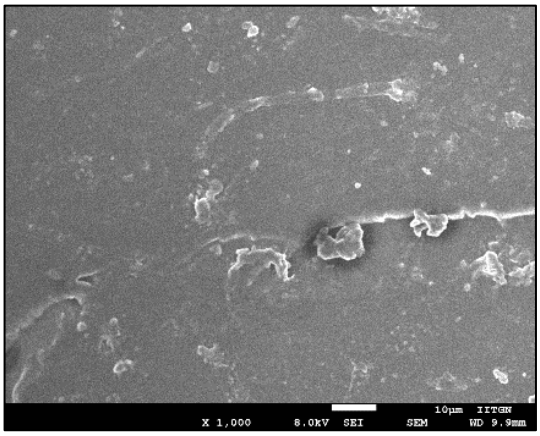
Pristine membrane (Cross section)



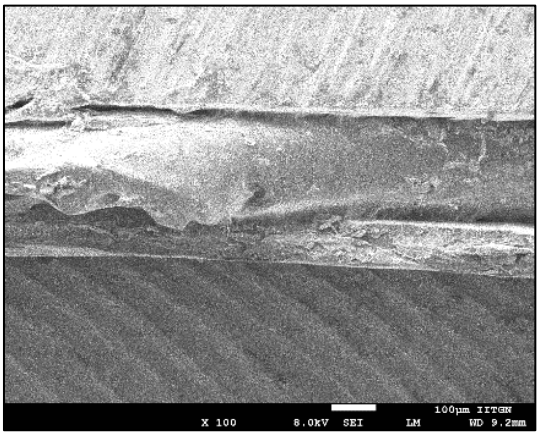
Used membrane (Cross section)

Fig. 4.30 SEM micrographs of cross section and top surface of AAV membrane under different magnifications used in present study.

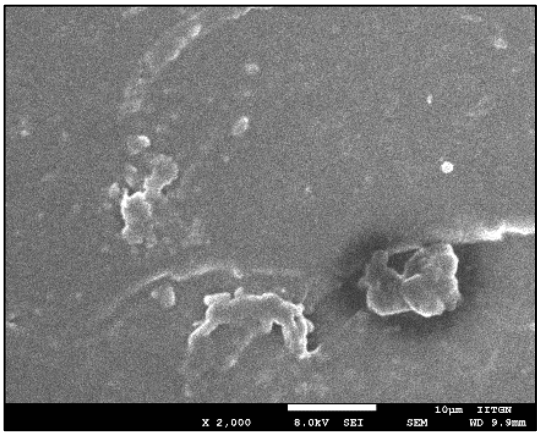
The microgram of the pristine membrane suggests the appearance of a compact and smooth surface without much visible pores. The absence of any surface irregularities or cracks signifies homogeneity and compactness of the membrane. This probably confirms good compatibility between ion exchange functional group and the polymer matrix. The cross-section of the anion exchange membranes was also found out to be densely porous and compact, facilitating the electrodialysis process. It is assumed that the pores generate easy flow channels for the counter-ion transportation. A few white smudges on the top surface of the pristine membrane were probably due to the improper adjustment of the scan. The scan pattern might have become nonlinear, particularly at the edges of the image at high magnifications. On the other hand, a perusal of the top surface of the used membrane reveals that the pores were shrouded with a slim layer, as a result of ionic transport experienced by the AAV membrane. With higher magnification (5000) the clusters were also visible almost on the entire surface. Moreover, there was a slight difference in pore morphology in the regions close to the outer surface as compared to the rest of the membrane. The appearance of pleat and cluster on the edges of the outer surface of the used membranes could be due to dehydration and shrinkage of the polymer. Taken together the observations from the SEM analysis suggest that the skin layer of the pristine membranes had a homogeneous morphology suitable for the transport of ions during the electrodialysis process. The AAV membrane was able to deliver favorable ionic conducting performance with improved electrochemical characteristics. However, the impact on the polarization phenomenon could not be ascertained under the present experimental setup.



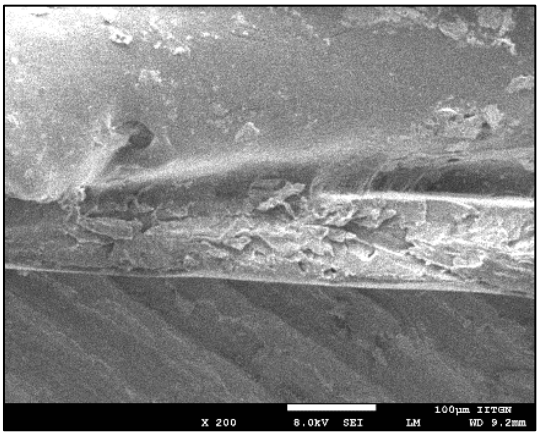
Top surface, Magnification 1000×



Cross section, Magnification 100×



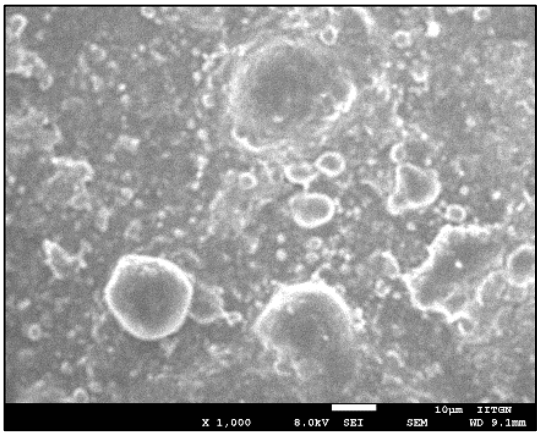
Top surface, Magnification 2000×



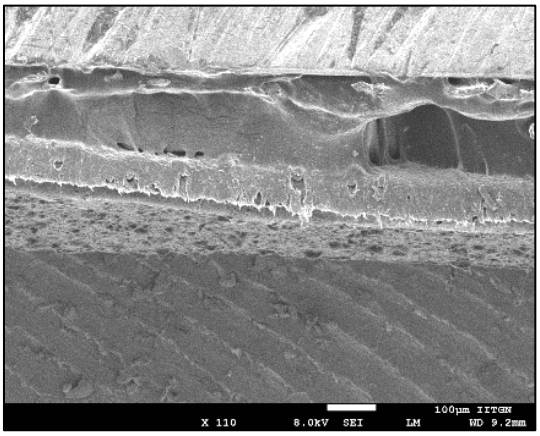
Cross section, Magnification 200×

Fig. 4.31 SEM micrographs of cross section and top surface of AMV membrane under different magnifications used in present study.

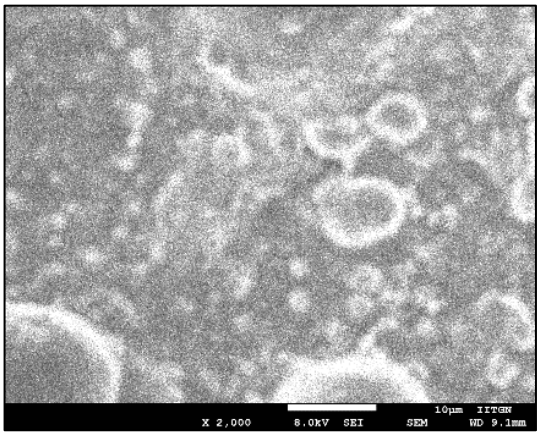
The SEM images of the surfaces, as well as the cross-sections of the pristine Selemion AMV membrane at different scales, are shown in Fig. 4.31. The images of the Selemion AMV membrane are similar to those published in the literature (Le et al. 2009). The surface topography of the Selemion AMV membrane appears smooth, dense and homogenous without much visibility of pores or fissures. The cross-section of the anion exchange membranes was also found out to be densely porous and compact.



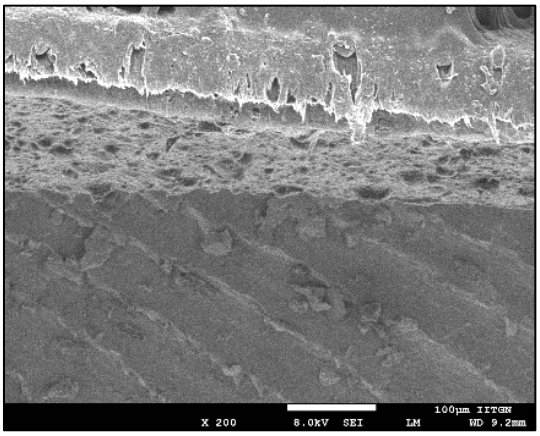
Top surface, Magnification 1000×



Cross section, Magnification 100×



Top surface, Magnification 2000×



Cross section, Magnification 200×

Fig. 4.32 SEM micrographs of cross section and top surface of IPA membrane under different magnifications used in present study.

Fig. 4.32 represents the SEM images of the surfaces as well as the cross-sections of the pristine IPA membrane at different magnifications. There are no visible cracks or irregularities on the surface signifies the homogeneity and compactness of the membrane which clearly confirms the good compatibility between ion-exchange functional group polymer matrix.

CHAPTER 5

Conclusions and Future Scope

5.1 Conclusions

Electrodialysis of model spent liquor of sulfuric acid was extensively investigated in a flat sheet ED module made of acrylic and commercially available anion exchange membranes for a wide range of operating conditions. Low-cost electrodes such as graphite and SS 316L were tested under electrodialytic conditions for acid separation and their effect on the quality of anolyte was investigated. Effect of various physico-chemical parameters such as initial catholyte concentration, current density on molar flux, current efficiency, the extent of sulfuric acid separation and voltage requirements were examined using batch ED process. In addition, a cascaded ED process consisted of six electrodialyzers in series was designed to enrich sulfuric acid concentration and operated with graphite electrode and Selemion AAV, Selemion AMV and IPA anion exchange membranes. The performance of the system was critically analysed in terms of acid concentration, operating time, current efficiency, voltage requirements, and energy consumption. The cascaded system allowed the enrichment of solution up to 28 wt. % and developed a set of performance parameters. Estimation of energy consumed by ED along with economic analysis was carried out and compared with the conventional evaporation process. Transport mechanism of ions across the anion exchange membrane was studied and an equation relating voltage requirements and molar flux with process performance parameters was developed.

The salient findings and significant conclusions of the present study are outlined below.

- Electrodialysis was found to be an efficient and powerful method for the separation and concentration of sulfuric acid from a model spent acidic solution of sulphuric acid.

- The material of construction of the electrodes played an important role in the performance of ED. Whilst SS 316L as anode material was prone to oxidation, graphite could be a suitable option in terms of overall performance in the range of current density from 2 to 30 mA cm^{-2} beyond which its disintegration was found making it unusable. There was a need to replace the graphite electrode after long time run. The electrode selected must be

inert and should run for a longer time. This suggests that an appropriate choice of the electrode is desirable.

- Applied current density and initial catholyte concentration have a profound influence on molar flux as well as current efficiency. Molar flux increased almost linearly with initial catholyte concentration and current density. It was found to increase for current densities of 10 mA cm^{-2} and above, however for lower current densities, 2 and 4 mA cm^{-2}, the enhancement was marginal. The maximum molar flux was estimated to be 10.52×10^{-8} mol cm^{-2} s^{-1} at 4.45 wt. % initial catholyte concentration and 30 mA cm^{-2} applied current density.

- Current efficiencies were found to increase with initial catholyte concentration whereas the reverse trend was observed with an increase in current density. Efficiencies were varied in the range from 50 to 70% for applied current densities 10, 20 and 30 mA cm^{-2} and initial catholyte concentration in the range from 2 to 4.5 wt. %. Even at low current densities, such as 2 and 4 mA cm^{-2}, the current efficiencies were observed to increase in the range from 78.8 to 85.23%. No negative effects such as bubble formation at the surface of the electrode, volume change, temperature rise or water splitting were observed at lower values of current density and this might be the possible reason for obtaining higher current efficiencies.

- Applied voltage had to be maintained in the range from 6 to 2.3 V with the increase in catholyte initial concentration from 2 to 4.5 wt. %, while the same was found to increase with current densities from 10 to 30 mA cm^{-2} and reported to be very high (> 10 V) while treating dilute (1±0.15 wt. %) solution at a high value of current density (30 mA cm^{-2}). ED might be an economical, less energy-intensive process when operated at low current densities. Separation of sulfuric acid also increased with increase in current density and found almost 99% with dilute solution supports the possibility to recover almost all acid contents from spent solution, making left-over catholyte dischargeable with minimal cost of treatment and concentrated anolyte to be recycled or reused.

- The present work developed a cascaded ED process to purify and concentrate sulfuric acid from spent acidic liquor. A cascaded electrodialysis system consisted of six electrodialyzer was found capable of increasing sulfuric acid concentration up to 28 wt.

% effectively and efficiently with ion exchange membranes namely Selemion AAV, Selemion AMV and IPA. Proton leakage through anion exchange membrane, acid back diffusion, concentration polarization and solution conductivity were considered to be the limiting factors for acid enrichment and their effects were found significant on current efficiency and applied voltage.

- Under present experimental conditions, the ability of Selemion AMV membrane was observed to be higher compared to the other two membranes to enrich acidic solution. Voltage and time requirements and consequently energies consumed in all the stages during the process were observed to be lower with Selemion AMV membrane and in the order AMV<AAV<IPA. The fluxes of sulfuric acid were observed to be the highest for AMV membrane and the smallest for IPA membrane. Current efficiencies were varied in the range of 50 to 60 % initially and then decreased to lower values with all the three membranes and observed higher in order AMV>AAV>IPA. Higher acid recovery, higher efficiency and lesser electrical energy utilisation are the key factors in terms of the commercial viability of the process. Major differences were observed in the performance of Selemion AMV membrane with other two AEMs, but IPA membrane performed equivalent to Selemion AAV, a low proton leakage membrane to enrich sulfuric acid concentration.

- Energy estimations for dilute sulfuric acid (concentration 1 to 5 wt. %) were found to decrease with increasing concentration for both ED and EV processes. An economic evaluation of ED and EV were almost identical for concentration enhancement from 1 to 5 wt. %. Integration of ED and EV processes could result in approximately 21 % and 24 % cost saving compared to standalone ED and EV respectively. It is more economical to concentrate solution up to intermediate level with ED followed by further concentration using EV. Enrichment of sulfuric acid solution by cascaded ED process seems to be costly due to the high cost of power consumption, cost of electrode replacement, and membrane.

- An attempt was made to apply the Nernst-Planck equation to calculate various fluxes. The contribution of diffusive flux, as well as membrane potential based flux calculated either in presence or absence of current, was very less as against practical flux obtained in the presence of applied electric current. The molar flux was predominantly due to the influence of the applied electric field. An equation was developed to predict

the molar fluxes and voltage required which matched satisfactorily with experimental values with minor standard square deviations. The developed equation helps to predict the molar flux and voltage requirements and hence estimates the time and power consumption for the desired separation and concentration.

5.2 Original contribution by the thesis

Present work explores the suitability of low-cost electrodes such as graphite and SS 316L for electrodialytic recovery and concentration of sulfuric acid from a spent acidic solution. In this work, ED performance for the studied electrodes was evaluated based on experimental results in terms of molar flux, current efficiency, the extent of acid separation and energy consumption. This work also explores the amenability of ED to be used commercially either as a stand-alone system or integrated with evaporation for the enrichment of dilute sulfuric acid solution. The data obtained in the present study would be useful as guidelines for scale-up of electrodialysis. The present work provides a complete set of process operating variables such as operating time and voltage requirements and also suggests a membrane effective for the enrichment of sulfuric acid solution using cascaded ED process that may be useful for large scale operation. An equation relating process variables with molar flux and voltage requirements was developed and compared with experimental data. Approximate cost analysis was also carried out for the proposed process. Two full-length research articles based on the present work have already been published in the international peer-reviewed journals. Other original outcomes of present work will also be published in the journal of international repute.

5.3 Future scope of study

Results of this study demonstrate that an appropriate choice of the electrode and operating conditions is an essential prerequisite for the efficient electrodialysis separation process. Based on the experimental results, it is clear that the graphite can work efficiently in the separation of sulfuric acid under electrodialytic conditions. But it performs poorly at higher current density and applied voltage thereby necessitating its frequent replacement after prolonged operation. This demands the further work in the direction to improve the stability of the graphite electrode. If this could be done a considerable cost reduction could be accomplished if compared with the cost of the platinum electrode. Improvements in the ED process performance with surface-modified electrodes or coating on the surface could also

provide a future scope for research. Electrodialysis has been proven to be an efficient technique for separation and concentration compared to conventional and some membrane-based technologies. Though ED is technically viable, enrichment or separation of the sulfuric acid solution by ED process is costly due to the high cost of power consumption, cost of electrode replacement, and membrane. If alternate/cheaper sources of electricity are available, the operating cost may be reduced and ED could become an economically viable option. Furthermore, the instability of ion exchange membranes in the strongly acidic environment and proton leakage during electrodialysis processes are the main factors limiting the increase of the concentration of sulfuric acid. Therefore, extensive work is required to improve the characteristics of the anion exchange membranes that are particularly used for acid enrichment.

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Appendices

MATLAB programmes for the development of equation relating molar flux and voltage requirements with process variables.

CASE 1: Program for equation relating molar flux with initial catholyte and anolyte concentration and current density.

```
mydata= xlsread('AAV_flux_J.xlsx');
Jp=mydata(:,1);
Ic=mydata(:,2);
Cct=mydata(:,3);
Cat=mydata(:,4);
dC=Cct-Cat;

P0_V=[1.096497593
0.504528918
0.718062836
0.108657975
-0.002756387
3.246773328];
myP = fmincon(@(P) diffSq_modelPr_V(P,Jp,Ic,Cct,dC),P0_V,[],[])

Jm=myP(1)*Ic.^myP(2)+ myP(3)*Cct.^myP(4)+ myP(5)*dC.^myP(6) ;
xlswrite('AAV_flux_J.xlsx',Jm,'Sheet1','E');

n=size(Jp,1);
plot(1:1:n,Jp,'-.*b',1:1:n,Jm,'--or')

function funR_J = diffSq_modelPr_V(P,Jp,Ic,Cct,dC)
Jmodel=P(1)*Ic.^P(2)+ P(3)*Cct.^P(4)+P(5)*dC.^P(6) ;
funR_J=sum((Jp-Jmodel).^2);
end

myP =

    0.1698
    1.1491
    9.2267
   -4.8826
    0.3961
```

CASE 2: Program for equation relating applied voltage with initial catholyte and anolyte concentration and current density.

```
mydata= xlsread('AAV_flux_V.xlsx');
Jp=mydata(:,1);
Ic=mydata(:,2);
Cct=mydata(:,3);
Cat=mydata(:,4);
dC=Cct-Cat;

P0_V=[1.096497593
0.504528918
0.718062836
0.108657975
-0.002756387
3.246773328];
myP = fmincon(@(P) diffSq_modelPr_V(P,Jp,Ic,Cct,dC),P0_V,[],[])

Jm=myP(1)*Ic.^myP(2)+ myP(3)*Cct.^myP(4)+ myP(5)*dC.^myP(6) ;
xlswrite('AAV_flux_V.xlsx',Jm,'Sheet1','E');

n=size(Jp,1);
plot(1:1:n,Jp,'-.*b',1:1:n,Jm,'--or')

function funR_J = diffSq_modelPr_V(P,Jp,Ic,Cct,dC)
Jmodel=P(1)*Ic.^P(2)+ P(3)*Cct.^P(4)+P(5)*dC.^P(6) ;
funR_J=sum((Jp-Jmodel).^2);
end

myP =
    0.5166
    2.7184
   -0.3011
   -0.0341
    1.9616
```

Sample data calculations

Catholyte initial concentration = 4.45 wt. %

Catholyte final concentration = 2.26 wt. %

Molecular weight of sulfuric acid = 98.079 gm/gmol

Volume of catholyte = 210 ml

Membrane effective area = 49.5 cm^2

t= 150 minutes

Current supplied = 1500 mA=1.5 A

Current density = 1500/4.9 = 30.3 mA cm^{-2}

(1) Molar flux

$$= \frac{(4.45-2.26)\times 210}{100 \times 49.5 \times 98.079 \times 150 \times 60}$$

= 10.52×10^{-8} gmol cm^{-2} s

(2) Current efficiency

One faraday represents one mole of electrons. It is equal to 96,485 coulombs. The amount of substance transferred depends upon the amount of electricity passed. One faraday of charge will transfer one-gram equivalent of any substance. 96485 charge will transfer 49.0 gm of sulfuric acid.

Actual amount of substance transferred from catholyte to anolyte in 150 minutes

$$= \frac{(4.45-2.26)\times 210}{100}$$

= 4.6 gm.

Passage of 1.5 A for 150 minutes will move

$$= \frac{1.5 \times 150 \times 60 \times 98}{2 \times 96485}$$

= 6.856 gm of sulfuric acid

Current efficiency (%)

= (gm of sulfuric acid actually transferred / gm of sulfuric acid transferred ideally based on current supplied) × 100

$$= \frac{4.46 \times 100}{6.856}$$

= 67 %

(3) Sulfuric acid separation (%)

$$= \frac{(4.45 - 2.26) \times 100}{4.45}$$

= 49.2 %

(4) Energy consumption

Energy consumed to increase 210 ml anolyte concentration from 1 to 2 wt. % in 150 minutes with current supplied 1 A and applied voltage of 10 V.

$$= \frac{10 \times 1 \times 150 \times 60}{210}$$

= 428.6 kJ/l

Research Publications

Journal

1. Sheth B., Nath K., Analysis of molar flux and current density in the electrodialytic separation of sulfuric acid from spent liquor using an anion exchange membrane, ***Korean J. Chem. Eng.*** *(Springer)* 35 (2018) 1878–1888.
2. Sheth B., Nath K., Effect of selected process parameters on the electrodialytic separation and concentration of sulfuric acid using graphite electrodes. ***J. Chem. Eng. Comm***. *(Taylor & Francis)* 207 (3) (2019) 295-305.
3. Sheth B., Nath K., Concentration of sulfuric acid from spent liquor by cascaded electrodialysis using an interpolymer anion exchange (IPA) membrane**.** ***Asian J. Chem***. 32 (2020) (In press).

Conference proceeding

1. Iyer N., Sheth B., Nath K., Studies on the recovery or separation of sulfuric acid from waste liquor (spent acid) using ion-exchange membrane-based separation techniques. *National Symposium on Advances in Separation and Purification Science & Technology (NSST),* GCET, Vallabh Vidyanagar, Anand, September (2016).
2. Momin J., Sheth B., Performance evaluation of membrane separation techniques to concentrate sulfuric acid. *International conference at Paradigm shift in Chemical Engineering Education*, *Process and Technology* organized by The Institution of Engineers (India), Gujarat, on 16-17th September (2017).