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Application of an electrodialysis process to recover nitric acid from aluminum finishing industry waste

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ABSTRACT

In this study, experiments were conducted with a conventional electrodialysis (ED) process to recover nitric acid from rinsing-wastewater originated in the aluminum finishing industry. A laboratory-scale ED cell was used, and the optimal operating conditions and parameters were defined in these tests. Five different external voltages (10, 15, 20, 25, and 30 V) were applied to the ED system to determine the appropriate potential difference. Conductivity, pH, acidity, and quality of recovered nitric acid were monitored continuously. The maximum conductivity removal was achieved as 90% when the potential difference was applied as 25 V. The efficiency of the ED process was calculated through current density, energy consumption, etc. The specific energy consumption was calculated as 0.11 kWh/mol when the potential was adjusted to 15 V. Applicability of the method for recovery of nitric acid was examined. With the aim of zero pollutant emissions, the ED process might be of significant interest to the aluminum industry, providing a closed-loop acid usage in aluminum anodizing process, reducing the environmental and economic burdens.

Keywords: Aluminum industry; Nitric acid recovery; Electrodialysis process; Rinsing wastewater

1. Introduction

The aluminum anodizing process is among the most extensively used surface treatment processes. The process is used for improving appearance, aesthetics, and abrasion resistance, and it also helps in preventing corrosion. Elements such as copper, manganese, and silica in aluminum cause black stain on the surface of the aluminum profiles during etching or chemical polishing processes with caustic. After caustic baths, the aluminum is cleaned in 30%–50% nitric acid baths to remove those stains. Nitric acid bath needs to be replaced periodically as the concentration of impurities such as aluminum and other additivities increase in time. Disposal of nitric acid baths' effluent, to the environment, is hazardous due to the high concentration level of nitrate, acidity, and aluminum present in the waste acid. The extensively applied disposal method for a spent nitric acid stream is the discharge to sanitary sewer system after neutralization with caustic. However, the cost of neutralization and the amount of sludge production are significantly high in this process. Moreover, the disposal of the spent acid solutions causes the loss of valuable raw materials [1]. Solvent extraction is another standard method used for the recovery of raw materials from waste acid streams [2–4]. Electromembrane processes, including membrane electrolysis, electrodialysis (ED), and diffusion dialysis, are extensively being studied for the recovery of acid and base from acidic and alkaline waste streams [5,6]. The ED is the ion separation process from an ionic solution into a concentrated stream through ion exchange membranes under the influence of the electrical

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area. The ED process is used in a wide range of fields such as salty textile wastewater treatment [7], the food industry for pH correction [8], acid recovery [9], etc.

Chavan et al. [10] have studied diffusion dialysis with a hybrid anion-exchange membrane for the recovery of nitric acid from the acidic waste stream and achieved 90% recovery efficiency. Since the studies in the literature focus on the treatment of nitric acid baths, there was little information about the treatment of rinsing-wastewater originated in aluminum finishing processes. Aluminum is rinsed with deionized water after being immersed in a nitric acid bath to remove residual nitric acid from the surface. The rinsing wastewater contains nitric acid and aluminum ions; thus it requires treatment before being discharged to the environment or the sewage system. Zhuang et al. [11] have studied the recovery of waste acid that originates from the foil industry through the use of diffusion dialysis and ED with bipolar membranes. They have reported that the process reduces the environmental effect of the foil industry and enables cost-effective and sustainable production for the foil industry. Zhang et al. [12] have integrated diffusion dialysis and conventional ED process to recover HCl from simulated chemosynthesis aluminum wastewater. They have achieved a 74.9% acid recovery ratio while the aluminum leakage ratio was 12.2% with 0.41 kWh energy consumption. On the other hand, diffusion dialysis and ED processes can be applied for the recovery of alkaline solutions in the aluminum industry. Yan et al. [6] have used diffusion dialysis and ED processes to treat alkaline solutions generated in the aluminum industry and achieved OH^- recovery ratio and $Al(OH)_4^-$ ratio 6.3% and 0.6%, respectively.

In this study, it is aimed to recover water and nitric acid from rinsing wastewater by using the ED process. In the ED process, the ion exchange membrane allows only the transfer of proton and nitrate and other metal ions remain in the influent stream. The pH of the influent stream increases through the removal of the acid and metal ions start to settle down with the formation of metal hydroxide solids. After the settling process, the supernatant may be used again at the rinsing process and also the recovered nitric acid can be added to a nitric acid bath.

2. Material and methods

In this study, rinsing-wastewater solutions -which contain nitric acid and aluminum ions- that was originated from an aluminum anodizing industry have been treated by using the ED process to recover nitric acid and water. Water quality parameters such as acidity, electrical conductivity, and pH were monitored inside the rinsing-wastewater according to standard methods [13]. Rinsing-wastewater solutions were brought to the laboratory from an aluminum industry located in Kocaeli-Turkey. Samples were analyzed to determine acidity and metal ion concentration. Then, the solution is filtered from a cartridge filter to remove suspended solids within the sample. Finally, samples were treated with the ED process.

2.1. ED unit

The laboratory-scale ED unit has been purchased from Pccell Company founded in Germany. Specifications of the ED unit, electrodes, and ion exchange membranes are given in Table 1. Anion exchange membranes (PC Acid 60) and standard cation exchange membranes (PC-SK) were used. Spacers were installed between two ion-exchange membranes to facilitate liquid flow. A schematic diagram of the ED system is given in Fig. 1. Voltage was kept constant by using the direct current (DC) power supply for all batch experiments since conductivity decrease in the waste acid compartment during operation causes a current drop. Flow rates of the solutions were adjusted between 4–8 L/h with centrifugal pumps. Pressure gauges were mounted to pipelines to control transmembrane pressure and keep it at zero.

Dilute nitric acid (0.1 M) solution and waste HNO_3/Al^{3+} stream were supplied between cation and anion exchange membranes, as shown in Fig. 2. The dilute HNO_3 aims to supply conductivity in the concentrate compartment, and the conductivity of the 0.1 M HNO_3 is measured about 4.5 ms/cm. H^+ and NO_3^- ions transferred to concentrate acid compartments while Al^{3+} ions remained in the waste acid compartments and left the ED unit with a dilute solution. In continuous experiments, the ion-exchange membranes were removed from the reactor and rinsed with the deionized water to clean the membrane surface.

2.2. Measurements

Electrical conductivity and pH changes in waste and concentrate acid compartments were monitored continuously using Hach SC1000 multimeter (Düsseldorf, Germany). Current and voltage values from the DC power supply were also saved on the computer. Samples were collected from waste and concentrate in intervals of time to monitor Al^{3+} concentrations, which were measured by using test kits in the UV-Vis spectrophotometer (HACH DR5000, Düsseldorf, Germany). The acidity of the samples was determined by using 0.1 N NaOH according to Standard Methods 2310 Acidity method [13]. The concentration of H^+ was analyzed by titration with a calibrated Na_2CO_3 solution in the presence of methyl orange as an indicator.

2.3. Energy consumption and operating cost

The significant portion contributing to the operating cost of an ED treatment process arises from energy expenses. Maintenance and labor costs, which are proportional to the size of ED treatment plants, should also be considered during the calculation of the overall operating cost. In an ED process, energy costs include energy consumption for pumping and

Table 1
ED unit specifications

Membrane size	110 × 110 mm
Active membrane area	64 cm^2 per membrane
Anode	Pt/Ir-coated titanium
Cathode	V4A steel
Electrode housing material	Polypropylene
Maximum current	5 A
Maximum voltage	30 V/cell
Nominal flow rate	4–8 L/h

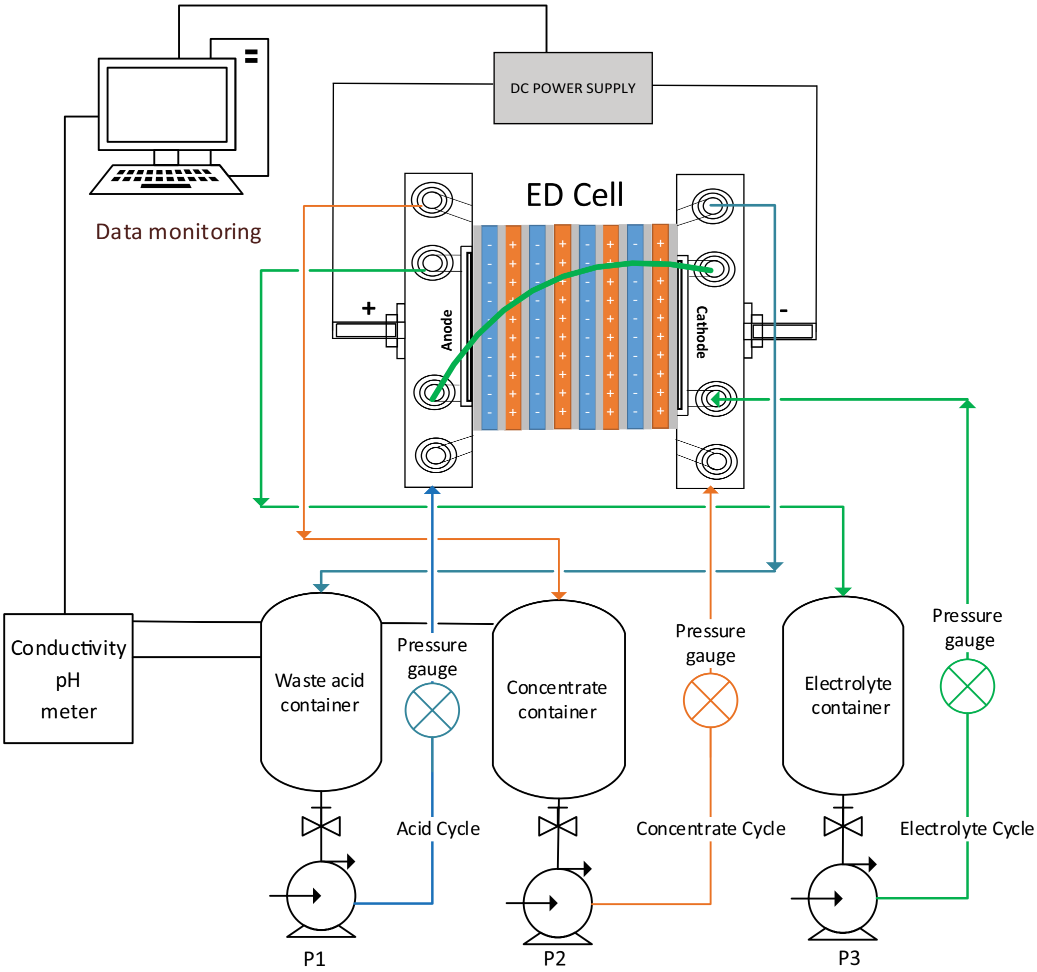

Fig. 1. Schematic representation of the batch electrodialysis process.

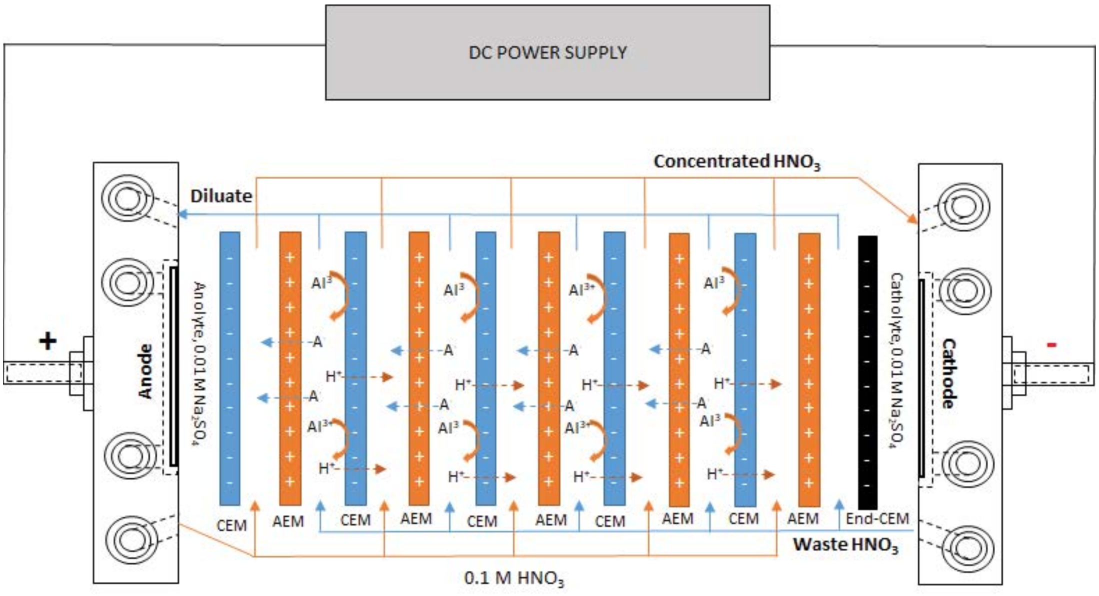

Fig. 2. Schematic representation of the ED cell configuration for recovery of waste acid. (CEM: cation exchange membrane, AEM: anion exchange membrane, End-CEM: end cation exchange membrane, A-: anion (NO_3^-etc.).

energy for transferring ions from the dilute compartment to concentrate compartment through ion-exchange membranes. Energy consumption of the ED process was calculated according to the following equations [14];

$$E_{\text{req}} = U \cdot I \cdot t \tag{1}$$

In Eq. (1) E_{req} is the required energy (kWh), U is the voltage of the cell (V), I is the current (A), and t is the processing time (h).

$$E_{\text{spe}} = \frac{E_{\text{req}}}{n_{\text{acid}}} \tag{2}$$

In Eq. (2) E_{spe} is the specific energy consumption (kWh/mol acid), n_{acid} is the mole of acid in the concentrate compartment.

3. Results

In this study, five different potential differences were applied to the ED process to find out appropriate voltage by comparing the change in conductivity values of rinsing-wastewater in time. In the first step of the ED process, nitric acid containing rinsing-wastewater was fed to the system, and the acid concentration was increased in the concentrate compartment while it was decreasing in the dilute compartment. During the treatment process, continuous measurement of pH and electrical conductivity was performed to monitor change in acid concentration. The results obtained from these measurements are being discussed in this section.

3.1. Nitric acid recovery

The first set of experiments for the treatment of rinsing-wastewater were conducted by applying 30 V potential to the ED unit, then the experiments were repeated by decreasing potential 5 V after each test. The initial electrical conductivity value of the rinsing-wastewater was recorded as 90 mS/cm, and it was reduced to 7.7 mS/cm in 20 min when 30 V potential was applied (Fig. 3a). The decrease in conductivity of the rinsing-wastewater was calculated as 91% for 30 and 25 V potentials, and 86% of the other applied potentials. The processing time increased with decreasing applied potential. However, the processing time needed for reducing the electrical conductivity of the rinsing-wastewater was recorded as minimum value when 25 V potential difference was applied (Fig. 3a). It can be said that the limiting current density value for the ED system exceeded when 30 V applied and the processing time increased after 25 V due to the higher resistivity. Regarding the change in electrical conductivity values, a similar trend with the dilute compartment was seen in the concentrate compartment (Fig. 3b). The increase in conductivity of the concentrate compartment was mainly caused by nitric acid arising from the rinsing-wastewater. However, some Al^{3+} ions leaked from the dilute compartment to the concentrate compartment and increased the conductivity of the concentrated acid solution. The conductivity of the concentrate acid solution reached to maximum of 71 mS/cm when the applied potential was adjusted to 15 V. The lowest conductivity value of the concentrate acid solution was recorded as 55.9 mS/cm when 30 V was applied to the ED unit. It is possible to increase the concentration of the concentrated acid solution by keeping the same solution at the concentrate container while treating rinsing-wastewater in continuous flow. Experiments were conducted to examine maximum acid concentration that can be obtained with the ED process, and the results are given in section 3.2.

While high ion and organic concentrations in wastewater may cause membrane clogging, low ion concentrations may cause excessive energy consumption. Varying mobility between anions and cations causes differences in resistance of membranes [15]. Larger anions exhibit lower mobility, which results in higher resistance when passing through the membrane. This is the reason why the voltage at the anion-exchange membrane is higher than at the cation-exchange membrane, where inorganic cations will find less resistance for crossing the membranes [16]. The organic content of the

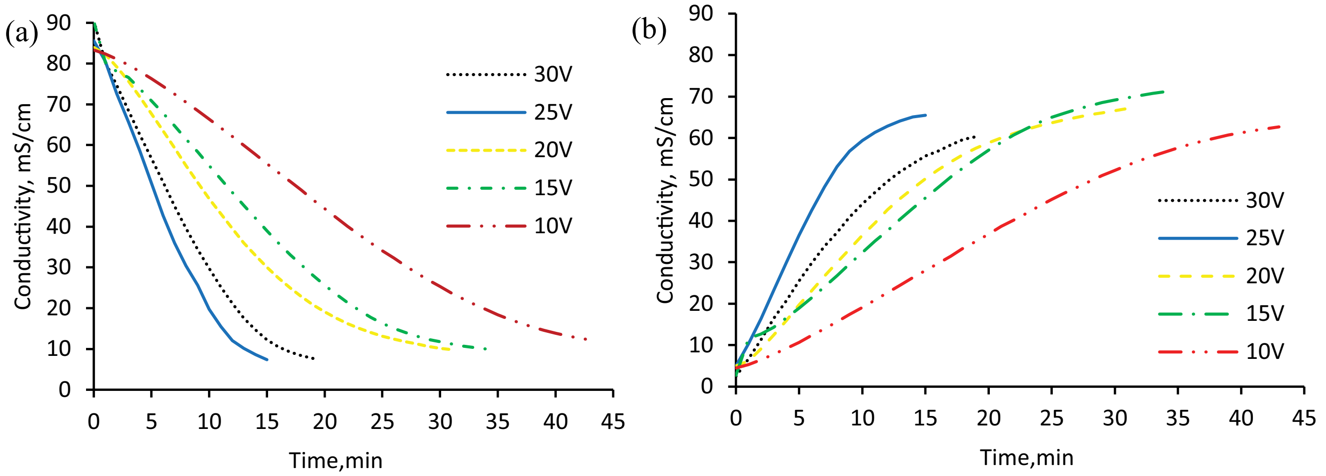

Fig. 3. Graphs of conductivity vs. time for the ED studies under various applied potential differences; (a) the dilute compartment and (b) the concentrate compartment.

wastewater generated from the aluminum industry is very low, and the mobility of H^+ ions is high. Thus, after optimum reaction time in which over %90 acid was recovered, the rapid increase in the cell resistance was attributed to decreasing conductivity and remaining aluminum concentration in the dilute during the ED treatment.

The acidity of the rinsing-wastewater was measured as 4,085 mg/L $CaCO_3$, and the acidity values of effluent solutions after the ED process are given in Fig. 4a. The acidity of the rinsing-wastewater decreased to 2,250 mg/L $CaCO_3$, which means 45% of the acid was recovered.

As the applied potential of the ED process decreased, the removal of the acidity decreased. This can also be seen in Fig. 3a. On the other hand, no relation was observed between the applied potentials and concentrations of recovered acid (Fig. 4b). The higher acid concentrations that were obtained in the concentrate compartment were caused by the dissociation of water at the surface of the anion exchange membrane. The high resistivity of the system caused dissociation due to the over limiting current density [17].

The color of the rinsing-wastewater solutions turned to yellow during the operation of the ED process. It is known that the color of the nitric acid turns yellow with the presence of NO_2 in the solution. The color change of the rinsing-wastewater was attributed to the formation of NO_2 by the reduction of NO_3^- with the influence of the electricity. The absorbance values of the rinsing-wastewater and the effluents of the dilute compartments are given in Fig. 5.

The absorbance value of a solution caused by yellow color should be determined by adjusting the wavelength between 565–590 nm. It is clear from Fig. 5 that almost the same reduction degree of NO_3^- achieved and the applied voltage did not affect the formation of NO_2 in the rinsing-wastewater. However, the absorbance values of the solutions under different applied potential values were different from each other due to the concentration of dissolved metal salts within the solutions, and no correlation was found between the applied potential and absorbance values.

3.2. Concentrating acid in the ED process

In the aluminum industry, the acid and water should be separated to get concentrated acid and desalinated wastewater for recycling the acid and water in the anodizing and anodizing rinsing processes. The nitric acid concentration in the ED brine should be increased because higher acid concentration is required in the nitric acid bath. Without the reuse of acid and alkali solutions, it is not possible to reach a circular economy concept in the aluminum industry. The dilute of the ED can be recycled as make-up water in the baths as conductivity up to 200 mS/cm is acceptable in the rinsing process. To increase the acid concentration in the concentrated cell, the wastewater of the standing mixed rinsing baths is continuously treated with the ED, where the concentrate can be led into the process bath due to the high concentration. For this purpose, the ED bench reactor system was run with 0.5 L of nitric acid rinsing-wastewater without discharging the concentrated acid solution to get higher HNO_3 concentration in the concentrated cell. When the conductivity reached the set final value of 8 mS/cm, dilute was replaced with a 0.5 L raw waste acid solution, and this step was repeated for nine cycles.

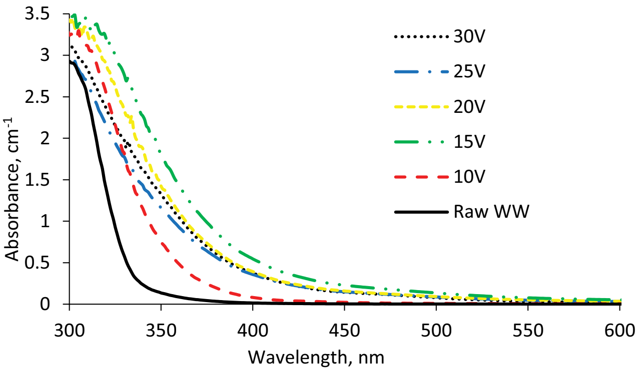

Fig. 5. Absorbance values of rinsing-wastewater and effluents of the dilute compartment in the ED process under different applied potentials.

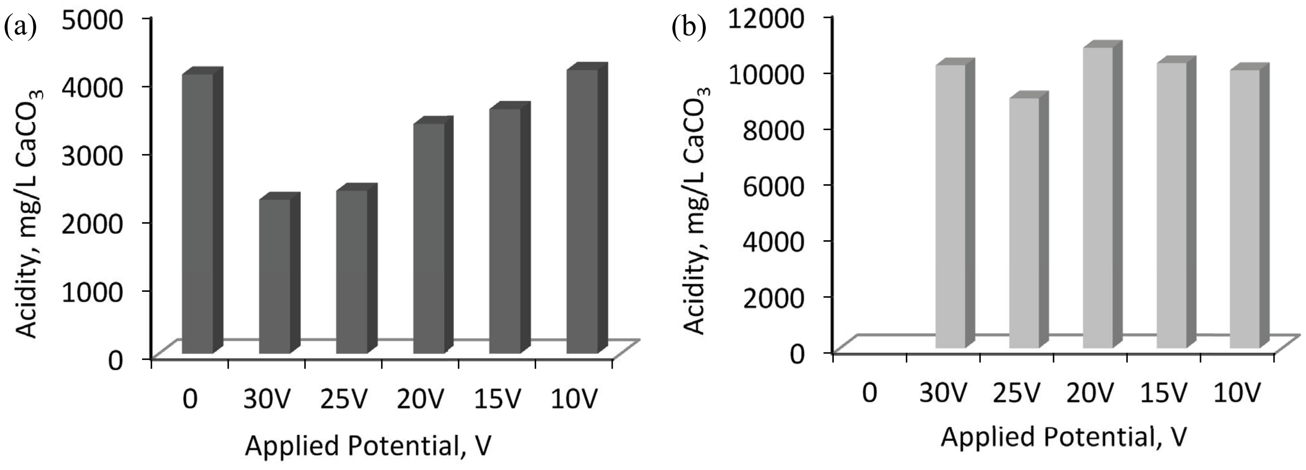

Fig. 4. Graphs of acidity vs. the applied potential for (a) the dilute compartment and (b) the concentrate compartment.

As previously reported, the product was almost demineralized after 20 min and the same pH, the conductivity and the current intensity profiles were observed in time during the first two cycles, and about 80% of nitric acid was recovered in the reused brine. The conductivity of the nitric acid reached 330 mS/cm as given in Fig. 6. The acid concentration in the brine increased at each cycle but the required time to reach 8 mS/cm is increased after the 3rd cycle. The extending period in the ED system was attributed to increasing pH level, and high Al^{3+} concentration in the dilute solution as inorganic alum may cause fouling on the cation exchange membrane even at pH 3. In the fifth cycle, the processing time reached to the maximum level (130 min.) then the ion exchange membranes were removed from the reactor and rinsed with deionized water to clean the membrane surface. The effect of the cleaning process is seen at the sixth cycle as the processing time decreased to 47 min.

The current density values started at 60 and 80 mA/cm^2 for the first and second cycles, respectively (Fig. 7). After the second cycle, the current density started at 20 mA/cm^2. The sharp decrease in current density values was attributed to the clogging caused by Al^{3+} ions, which precipitated on the membrane surface. Furthermore, the time required for one cycle has increased.

3.3. Energy and current density calculations

Applied external voltage closely correlates to system energy requirements. Thus, the current density and resistance across the cell, which is determined by the concentration and composition of the waste acid liquor, become important parameters along with treatment time. Fluctuating current densities were observed during the ED treatments due to the uncontrolled temperature in the cell (Fig. 8). It can be seen that at higher voltage, higher current density was achieved, and consequently, the time needed to achieve target conductivity value decreased.

The specific energy consumption of the ED process is given in Fig. 9. The specific energy consumption increased after 15 V potential difference and reached its maximum value when 25 V was applied to the ED system. According to the specific energy consumption of the ED process, the optimum applied potential was calculated when the applied potential was adjusted to 15 V.

4. Conclusion

In this study, the ED process was used for the recovery of waste acid, -that originates from aluminum anodizing

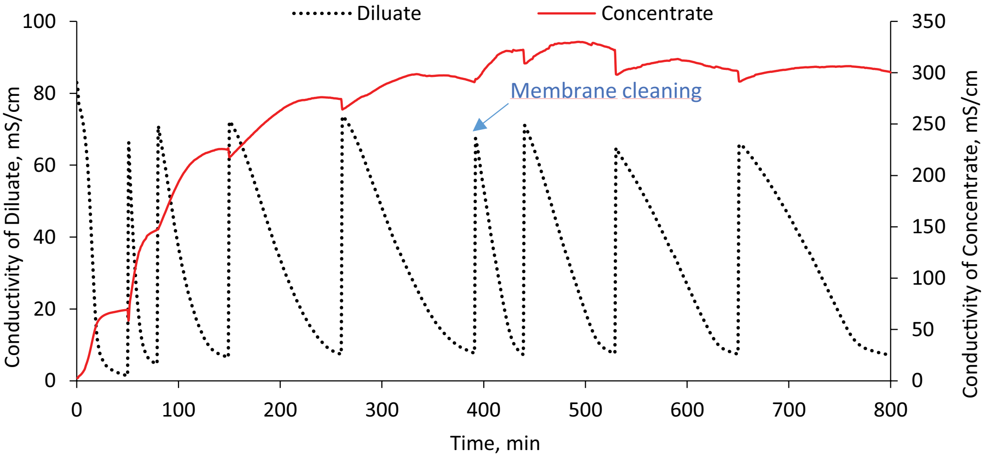

Fig. 6. Change in conductivity of concentrate and dilute compartments. The ED system was run with the same concentrate solution while the dilute solution was replaced when it reached to 8 mS/cm of conductivity value (The applied potential was 25 V).

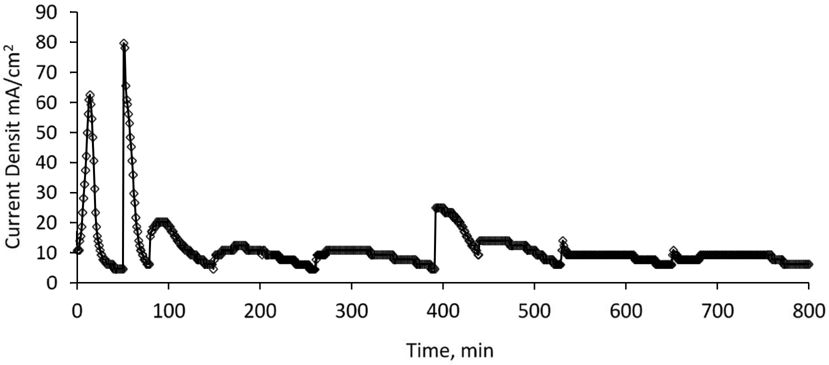

Fig. 7. Current density values for the continuous operation of the ED system without changing the concentrate compartment.

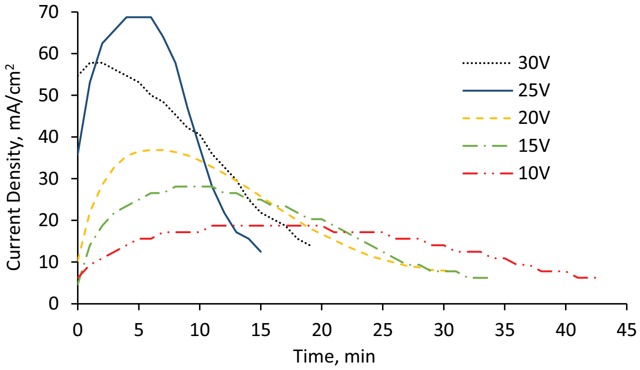

Fig. 8. Current density values for the continuous operation of the ED system without changing the concentrate compartment.

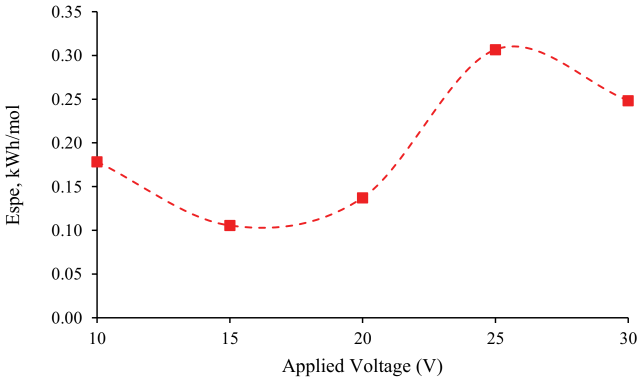

Fig. 9. Specific energy consumption of the ED process under applied potentials (10–30 V).

washing-scouring baths- to close to loop for economic and environmental benefits. The ED system recovered most of the waste nitric acid, and the effects of operational conditions were established for a better understanding of the ED process. Applied potential was optimized to maximize the productivity, which is adopted in a real system. Over 80% of acid recovery was achieved for all applied potentials. Increasing the applied potential decreased the treatment time; however, 20 V applied potential was found to be optimum in terms of the treatment time and energy consumption. The conductivity was set in the ED system for the recovery of the waste acid in a continuous cycle, the alum precipitation was observed on the membrane surface, and the desalination time to reach target conductivity increased after the 3rd cycle.

Considering acid and water recoveries results indicate that the application of the ED system for recovery and reuse of dilute acid wastes is efficient in addition to the environmental benefits. The continuous operations here indicate that the ED system can convert the waste acids to valuable concentrated nitric acid and clean water which are resulting in zero pollutant discharge in the aluminum industry.

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