The electrochemical investigation of salts partition with ion exchange membranes

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A B S T R A C T

The regenaration of acid and base from the solutions containing metallic salts was achieved by salt splitting method (SSM) using not only anion-exchange membranes (AEM) but also cation-exchange membrane (CEM). In these experiments, while the ion exchange membrane was anion-exchange membrane, acid solutions were used as an anolyte and different salts of potassium were used as a catholyte. In addition to these experiments, while the ion exchange membrane was cation-exchange membrane, base solutions were used as a catholyte and different salts of potassium were used as an anolyte. The effects of current density, initial concentrations of anolyte and catholyte solutions, the type of salt solution and the type of the ion-exchange membranes on the recovery ratio of bases and acids were investigated. The results of the experiments were investigated with the Statistical Package for Social Sciences (SPSS) program. The obtained results show that this technique can be used not only for recovering the acid and base wastes of industry but also for removing the impurities in order to obtain pure acids and bases in laboratory conditions.

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1. Introduction

An increasing world population with growing industrial demands has lead to the situation where the protection of the environment has become a major issue and crucial factor for the future development of industrial processes, which will have to meet the requirements of sustainable development. Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. The inherent advantage is its environmental compatibility, due to the fact that the main reagent, the electron, is a 'clean reagent'. The strategies include both the treatment of effluents and waste and the development of new processes or products with less harmful effects, often denoted as process-integrated environmental protection:

- *Cathodic and anodic treatment of effluents and waste*: this includes all techniques where toxic material is removed from gases, liquids or even solids at the final stage of an industrial process.
- *Process-integrated environmental protection*: this includes recycling of valuable material and substitution of waste-producing processes by a cleaner electrochemical technology with little or no waste production.

Removal and destruction of pollutant species can be carried out directly or indirectly by electrochemical oxidation–reduction processes in an electrochemical cell without continuous feed of redox chemicals. In addition, the high selectivity of many electrochemical processes helps to prevent the production of unwanted by-products, which in many cases have to be treated as waste [1].

There are attractive advantages of electrochemical processes such as versality, energy efficiency, amenability to automation and cost effectiveness. For this reason, the applications of electrochemistry for the protection of the environment have already been the topic of several books and reviews [2–9]. Among these applications, especially the treatment of spent acids containing metallic salts concerns several industries such as pickling and surface treatment. As a possible alternative, membrane technology is progressively replacing traditional techniques such as distillation, evaporation and pyrolysis, allowing acids to be reconcentrated with relatively low membrane areas [10]. For this reason, today various kinds of separation membranes have been widely studied and utilized industrially in various fields. The purpose of membrane research is to separate specific components from their mixture efficiently [11]. For example, as a membrane technology, electrodialysis (ED) is an attractive technique not only for treating waste acids [12] but also has found industrial use in such diverse applications as brackish water desalination [13], corn sugar solution demineralization, photographic emulsion preparation, radioactive solution concentration [14] and heavy metal recovery from plating rinse waters [15].

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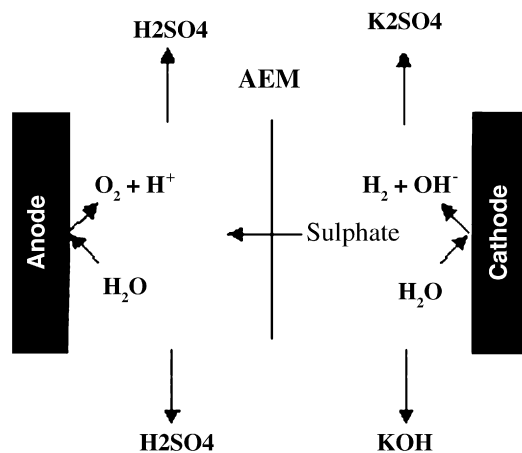 *E-mail address:* yoztekin@gmail.com (Y. Oztekin).

Fig. 1. The diagram used for electrohydrolysis experiments with AEM.

These methods are being replaced by membrane techniques such as electrohydrolysis (EHD), which has already been used for the treatment of heavy metal contaminated acids or electro-membrane techniques which allow acids to be concentrated with relatively low membrane areas [16].

Salt splitting is new technology dependent on the availability of modern membranes and EHD process. The process of salt splitting is a potentially important use for electrochemical technology [17]. The electrochemical splitting of salts by EHD to their original constituents is highly desirable to minimize chemical consumption and effluent treatment costs and to enable re-use of acids and bases [18].

Figs. 1 and 2 show a schematic diagram of a typical EHD cell employing a anion-exchange membrane (AEM) and cation-exchange membrane (CEM), respectively. In the first diagram, according to the applied potential, anions of salt solution transport to anolyte solution via the AEM where they combine with the hydrogen ions to increase the concentration of acid solution. In the cathode chamber there are some uncomplexed potassium ions because of the migration of their anions. These cations combine with the hydroxyl ions to form KOH. But in the second diagram, due to the potential difference, potassium ions migrate through the CEM towards the catholyte where they combine with the hydroxyl ions to form KOH. The uncomplexed sulphate ions (nitrate or chloride) combine with the protons to form H_2SO_4 (HNO_3, HCl). Both of these diagrams can compare for the performance of ion exchange membranes for salt splitting.
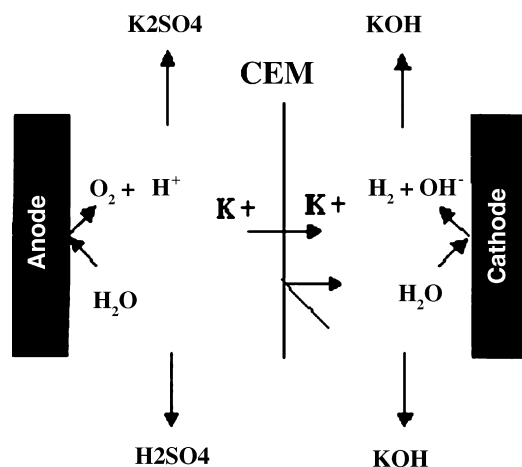

Fig. 2. The diagram used for electrohydrolysis experiments with CEM.

This paper reports data for the EHD of different salt forms of potassium with three types of commercial anion and cation-exchange membranes as functions of current density, initial concentrations and type of salt solution.

2. Experimental

2.1. Apparatus, membrane and solutions

The apparatus for EHD experiments is illustrated in Figs. 1 and 2, which is made from polyamide. Two chambers were attached by means of inserting two screws on their flanges with an/a AEM/CEM in between. The membrane was cut as a circle with a diameter of 30 mm and glued into the inner mounting wall of the two chambers with silicone rubber sealant to prevent any leakage between the chambers. The electrodes were fitted in the inner wall of apparatus and were symmetrically separated about 65 mm from the membrane surface. A stainless steel and Pt were used as a cathode and anode, respectively, and their active dimensions were 30 mm. The power supply used in experiments was capable of supplying a potential of up to 32 V and a direct current (DC) of up to 2 A. Three commercial AEMs (AHA, ACM and AMH) selected in this study were produced by the Japanese firm Tokuyama Soda Co. Ltd. and kindly supplied from Eurodia Co. and the CEMs selected in this work were CMB, CMS, CMX offered from Eurodia Co. Their main characteristics of the AEMs and CEMs are listed in Tables 1 and 2, respectively [19]. To ensure that the cation exchange membranes were initially in a proton form for this reason, the following steps were conducted for all membrane samples (7065 cm^2): Prior to use, all CEMs were treated with distilled water at 70 °C for 1 h, 0, 1 M HCl and 0.1 M NaOH at 50 °C for 1 h, respectively, to remove inorganic impurities. The resulting membranes were finally immersed in 1 M HCl solutions to transform membranes to their hydrogen form for 24 h. For the AEMs, all the initial three preparation steps are the same with CEMs except the fourth one that is the last immersion step. As a difference from CEMs, resulting AEMs are finally immersed in 1 M NaCl solutions to transform membranes to their chloride form for 24 h.

2.2. Experimental procedures and chemical analysis

An equal volume (250 mL) of the anolyte and the catholyte solution was filled in the respective chamber. The cathode chamber contained various salts of potassium ion having different concentration and the anode chamber contained acid solution for AEM experiments but base solution in cathode chamber and salts of potassium in anode chamber for CEM experiments having different type and concentration were chosen. The experiments were carried out at the constant current by changing the cell voltage according to the variation of the current. A stirring speed was adjusted as 500 rpm. Samples were taken at time intervals (for 15 min) from the cathode chamber for both of the experiment types to determine the base regeneration. The concentration of base was determined by titration using H_2SO_4 solution in the presence of brominethimol blue indicator. Each experiment was duplicated under identical conditions for 2 h. The results of the experiments were investigated with the Statistical Package for Social Sciences (SPSS) program in order to determine the statistical differences between the mathematical values of our results.

Analytical reagent grade KOH, K_2SO_4, KNO_3, KCl, H_2SO_4, HNO_3 and HCl were obtained from Merck Co. The anolyte and catholyte solutions were prepared by dissolving required concentrations of forms in deionized water.

Table 1
The properties of AEM

Membrane	AHA	AMH	ACM
Type	Strongly basic anion permeable	Strongly basic anion permeable	Strongly basic anion permeable
Form	Cl^-	Cl^-	Cl^-
Ion exchange capacity (mequiv./g)	0.5–3.0	1.3–1.5	1.4–1.7
Thickness (mm)	0.18–0.24	0.26–0.28	0.11–0.13
Characteristics	High mechanical strength	High mechanical strength	Low H^+ transport
Water content (%)	13–20	17–22	18–31

Table 2
The properties of CEM

Membrane	CMB	CMS	CMX
Type	Strongly acidic cation permeable	Strongly acidic cation permeable	Strongly acidic cation permeable
Characteristics	High mechanical strength (Na form)	Mono-cation permselective (Na form)	High mechanical strength (Na form)
Functional groups	Polysulphone	Polysulphone	Polysulphone
Electric resistance	2.5–6.0	1.5–3.5	1.8–3.8
Thickness (mm)	0.18–0.25	0.12–0.17	0.14–0.20
Burst strength	≥ 0.40	≥ 0.10	≥ 0.40

3. Results and discussion

3.1. Reactions involved in the electrolysis cell

The electrochemical splitting of potassium sulphate into sulphuric acid by electrohydrolysis (EHD) can be represented by the general reaction:

$$K_2SO_4 + 2H_2O \rightarrow H_2SO_4 + 2KOH \tag{1}$$

Electrohydrolysis is a process that combines selective ion transport through an ion-exchange membrane and electrochemical reactions at the electrodes. The anodic oxidation of water generates protons and oxygen [20]:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \tag{2}$$

The cathode reaction generates hydroxyl ion and hydrogen from water:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \tag{3}$$

The hydrogen and oxygen evolution reactions are potentially desirable by-products. Figs. 1 and 2 show schematic diagrams of a typical two-compartment EHD cell. As it was understood from these figures, according to the potential applied to the EHD cell; anions of salt solution transport to anolyte solution via the AEM where they combine with the hydrogen ions to increase the concentration of acid solution. By the way of this transportation in the cathode chamber some uncomplexed potassium ions formed because of the migration of their anions. These cations combine with the hydroxyl ions to form KOH. But in the diagram of CEMs, due to the potential difference, potassium ions migrate through the CEM towards the catholyte where they combine with the hydroxyl ions to form KOH. The uncomplexed sulphate ions (nitrate or chloride) combine with the protons to form H_2SO_4 (HNO_3, HCl). Both of these diagrams can compare for the performance of ion exchange membranes for salt splitting.

3.2. Equations used for calculations in the EHD experiments

The current efficiency relates the performance of a process to a theoretical maximum, and is therefore extremely useful for process evaluation. The current efficiencies, Φ, for potassium ion transport were calculated from:

$$\Phi = \left(\frac{nFV}{It} \right) \Delta C \tag{4}$$

where n is the number of electrons transferred, F the Faraday constant (96484.5 c/mol), V the volume of the electrolyte (dm^3), ΔC the change in concentration (mol/dm^3), I the electric current (A) and t is the time interval (s).

The potassium ion flux or permeation rate (J_K^+) expressed as equiv. $m^{-2} s^{-1}$, and transport number (t_K^+) were determined from:

$$(J_K^+) = \frac{(n_K^+)_{t+\Delta t} - (n_K^+)_t}{A . \Delta t} \tag{5}$$

where n_K^+ is the number of moles of potassium (mol) and A is the actual area of membrane (m^2).

3.3. Effect of current density on EHD

The various experiments were performed using 0.1 M H_2SO_4 solution and 0.1 M K_2SO_4 as an anolyte and a catholyte solution, respectively, in the cell of separating with ACM membrane to determine the effect of the current density to transport of sulphate ions due to this fact formation of bases in cathode chamber. For this reason, current densities such as 10 mA, 15 mA and 20 mA were applied to the cell of EHD. The results obtained from these experiments are demonstrated in Fig. 3. As it is known; EHD is an electrochemical
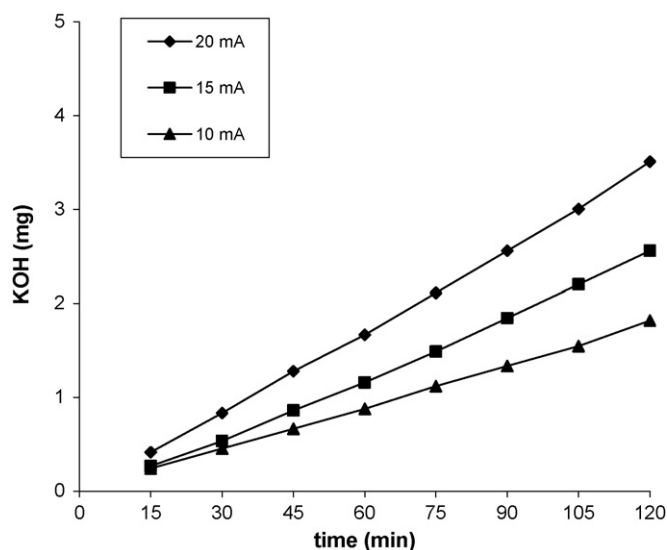
Fig. 3. The effect of current density on EHD for AS: 0.1 M H_2SO_4, CS: 0.1 M K_2SO_4 and AEM: ACM.

Table 3
ANOVA table of current density effect (tests of between-subjects effects, dependent variable: mgbase)

Source	Type III sum of squares	d.f.	Mean square	F	p-Value
Corrected model	17.243[a]	9	1.916	28.321	.000
Intercept	48.992	1	48.992	724.202	.000
Current density	3.444	2	1.722	25.452	.000
Time	13.800	7	1.971	29.141	.000
Error	.947	14	.068		
Total	67.182	24			
Corrected total	18.190	23			

F: result of *F*-test statistics; d.f.: freedom of degree; *p*-value: probability value

[a] $R^2 = .948$ (adjusted $R^2 = .914$).

separation process in which mineral salts and other ionic species are transported through ion selective membranes from one solution into another under the driving force of a direct current and when a DC voltage is applied, the electrical potential created becomes the driving force to move ions, with the membranes forming barriers to ions of opposite charge. As a result of this explanation and as it is seen in Fig. 3; the concentration of base, occurred in the cathode chamber increased with increasing the current density which was applied to the cell during the experiment in the order of 20 mA > 15 mA > 10 mA. These experiments were occurred with three different current density in eight different time section because of this it was thought that not only current density but also time could effect the base and acid formation in the chambers and as a result of this opinion two-way ANOVA was applied to the values. The statistical values of this part of this study are given in Tables 3 and 4. If Table 3, called ANOVA table, is investigated, it can be seen that group averages are different from each other with the important level on the account of possibility value in terms of current density is smaller than the selected trip level ($p = 0 < \alpha = .05$). It means that according to the current density values as 20 mA, 15 mA and 10 mA, group averages are different from each other statically. If the values are investigated in terms of time, the same comments are valid and possibility value in terms of time is smaller than the selected trip level ($p = 0 < \alpha = .05$) because of this group averages due to 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min are accepted different from each other with the important level. The differences in the group average of current density in terms of mg base measurement were explained with the two-way ANOVA method. In order to determine which of them are different from each other, among the multiple comparison testes, Tukey's honest significant difference test (Tukey's HSD test) were used. The differences between the values were supported with the multiple comparison table which is given as Table 4 ($p = .002 < \alpha = .05$, $p = 0 < \alpha = .05$, $p = .035 < \alpha = .05$).

This alignment and the comments are the same for the CEMs experiments. The concentration of acid occurred in the anode chamber and the concentration of base occurred in the cath-

Table 4
Multiple comparison table of current density effect (dependent variable: mgbase, Tukey HSD)

| Current density, I (mA)	Current density, J (mA)	Mean difference, $I - J$	S.E.	p-Value
20	15	.5563*	.13005	.002
	10	.9213*	.13005	.000
15	20	−.5563*	.13005	.002
	10	.3650*	.13005	.035
10	20	−.9213*	.13005	.000
	15	−.3650*	.13005	.035

Based on observed means.

* The mean difference is significant at the .05 level.

ode chamber increased with increasing the current density which was applied to the cell during the experiment in the order of 45 mA > 30 mA > 15 mA. This study has led us to the conclusion that an increase of the current density gives a more concentrated acid [21].

Operations below the limiting current are desirable for most electrolysis processes. When the cell voltage (V) across the cell is increased and the limiting current density (i) of the membrane reached, the cell voltage against current density plot typically exhibits a plateau or point of inflection. A plot of V/i vs. $1/I$ (resistance vs. reciprocal current) will typically exhibit a minimum when the limiting current density is reached [22]. In our study no limiting current was apparent in any case. However, this lack of identifiable limiting current is probably due to the fact that ion transport through the membrane is for both potassium ions and hydrogen ions generated by the EHD.

3.4. Effect of membrane types on electrolysis

The various experiments were performed using 0.1 M H_2SO_4 solution and 0.1 M K_2SO_4 as an anolyte and a catholyte solution, respectively, in the cell of separating with different anion exchange membrane to determine the effect of type of the membrane to transfer of sulphate ions. In these experiments; anion exchange membranes such as ACM, AMH and AHA were used for this aim. The variation of the increased amount of base solution in the catholyte chamber with time is plotted in Fig. 4 for three commercial anion exchange membranes. Although in all cases the amount of anion transported from one chamber to the other one through the membrane increased for all membranes, there was a significant increase for ACM membrane which had a macro porous structure and water content between 0.31 and 0.18 as given in Table 1. If the transport efficiency of AHA and AMH was compared, it could be clearly seen that anion transport efficiency of AMH membrane was higher than AHA because of the differences of their water content. For this reason, for the three commercial anion exchange membranes the order of the amount of transported anion was ACM > AMH > AHA. These mathematical comments were supported with the SPSS assessments. But there were no changes in the explanations. In order to determine the effect of the membrane type on the formation of acids and bases in the chambers, three different commercial ion exchange membrane in eight different time section were used
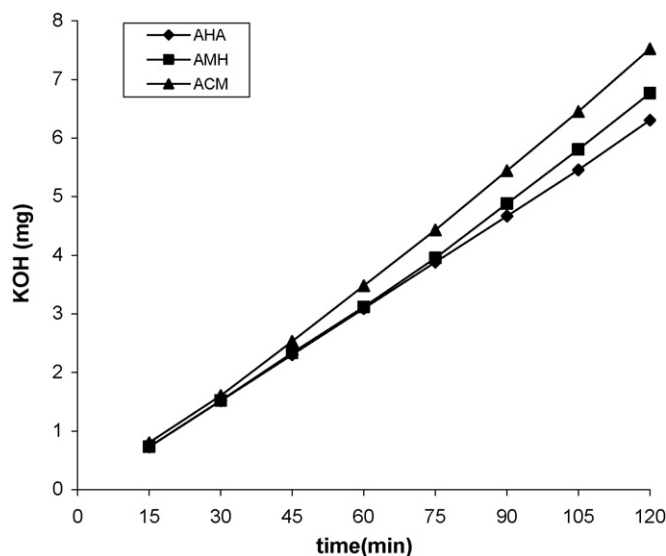
Fig. 4. The effect of membrane types on EHD or AS: 0.1 M H_2SO_4, CS: 0.1 M K_2SO_4 and CD: 45 mA.

Table 5
ANOVA table of membrane type effect (tests of between-subjects effects, dependent variable: mgbase)

Source	Type III sum of squares	d.f.	Mean square	F	p-Value
Corrected model	97.970[a]	9	10.886	238.340	.000
Intercept	330.940	1	330.940	7245.923	.000
Membrane	1.289	2	.644	14.111	.000
Time	96.681	7	13.812	302.405	.000
Error	.639	14	.046		
Total	429.550	24			
Corrected total	98.610	23			

F: result of F-test statistics; d.f.: freedom of degree; p-value: probability value.

[a] $R^2 = .994$ (adjusted $R^2 = .989$).

because of this there was an effect not only membrane type but also time on the base and acid formation in the chambers and as a result of this opinion two-way ANOVA was applied to these values. The statistical values of this part of this study are given in Tables 5 and 6. If Table 5 is investigated, it can be seen that group averages are different from each other with the important level on the account of possibility value in terms of membrane type is smaller than the selected trip level ($p = 0 < \alpha = .05$). It means that according to the membrane types as AHA, ACM and AMH, group averages are different from each other statically. If the values are investigated in terms of time, the same comments are valid and possibility value in terms of time is smaller than the selected trip level ($p = 0 < \alpha = .05$) because of this; group averages due to 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min are accepted different from each other with the important level. The differences in the group average of membrane types in terms of mg base measurement were explained with the two-way ANOVA method. In order to determine which of them are different from each other, among the multiple comparison testes, Tukey's HSD test were used. The differences between the values were supported with the multiple comparison table which is given as Table 6. When the multiple comparison table is examined, it is understood that the average of ACM membrane type showed differences due to both of the AEMs; AHA and AMH ($p = 0 < \alpha = .05$ vs. $p = .004 < \alpha = .05$). On the other hand the differences between the membrane type as AHA and AMH has not importance in point of statistic ($p = .513 > \alpha = .05$).

The cation exchange membranes selected in this study were CMB, CMS, CMX and their properties are the same except the properties such as their capacity of ion-exchange, thickness and capacity of water retention. According to Eqs. (2) and (3), their explanations and the constants given in Table 2, it can be easily said that the concentration of base solution occurred in the cathode chamber increased in that order: CMB > CMS > CMX. The differences on experiments' results about the types of membranes are explained with the structure of the membranes (Table 2). The ion exchange capacity of membranes increased CMB > CMS > CMX, for this reason according to the generation of hydrogen ion and hydroxyl ion due
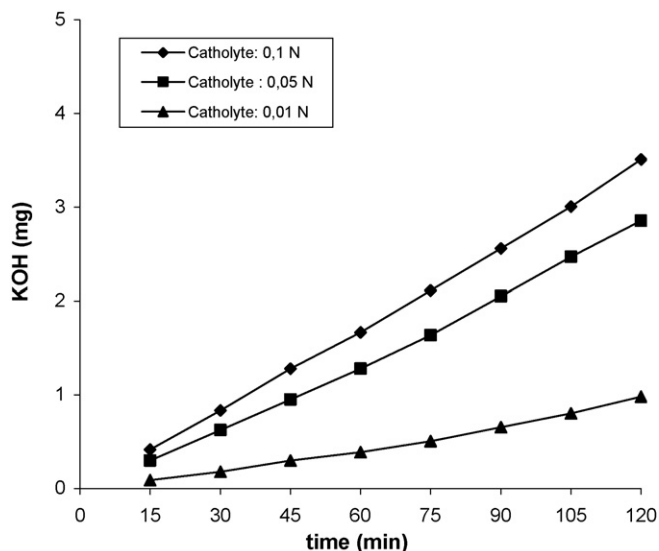
Table 6
Multiple comparison table of membrane type effect (dependent variable: mgbase)

Membrane, I	Membrane, J	Mean difference, $I - J$	S.E.	p-Value
AHA	AMH	−.1207	.10686	.513
	ACM	−.5407[*]	.10686	.000
AMH	AHA	.1207	.10686	.513
	ACM	−.4200[*]	.10686	.004
ACM	AHA	.5407[*]	.10686	.000
	AMH	.4200[*]	.10686	.004

Based on observed means.

[*] The mean difference is significant at the .05 level.

Fig. 5. The effect of the concentration of the salt solution on EHD for AS: 0.1 M H_2SO_4, AEM: ACM and CD: 20 mA.

to the reactions (2) and (3), mequiv. K ion per g migrate through the cation exchange membrane increased in this order.

3.5. The effect of the concentration of the salt solution

The experiments were performed using 0.1 M acid solution and K_2SO_4 having different concentrations as an anolyte and a catholyte solution, respectively, in the cell of separating with ACM membrane. These experiments were repeated for other two of the AEMs. Not the results but the comments were the same because of this, AHA and AMH membrane results were not given in this section. The current density was applied as 20 mA to the EHD cell. $1 \times 10^{-1}, 5 \times 10^{-2}$ and 1×10^{-2} M K_2SO_4 solutions were used for each experiment. The results obtained from these experiments are shown in Fig. 5 and its order is like that: $1 \times 10^{-1} > 5 \times 10^{-2} > 1 \times 10^{-2}$ M K_2SO_4. The reason of these results is the amount of the anion that transferred from the cathode to the anode chamber. As a result of the highest values of the amount of being transferred, the amount of uncomplexed potassium cation in the cathode cell and due to this fact the amount of the base formed in the cathode chamber become more. These experiments' results were evaluated with the statistical analysis. For this reason, the experiments were performed with three different concentration of catholyte solution in eight different time section because of this as it was thought in the previous sections that not only concentration but also time could effect the base and acid formation in the chambers and as a result of this opinion two-way ANOVA was applied to the values. The statistical values of this part of this study are given in Tables 7 and 8. If Table 7 is investi-

Table 7
ANOVA table of catholyte concentration effect (tests of between-subjects effects, dependent variable: mgbase)

Source	Type III sum of squares	d.f.	Mean square	F	p-Value
Corrected model	20.848[a]	9	2.316	14.343	.000
Intercept	41.186	1	41.186	255.027	.000
Catholyte	8.729	2	4.365	27.026	.000
Time	12.119	7	1.731	10.720	.000
Error	2.261	14	.161		
Total	64.295	24			
Corrected total	23.109	23			

F: result of F-test statistics; d.f.: freedom of degree; p-value: probability value.

[a] $R^2 = .902$ (adjusted $R^2 = .839$).

Table 8
Multiple comparison table of catholyte concentration effect (variable: mgbase, Tukey HSD)

Catholyte, I	Catholyte, J	Mean difference, $I - J$)	S.E.	p-Value
0.1N	0.05N	.3988 1	.20093	.153
	0.01N	.4313[*]	.20093	.000
0.05N	0.1N	−.3988	.20093	.153
	0.01N	1.0325[*]	.20093	.000
0.01N	0.1N	−1.4313[*]	.20093	.000
	0.05N	−1.0325[*]	.20093	.000

Based on observed means.
[*] The mean difference is significant at the .05 level.

gated, it can be seen that group averages are different from each other with the important level on the account of possibility value in terms of concentration is smaller than the selected trip level ($p = 0 < \alpha = .05$). It means that according to the concentration values as 1×10^{-1}, 5×10^{-2} and 1×10^{-2} M, group averages are different from each other statically. If the values are investigated in terms of time, the same comments can be said and possibility value in terms of time is smaller than the selected trip level ($p = 0 < \alpha = .05$) because of this group averages due to 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min are accepted different from each other with the important level. In order to determine which of them are different from each other, among the multiple comparison testes, Tukey's HSD test were used. The differences between the values were supported with the multiple comparison table which is given as Table 8. When Table 8 is examined, it is understood that the average of 0.01N catholyte concentration showed differences due to both of the 0.1N and 0.05N catholyte concentration ($p = 0 < \alpha = .05$ vs. $p = 0 < \alpha = .05$). On the other hand the differences between the 0.1N and 0.05N catholyte concentration have not importance in point of statistic ($p = .153 > \alpha = .05$).

The same experiments were performed with CMB as a CEM. In these experiments, 0.01 M KOH solution and K_2SO_4 having different concentrations were used as a catholyte and an anolyte solution, respectively. The current density was applied as 45 mA to the EHD cell. 1×10^{-1}, 2×10^{-1}, 3×10^{-1}, 4×10^{-1} and 5×10^{-1} M K_2SO_4 solutions were used for each experiment. The transport numbers were lower for the lower concentrations of salt solution used. The Faradic process at the anode results in the generation of free protons in the feed compartment. This leads to a reduction in current efficiency for potassium transport, due to the competing transport of potassium and hydrogen ions across the CEM. In addition, as the extent of salt splitting increased the current efficiency decreased and a fall in the transport number was observed with time, since protons were more mobile than the potassium ions. Bearing in mind that the limiting current density, and hence current efficiency is broadly proportional to concentration, the salt concentration should be as high as possible, being limited by solubility or post-electrolysis process requirements [20]. The results obtained from these experiments are showed similarity with the results obtained from AEMs in the basic of this study and its order is like that: $1 \times 10^{-1} < 2 \times 10^{-1} < 3 \times 10^{-1} < 4 \times 10^{-1} < 5 \times 10^{-1}$ M K_2SO_4.

It was understood that from the experiments that were made in order to determine the effect of the salt concentration to the regeneration of base solution, the amount of base solution formed in the cathode chamber for both the membrane experiments increased as an effect of salt concentration.

3.6. The effect of the composition of salt solution

In order to investigate the effect of different anions for EHD process, the experiments were performed by using 0.1 M KCl, KNO_3 vs. K_2SO_4 as a catholyte solution. In these experiments, both of the cells

Table 9
ANOVA table of salt solution type effect (tests of between-subjects effects, dependent variable: mgbase)

Source	Type III sum of squares	d.f.	Mean square	F	p-Value
Corrected model	141.168[a]	9	15.685	45.326	.000
Intercept	459.900	1	459.900	1328.988	.000
Salt composition	15.862	2	7.931	22.918	.000
Time	125.306	7	17.901	51.729	.000
Error	4.845	14	.346		
Total	605.913	24			
Corrected total	146.013	23			

F: result of F-test statistics; d.f.: freedom of degree; p-value: probability value.
[a] $R^2 = .967$ (adjusted $R^2 = .945$).

Table 10
Multiple comparison table of salt solution type effect (dependent variable: mgbase, Tukey HSD)

Salt composition, I	Salt composition, J	Mean difference, $I - J$	S.E.	p-Value
Sulphate	Chloride	−.6888	.29413	.083
	Nitrate	−1.9625[*]	.29413	.000
Chloride	Sulphate	.6888	.29413	.083
	Nitrate	−1.2738[*]	.29413	.002
Nitrate	Sulphate	1.9625[*]	.29413	.000
	Chloride	1.2738[*]	.29413	.002

Based on observed means.
[*] The mean difference is significant at the .05 level.

were separated with ACM membrane from each other and 45 mA was applied to the electrolysis cell. The results obtained from these experiments are shown in Fig. 6. As it is seen from Fig. 6, the experiments were performed with three different salt solution in eight different time section as a result of this the question is occurred such as: which effects the formation of base and acid in the chambers? "Time?" or "Salt solution type?" or "both of them"? In order to find the answer of this question two-way ANOVA method was applied to the values. The statistical values of this part of this study are given in Tables 9 and 10. If Table 9 is investigated, it can be seen that group averages are different from each other with the important level on the account of possibility value in terms of salt solution type is smaller than the selected trip level ($p = 0 < \alpha = .05$). It means that according to the salt solution types group averages are
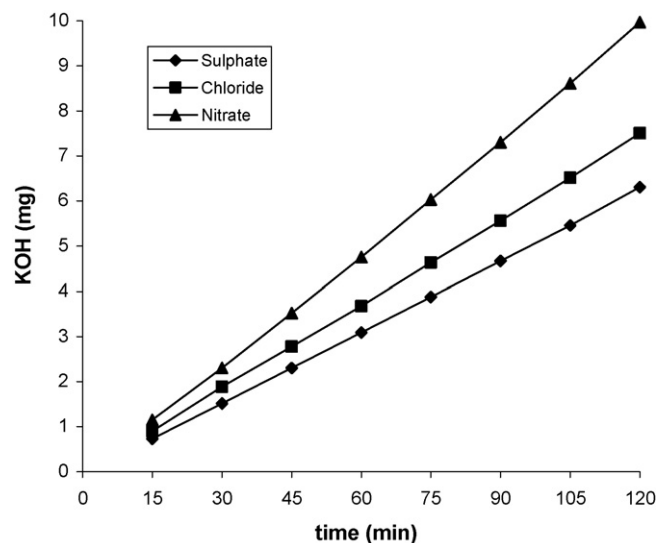
Fig. 6. The effect of the composition of salt solution on EHD for AS = CS: 0.1 M, AEM: AHA and CD: 45 mA.

different from each other statically. If the values are investigated in terms of time, the same comments can be said and possibility value in terms of time is smaller than the selected trip level ($p = 0 < \alpha = .05$) because of this group averages due to 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min and 120 min are accepted different from each other with the important level. In order to determine which of them are different from each other, among the multiple comparison testes, Tukey's HSD test were used. The differences between the values were supported with the multiple comparison table which is given as Table 10. When Table 10 is examined, it is understood that the average of the values obtained via the usage of nitrate ions as salt showed differences due to both of the chloride and sulphate ($p = 0 < \alpha = .05$ vs. $p = .002 < \alpha = .05$). However the differences between the sulphate and nitrate salts were not found as important in the point of statistic ($p = .083 > \alpha = .05$). Sulphate transport order with respect to different catholyte solutions through AHA anion exchange membrane was obtained as $KNO_3 > KCl > K_2SO_4$ when the concentration of anolyte solution was 0.1 M acid forms of salts. In the experiments, it was obtained that the recovery values of base have variation which depends on radius of these ions in these salts of potassium. The radius order of these ions is like that: $SO_4^{2-} > Cl^- > NO_3^-$. Due to the biggest radius of the ion such as SO_4^{2-}, the transportation of this ion was lower than the other ions (Cl^-, NO_3^-), because of this the formation of base was less than the others. The comments that were made for the other ions of salts are the similar with sulphate.

4. Conclusions

There is a demand for industrial processes for recycling salts, for example potassium sulphate, potassium nitrate and potassium chloride, by splitting them electrochemically into their corresponding acids and bases. But, until now, the permselectivities of anion exchange membranes (AEMs), have been insufficient and have not proved suitable for cost-effective applications. In experiments, using the anion exchange and cation exchange membrane for potassium salts electrolysis, no effective H^+ ion leakage, i.e. 100% permselectivity, has been observed for concentrations of up to about 7–8 wt.% acid and bases. A transport model is presented that explains all of the results, and is based on two properties of mono and multivalent anions. On the one hand, multiply charged anions can interact with the fixed ions of the membrane, reducing its ability to stop H^+ ion leakage out of the anolyte. On the other hand, they can combine with H^+ ions and then transport them in the desired direction into the anolyte. These opposing effects influence the overall permselectivity of anion exchange membranes. This process performed as an effect of the current density, concentration, membrane permeability, salt form of potassium.

The results show that anion-exchange membranes allow the transfer of anions such as SO_4^{2-}, Cl^-, NO_3^-, particularly the ACM which is the most efficient than AHA and AMH membrane. On the other hand; it was determined that the current density was important because of transporting of the ions from one cell to the other one through the membrane and the best results were obtained while the current density was applied as 45 mA. For this reason, in the other experiments such as studying of the effect of the concentrations, composition of salt solution, ACM membrane were used

as anion-exchange membrane and 45 mA was applied to the cell as current density. With increasing in the salt concentration, the amount of the base formed in the catholyte chamber for AEM and for CEM experiments increased. In addition to this the amount of the base formed in the catholyte chambers changed due to the radius of anions in the salt compound.

The obtained results show that this technique can be used not only for recovering the acid and base wastes of industry but also for removing the impurities in order to obtain pure acids and bases in laboratory conditions.

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