



Concentration of Sulfuric Acid from Spent Acidic Liquor by Cascaded Electrolysis Using an Interpolymer Anion Exchange Membrane

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Cascaded electrolysis system has been developed for increasing the concentration of sulfuric acid from aqueous solution using an interpolymer anion exchange (IPA) membrane. Enrichment process was carried out in a cascade of six electrolysers at 20.2 mA/cm² current density. The performance of the process was evaluated rigorously in terms of current efficiency, voltage requirements and processability to enrich the acid concentration. The bench-scale experimental results exhibited the ability of membrane to perform as a low proton leakage membrane and to enrich the sulfuric acid concentration up to 27.93 wt. %. The higher values of current efficiencies were reported to be in the range of 50 to 60 %. Proton leakage through the 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 voltage requirement.

Keywords: Cascaded electrolysis, Concentration enrichment, Interpolymer anion exchange membrane, Sulfuric acid.

INTRODUCTION

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 wastes list. Metal finishing units particularly iron and steel industries are the significant contributors of waste streams where hydrochloric acid and sulfuric acid are used as principal acids and the resulting metal salts are ferrous chloride and ferrous sulfate, respectively [1]. Recovering the dilute acid is not only profitable to the manufacturer but also imperative to environmental protection [2]. Acids can be recovered using different conventional as well as advanced separation methods amongst which electrolysis is found effective and serves the purpose of purification as well as concentration [3-5]. Electrolysis is an electromembrane process holds much promise for the treatment of acidic effluents [6,7]. It has been reported in the literature that an enrichment of sulfuric acid solution by electrolysis is affected by the properties of the

ion exchange membrane (AEM) and limited to certain value due to its proton leakage characteristics [8]. Most of the researchers have used either low proton leakage [4] or tailored membrane [3,5] to enrich the sulfuric acid solution. Development of multi-stage electrolysis system to increase sulfuric acid concentration up to the maximum possible value using an interpolymer anion (IPA) exchange membrane has not been reported and remains an area of research in separation science, which requires further insight. The acid enrichment by electrolysis is influenced not only by proton leakage but acid back diffusion [4,9], concentration polarization [10-12] and conductivity of solution [13] also play a key role. These factors affect the process performance in terms of current efficiency [14,15] and voltage requirements [16,17] that together affect the operating cost of the system.

Furthermore, mostly researchers employed the costly electrodes such as platinum, titanium coated with platinum or other metal oxides that effect the costing of the system. Present work employed graphite as material of electrode that can be consi-

dered as cost-effective material and can sustain in acidic medium compared to other low-cost metals such as stainless steel [17,18].

In present work, a cascaded electro dialysis process was developed to concentrate sulfuric acid using IPA membrane, graphite electrode and an electro dialysis module made up of acrylic. A cascaded electro dialysis system consisted of six electro dialyzer in series was operated at constant current density of 20 mA cm^{-2} (a value found suitable on the basis of several batch experiments) [15,17] in a stage-wise manner. Indigenous interpolymer anion exchange membrane membrane was used in this study and its performance was examined rigorously in terms of extent of acid concentration, current efficiency and voltage requirements. The membrane used in the electro dialysis process was found capable of increasing the acid concentration from 5 to 27.93 wt.% effectively and efficiently without any additional cost requirements as there were no other moving elements present in the system. The concentrated acid can be used as battery acid in lead acid batteries with little makeup of fresh sulfuric acid. The exit stream sulfuric acid concentration was reduced to less than 0.25 wt.% reducing the load for further treatment before discharge and making it less harmful to the environment.

EXPERIMENTAL

All the chemicals used in the present study were of analytical grade (AR) supplied by Finar Ltd. (Mumbai, India) and used as received without further purification. Preparation of stock solutions was carried out with deionized water, having a conductivity of $20 \mu\text{S cm}^{-1}$, produced from a reverse osmosis system. An interpolymer anion exchange membrane (IPA) produced and supplied by CSMCRI, Bhavnagar, India was used in the present study. It was an interpenetrating network (IPN) based ion-exchange membrane and possesses an excellent combination of both electrochemical and mechanical properties [19]. The characteristics of the membrane are presented in Table-1. The membrane was soaked in the feed solution for more than 24 h prior to its use in the electro dialysis cell. Commercially available graphite sheets were used as electrodes.

General procedure: A proposed system flow diagram is shown in Fig. 1. A 5 % wt. synthetic solution of sulfuric acid was taken as an initial feedstock. Each electro dialyzer module consisted of an acrylic sheet was partitioned into an equal volume by IPA membrane providing an effective area of 49.5 cm^2 . Each experiment was started with 210 mL of anolyte and catholyte solution of equal concentration with fresh electrodes. Electro-

TABLE-1
CHARACTERISTICS OF THE MEMBRANE
USED IN PRESENT STUDY

Membrane type	IPA
Structure properties	Anion LDCE/HDPE
Permselectivity (%)	92
Area resistance ($\Omega \text{ cm}^2$)	2.0-4.0
Exchange capacity (meq. g^{-1})	0.8-0.9
Thickness (mm)	0.16-0.18

dialyzers were operated at a current density of 20.2 mA/cm^2 maintained constant by controlling voltage variation by multiple power supply (model-PSD3304, ScientiFic). Each experiment was run more than 15 h and anolyte and catholyte concentrations were measured at a regular time interval. Frequent stirring was provided to both the compartments to maintain the homogeneity of the solution during the experiment.

Detection method: Conductivity of dilute sulfuric acid solution was measured by a Chemiline digital conductivity meter CL 220 manufactured by Aqua Mart, Kolkata, India. Anolyte and catholyte solutions were analyzed titrimetrically using NaOH solution. Current efficiency is the actual current utilized for the movement of ions from catholyte to anolyte through an ion exchange membrane [15,20]. It was calculated using eqn. 1.

$$\eta = \frac{z(C_{co} - C_{cf})V_l F}{It} \quad (1)$$

where F is Faraday constant, I is current (mA), z valence number of ions. C_{cf} and C_{co} are the final and initial catholyte concentrations, t is time and V_l is the volume of catholyte solution. The energy required to increase anolyte concentration (E_{ED}) was calculated using eqn. 2 to obtain its value in kJ/L of final anolyte solution (V_{fa}) [15,21,22] at the corresponding values of applied voltage (V).

$$E_{ED} = \frac{VIt}{V_{fa}} \quad (2)$$

FTIR and FESEM analysis: The presence of organic functional groups on the membrane surface was analyzed by the Fourier transform infrared spectroscopy (Perkin-Elmer Spectrum GX) using a wave number range of $4000\text{-}400 \text{ cm}^{-1}$ at a resolution of 4.0 cm^{-1} with an acquisition time of 1 min. The outer surface topologies of IPA membrane were investigated *via* field emission scanning electron microscopy (FE-SEM) using JEOLFE-SEM (JSM-6701F) at 5 kV. For cross

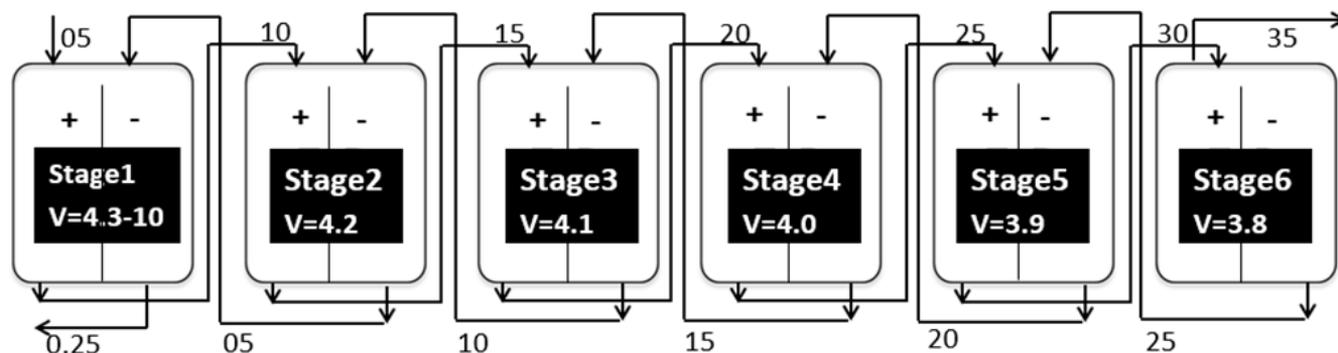


Fig. 1. Schematic diagram of cascaded electro dialysis process used in the present study, numbers indicate sulfuric acid concentration by weight %

sectional analysis, cryogenically fractured membrane samples under liquid nitrogen were freeze-dried overnight and sputtered with a thin layer of platinum using JEOL JFC-1600 auto fine coater.

RESULTS AND DISCUSSION

In electrodialysis, the transfer of ions from upstream side to the downstream side of the membrane is strongly influenced by acid back diffusion and concentration polarization. Along with this, the variation in solution conductivity with acid enrichment also affects the process. In addition, a proton leakage characteristics of the membrane plays a key role in enrichment of acidic solution.

Stage-wise concentration enrichment: Results obtained during stage-wise sulfuric acid concentration using an IPA membrane are given in Table-2 and also shown graphically in Fig. 2. As shown in Fig. 2a, a first stage took almost 660 min 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 min for each 5 wt.% concentration enrichment. Stages 5 and 6 as could not produce satisfactory results. Results obtained with stage 6 are shown in Fig. 2b. These observations were in good agreement with the observations reported by Yongtao *et al.* [3] regarding the prod-

uction 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.

Fig. 2 represents how the concentration gradient changed during the process of transfer of sulfate ions from catholyte to anolyte. The concentration gradient increased from initial value zero at $t = 0$ min to a higher value with enrichment of anolyte solution with time. Back-diffusion results from concentration gradient across the ion-exchange membrane (IEM) and increases with an increase in the concentration ratio between the streams separated by IEM [4,10]. Apart from this, concentration polarization is an inherent, inevitable and fundamentally important phenomena in electromembrane processes [10-12]. In the case of electrodialysis, the effect of concentration polarization in the liquid film formed at the upstream side of the 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, sulfate ion concentration becomes a lower interface than in the bulk solution. The depletion of permeating ion increases the electrical resistance [16]. On the other hand, sulfate ions concentration was 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 electrodialysis renders the impact of concentration

TABLE-2
STAGE WISE CATHOLYTE CONCENTRATION REDUCTION AND ANOLYTE CONCENTRATION ENRICHMENT WITH TIME AND APPLIED VOLTAGE AT A CONSTANT CURRENT DENSITY OF 20 mA/cm² AND GRAPHITE ELECTRODE

Stage No.	Applied voltage (volt)	Time (min)	Anolyte concentration (wt. %)		Catholyte concentration (wt. %)		Maximum concentration gradient (wt. %)	Energy (kJ/L of final anolyte solution)
			Initial (C_{ao})	Final (C_{af})	Initial (C_{ao})	Final (C_{af})	$\Delta C = C_{af} - C_{cf}$	
1	4.3-10	660	4.90	9.56	4.90	0.25	9.31	1100
2	4.2	840	10.29	15.44	10.29	5.15	10.29	1078
3	4.1	840	15.19	20.09	15.19	10.05	10.04	1052
4	4.0	840	20.58	25.48	20.58	15.44	10.04	1026
5	3.9	840	25.48	27.93	25.48	23.03	4.90	–
6	3.8	840	29.40	31.85	29.40	27.93	3.93	–

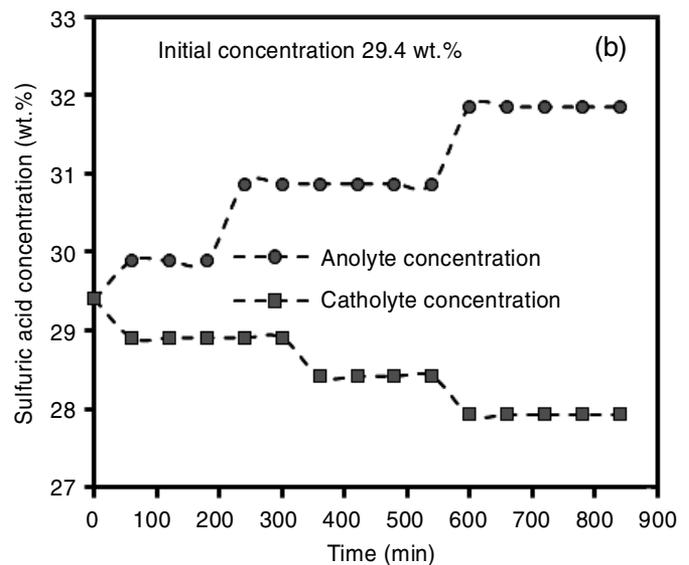
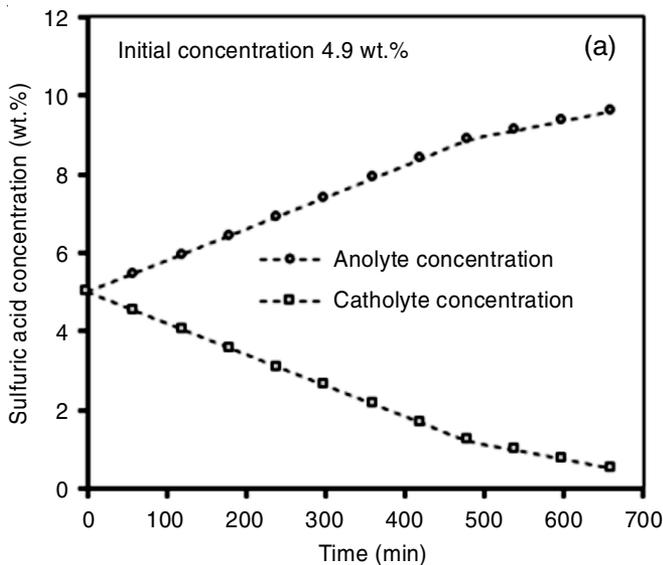


Fig. 2. Stage wise sulfuric acid concentration enrichment at initial concentration of (a) 4.9 wt. % and (b) 29.4 wt.% at a constant current density of 20 mA/cm²

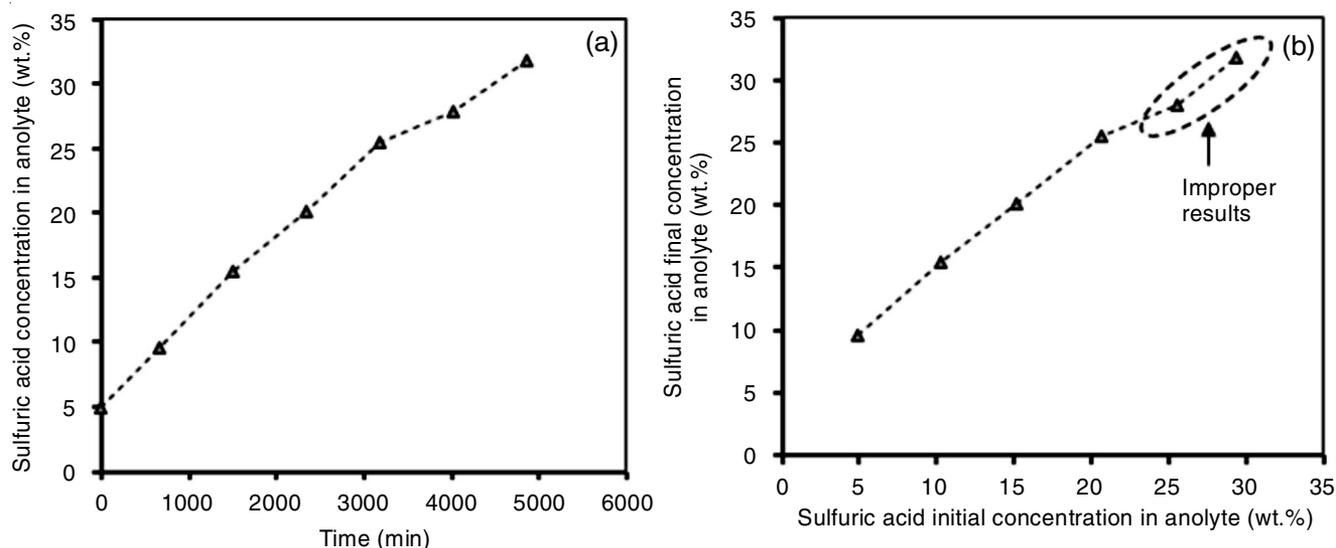


Fig. 3. (a) Sulfuric acid concentration enrichment with time and (b) Stage wise initial and final anolyte concentration

polarization adjacent to the IEM negligible [4] and hence the effect of concentration polarization can be neglected. The same becomes appreciable in batch electro dialysis where the fluid is stirred manually and hence it was essential to consider it.

The concentration of sulfuric acid was found to increase to the tune of 5 wt.% in stages 1 to 4 as shown in Table-2. When the membrane was tested under present experimental conditions, it could enrich sulfuric acid concentration up to 25.48 wt.% in approximately 3180 min in stages 1 to 4 as shown in Fig. 3a. However, the results obtained in stages 5 and 6 were not satisfactory. Starting with an initial concentration of 29.4 wt.%, after the completion of stage 6, the sulfuric acid concentration was reported to be 31.85 wt.% in 840 min. The anolyte concentration increased about 5 wt.% each in stages 1 to 4, but beyond stage 4 the results did not follow the same trend as highlighted by the dotted circle in Fig. 3b. These observations were in good agreement with the findings reported by Jaroszek *et al.* [4] for process with the recirculation of solution. Since AEMs were made of polymeric materials, their swelling, as well as proton leakage characteristic, affects the performance of the separation process by electro dialysis. The recovery of sulfuric acid by electro dialysis cannot be developed on an industrial scale because of the proton leakage of polymeric anion exchange membranes. Baltazar *et al.* [23] studied a proton leakage through different ion exchange membranes and showed that the characteristic of the membrane played an important role in the recovery of acid [23]. Water present in AEM acts as an excellent mediating agent for the proton leakage [24]. Proton leakage is a major problem associated with most commercial anion-exchange membranes, which makes them unsuitable to use to recover sulfuric acid [8]. Yongtao *et al.* [3] increased the sulfuric acid concentration up to 28.56 wt.% by using polyethylene heterogeneous membrane [3] whereas Jaroszek *et al.* [4] enriched sulfuric acid up to 3.5 mol/l using Selemion AAV membrane. Low proton leakage membranes such as Selemion AAV has been reported to be the best candidate for the concentration of sulfuric acid [4]. The IPA membrane used in the present study performed equivalent to a low proton leakage anion exchange membrane

and enrich the sulfuric acid concentration up to 27.93 wt.% in five consecutive electro dialyzers operated at a constant current density.

Effect of acid enrichment on current efficiency: Fig. 4 represents the effect of the increase of sulfuric acid concentration in anolyte on current efficiency for stage 1. Initially, high current efficiency in the range of 50 to 60% was observed, then after current efficiency decreased rapidly with the decrease in sulfuric acid concentration in catholyte less than 1 wt.%. The lowest value of current efficiency 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 [4,13]. This might be the reason for observing a rapid decrease in current efficiency. A similar trend was observed with all other stages of the cascaded electro dialysis process with the IPA membrane. In previous report [15], an effect of anolyte and catholyte concentration difference on current efficiency was reported for dilute sulfuric acid separation and current efficiency values were found below 50% for the case wherein anolyte concentration was greater

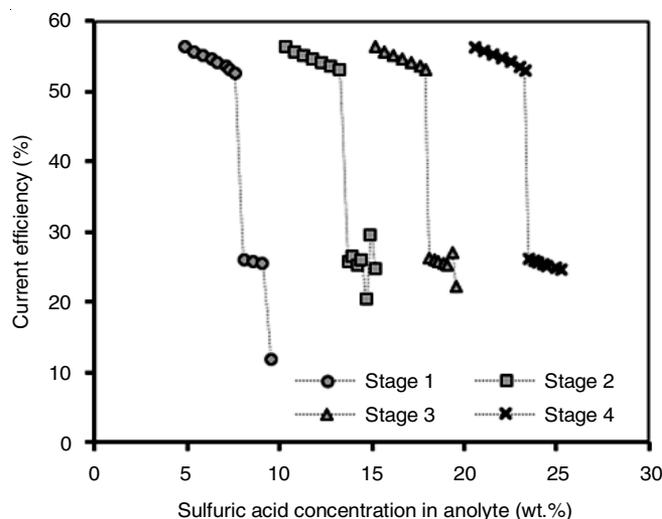


Fig. 4. Effect of sulfuric acid enrichment on current efficiency of stages 1 to 4 performed at a current density of 20 mA/cm²

than the catholyte concentration [15]. Additionally, it has been reported that in acid enrichment process, acid concentration reaches a limiting value at which the current efficiency falls to zero [8]. 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. Additionally, the conductivity of sulfuric acid solution plays a major role in the electrodynamic movement of sulfate ions through membrane. As reported in literature, the conductivity of sulfuric acid solution increases up to certain value and then decreases with acid concentration [25]. Thus, the concentrate resulted in an increase of voltage for the same current density. This may cause an overall current efficiency decrease [13]. 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.

Voltage and energy requirements: Fig. 5 shows that the voltage varied with time for stages 1 to 6 to maintain the current density at a constant value of 20 mA/cm² during sulfuric acid enrichment process. At the beginning of experiment, applied voltage was observed a little higher for about 30 min and then decreased to a lower value [21]. As shown in Fig. 5b, applied voltage decreased by 0.1 V for each stage of electrodialysis and then it was observed almost constant except for stage 1. This period might 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. 5a, for stage 1, when initial catholyte and anolyte concentration was 4.90 wt.%, an 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, catholyte was diluted to 0.25 wt.% concentration and had a conductivity of just 12 mS. Hence, 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. 5b. For stages 5 and 6, even a supply of higher voltage for a longer time could not increase the anolyte concentration much. On the basis of experimental results given in Table-2, it was clear that the voltage requirements were almost the same for all the stages except stage 1 to enrich sulfuric acid concentration under present experimental conditions. In spite of having the same voltage demands with all the stages, energy consumptions differed due to different time consumptions. Energy consumed to perform the separation is the key factor determining the overall efficiency of an electrodialysis 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 cm², the energy consumed during the acid enrichment process was calculated using eqn. 2 in kJ/L. Energy consumed to enrich sulfuric acid concentration stage-wise is also represented in Table-2 and 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 could be said that an energy required for each 5 wt.% concentration increment was almost constant.

FTIR and FESEM analysis: Interpretation of the FTIR spectrum can be of great help in determining the presence of functional groups in the ion-exchange membrane specimen.

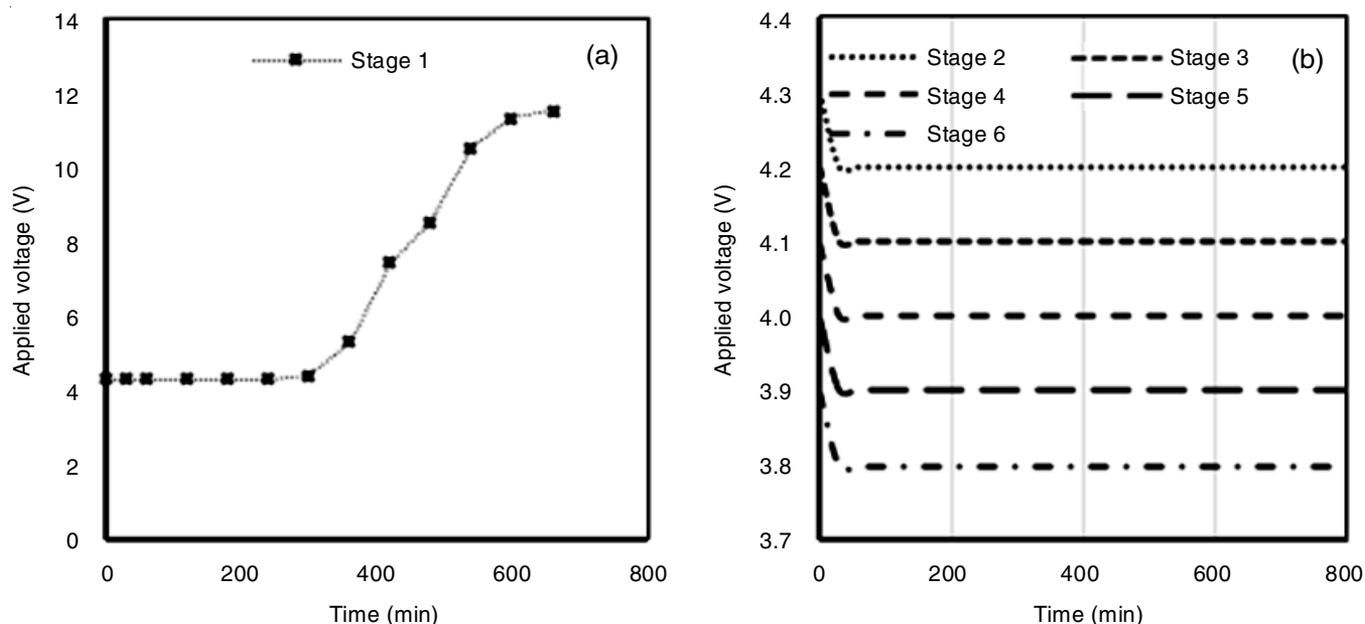


Fig. 5. Variations in voltage during acid enrichment in (a) stage 1 and (b) stages 2 to 6

A close inspection of FTIR spectra of the pristine membrane as presented in Fig. 6 indicates the presence of a number of sharp, medium and broad peaks in the entire range of 4000-400 cm^{-1} . Principal band assignments of FTIR spectra are presented in Table-3. The IPA ion exchange membrane was fabricated by copolymerization of styrene and divinyl benzene. The peaks at 3025.78 and 3071.83 cm^{-1} were associated with aromatic benzene system (C-H *str.*), which belongs to styrene. A strong absorption of C=C *str.* appeared around 1600 cm^{-1} . Aliphatic system (C-H *str.*) appeared below 3000 and 2980-2800 cm^{-1} . Alkane system C-H bending showed a broad peaks at 1480-1450 cm^{-1} . A distinctly characteristic broad absorption band (O-H *str.*) at 3400 cm^{-1} and the (C-O *str.*) at 1100 cm^{-1} . In finger print zone, it was difficult to assign bands due to overlapping and broadening of multiple bands. However, these bending absorptions were according to presence of aromatic and aliphatic system.

Wave numbers (cm^{-1})	Bands 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 ₂ X stretching vibrations presence of alkyl halide
1112.64; 1064.11	C-O primary, secondary alcohol
1034.90	C-O ether

Fig. 7 represents the SEM images of the surfaces as well as the cross-sections of pristine IPA membrane at different

magnifications. The images of the pristine membrane suggested the appearance of a compact and smooth surface without much visible pores. There were no visible cracks or irregularities on the surface signifies the homogeneity and compactness of membrane, which clearly confirmed a good compatibility between ion-exchange functional group polymer matrix.

Conclusion

In present work, a cascaded electro dialysis system consisted of six electro dialyzer with interpolymer anion exchange (IPA) membrane was found capable of enriching sulfuric acid concentration up to 27.93 wt.% effectively and efficiently in first five electro dialyzers operated at a constant current density of 20 mA/cm^2 . An IPA membrane used in this study performed equivalent to a low proton leakage membrane. The studied membrane was found to be limited to enrich the acid content beyond 27.93 wt.% due to the combined effects of proton leakage, acid back diffusion, concentration polarization and conductivity of the solution. Voltage requirements exceeded 10 V and higher during acid enrichment from 5 to 10 wt.% concentration and hence represented great influence of acid back diffusion and solution resistance on cell voltage. For acid enrichment beyond 10 wt.% concentration, a cell voltage was affected negligible by variation in solution concentration and varied in the range 3.8 to 4.2 V was found capable to maintain constant current density. Current efficiencies were also reported to be in the range of 50 to 60% for all stages which fallen rapidly after generation of about 7 wt.% concentration gradient. Current efficiencies were reported to be zero when acid concentration in anolyte approached in the range 27 to 32 wt.%. Energy consumption was found almost constant to enrich acid concentration by 5 wt.%. FTIR spectra of the membrane specimen indicated the copolymerization of styrene and divinyl benzene and the SEM analysis suggested that a skin layer of pristine membrane had a homogeneous morphology rendering it amenable for delivering favourable ionic conducting performance with the system studied. Table-4 represents the detailed information about the work that has been carried out by various researchers using different AEMs to enrich the sulfuric acid concentration. These observations

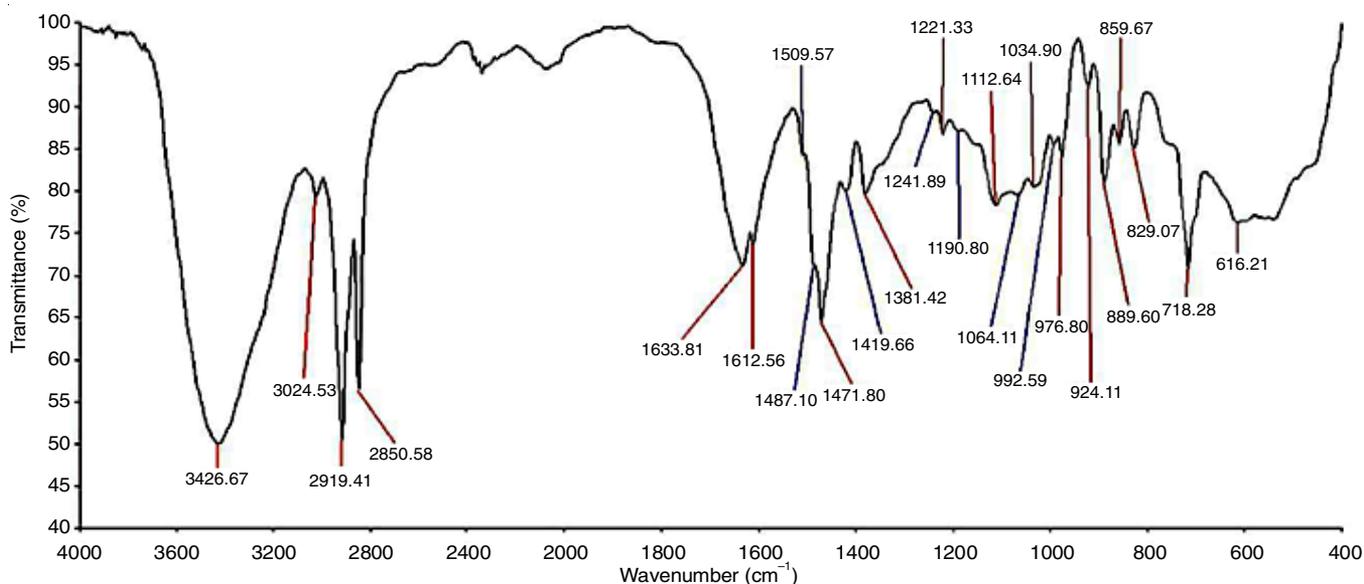


Fig. 6. FTIR spectra of IPA membrane

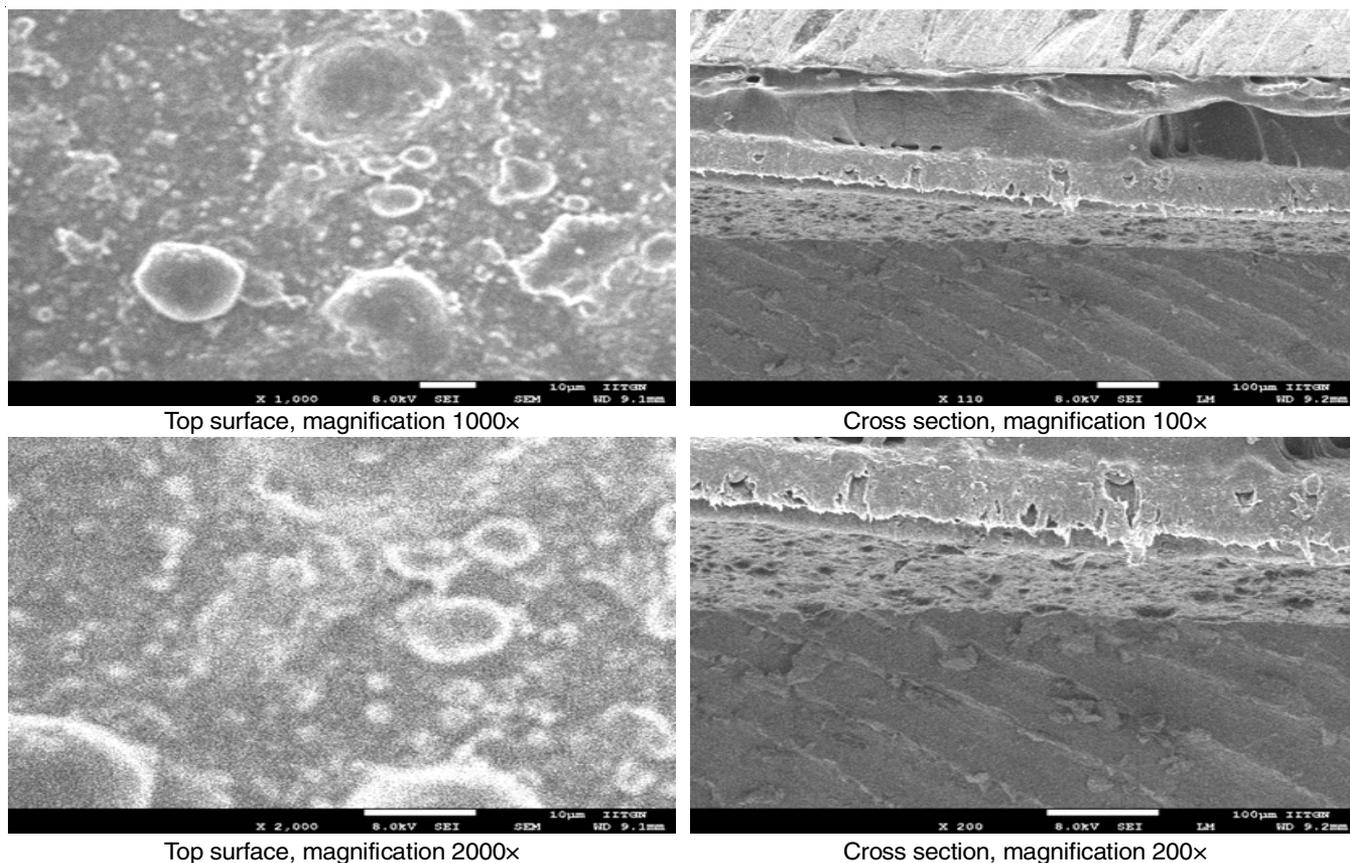


Fig. 7. SEM micrographs of cross-section and top surface of IPA membrane under different magnifications

TABLE-4
SULFURIC ACID ENRICHMENT BY ELECTRODIALYSIS USING DIFFERENT ANION EXCHANGE MEMBRANES

Feed	ED Configuration	Membranes used	Anode	Cathode	Concentration of Sulfuric acid obtained	Ref.
Model sulfuric acid solution (5 wt. %)	Acrylic flat sheet ED module, no solution re-circulation, no any moving element	IPA (Interpolymer anion exchange membrane)	Graphite	Graphite	27.93 wt. % at 20 mA/cm ² in 67 h	Present study
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. %	[23]
Copper electrorefining solution	Lab scale six compartments Electrohydrolysis cell	Ionac MA3475, Ionac MC3470	Platinum	Platinum	0.5 mol/L (\approx 5 wt. %) at 225 A/m ² current density in 12 h	[27]
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	[26]
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 (\approx 2.5 wt. %) at 15 mA/cm ² current density in 10 h	[6]
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. %	[3]
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	CF-210, CF-21	3.5 mol/L in 10 h	[4]
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 h	[5]

and conclusions are important for the selection of operating variables with IPA membrane to particularly electro dialysis processes which are used for acid enrichment along with factors influencing the process performance and may be a valuable help for the development of large-scale acid enrichment process.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Agrawal and K.K. Sahu, *J. Hazard. Mater.*, **171**, 61 (2009); <https://doi.org/10.1016/j.jhazmat.2009.06.099>
2. Z. Zhou and Z. Liu, *Chem. Eng. Process. Process Intensif.*, **46**, 1310 (2007); <https://doi.org/10.1016/j.cep.2006.10.008>
3. Y. Yongtao, N. Ping, Q. Guangfei, L. Junyan and Z. Qian, *J. Electrochem. Soc.*, **162**, E141 (2015); <https://doi.org/10.1149/2.0591509jes>
4. H. Jaroszek, W. Mikolajczak, M. Nowak and B. Pisarska, *Desalination Water Treat.*, **64**, 223 (2017); <https://doi.org/10.5004/dwt.2017.11385>
5. R. Xie, P. Ning, G. Qu, J. Li, M. Ren, C. Du, H. Gao and Z. Li, *Chem. Eng. J.*, **341**, 298 (2018); <https://doi.org/10.1016/j.cej.2018.02.012>
6. M.C. Martí-Calatayud, D.C. Buzzi, M. García-Gabaldón, E. Ortega, A.M. Bernardes, J.A.S. Tenório and V. Pérez-Herranz, *Desalination*, **343**, 120 (2014); <https://doi.org/10.1016/j.desal.2013.11.031>
7. A. Chekioua and R. Delimi, *Energy Procedia*, **74**, 1418 (2015); <https://doi.org/10.1016/j.egypro.2015.07.789>
8. A.T. Cherif, C. Gavach, T. Cohen, P. Dagard and L. Albert, *Hydrometallurgy*, **21**, 191 (1988); [https://doi.org/10.1016/0304-386X\(88\)90004-7](https://doi.org/10.1016/0304-386X(88)90004-7)
9. A.E. Simpson and C.A. Buckley, *Desalination*, **70**, 431 (1988); [https://doi.org/10.1016/0011-9164\(88\)85071-9](https://doi.org/10.1016/0011-9164(88)85071-9)
10. Y. Tanaka, *J. Membr. Sci.*, **216**, 149 (2003); [https://doi.org/10.1016/S0376-7388\(03\)00067-X](https://doi.org/10.1016/S0376-7388(03)00067-X)
11. X.T. Le, *J. Membr. Sci.*, **397-398**, 66 (2012); <https://doi.org/10.1016/j.memsci.2012.01.011>
12. M. La Cerva, L. Gurreri, M. Tedesco, A. Cipollina, M. Ciofalo, A. Tamburini and G. Micale, *Desalination*, **445**, 138 (2018); <https://doi.org/10.1016/j.desal.2018.07.028>
13. G.S. Luo, S. Pan and J.G. Liu, *Desalination*, **150**, 227 (2002); [https://doi.org/10.1016/S0011-9164\(02\)00978-5](https://doi.org/10.1016/S0011-9164(02)00978-5)
14. E. Güler Akgemci, M. Ersöz and T. Atalay, *Sep. Sci. Technol.*, **39**, 165 (2005); <https://doi.org/10.1081/SS-120027407>
15. B. Sheth and K. Nath, *Korean J. Chem. Eng.*, **35**, 1878 (2018); <https://doi.org/10.1007/s11814-018-0091-z>
16. H. Strathmann, *Ion Exchange Membrane Separation Processes*, Elsevier, edn 1 (2004).
17. B. Sheth and K. Nath, *Chem. Eng. Commun.*, **207**, 295 (2020); <https://doi.org/10.1080/00986445.2019.1587611>
18. H. Iken, R. Basseguy, A. Guenbour and A.B. Bachir, *Electrochim. Acta*, **52**, 2580 (2007); <https://doi.org/10.1016/j.electacta.2006.09.013>
19. R.K. Nagarale, G.S. Gohil and V.K. Shahi, *Adv. Colloid Interface Sci.*, **119**, 97 (2006); <https://doi.org/10.1016/j.cis.2005.09.005>
20. S. Koter, M. Kultys, B. Gilewicz-Lukasik and I. Koter, *Desalination*, **342**, 75 (2014); <https://doi.org/10.1016/j.desal.2013.10.025>
21. N. Zouhri, *Am. J. Appl. Chem.*, **1**, 75 (2013); <https://doi.org/10.11648/j.ajac.20130104.15>
22. J. Kroupa, J. Kincl and J. Cakl, *Desalination Water Treat.*, **56**, 3238 (2015); <https://doi.org/10.1080/19443994.2014.980972>
23. V. Baltazar, G.B. Harris and C.W. White, *Hydrometallurgy*, **30**, 463 (1992); [https://doi.org/10.1016/0304-386X\(92\)90100-E](https://doi.org/10.1016/0304-386X(92)90100-E)
24. Y. Lorrain, G. Pourcelly and C. Gavach, *Desalination*, **109**, 231 (1997); [https://doi.org/10.1016/S0011-9164\(97\)00069-6](https://doi.org/10.1016/S0011-9164(97)00069-6)
25. H.E. Darling, *J. Chem. Eng. Data*, **9**, 421 (1964); <https://doi.org/10.1021/je60022a041>
26. Y. Asari, N. Shoji, K. Miyoshi, D. Umeno and K. Saito, *J. Ion Exchange*, **22**, 53 (2011); <https://doi.org/10.5182/jaie.22.53>
27. L. Cifuentes, I. Garcia, R. Ortiz and J.M. Casas, *Sep. Purif. Technol.*, **50**, 167 (2006); <https://doi.org/10.1016/j.seppur.2005.11.021>