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# Salt splitting process application

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## ABSTRACT

The recovery of bases from solutions containing metallic salts were achieved in three compartment cells separated with commercial ion exchange membranes (IEMs) as anion exchange membrane (AEM) and cation exchange membrane (CEM). In the experiments, an equimolar quantity of acid, base and different salts of metal solutions were used as the anolyte and the catholyte solutions and the solution in the middle chamber of the cell, respectively. Effects of current, the type of ion-exchange membranes, the nature and the concentrations of the solutions on the recovery of bases were investigated. The results of the experiments were analyzed with the statistical package for social sciences (SPSS) program. The results obtained show that electrohydrolysis seems to be an applicable method for the recovery of bases from waste water at suitable conditions.

*Keywords:* Industrial wastes; Salt splitting; Regeneration of bases; Ion-exchange membranes

## 1. Introduction

Industrial countries are increasingly concerned with environment protection issues. One of the major concerns is the treatment of spent mineral acids since waste acids are produced by several industries such as those involved with pickling and surface treatment. These waste acids often contain metallic salts that are serious pollutants as well. Indeed, toxic effluents which are produced by various industries have to be treated before being thrown into the body water because of the very strict standards of discharge [1–4].

To date, spent acid solutions have been treated mostly either by neutralization, which leads to large amounts of sludge, or by traditional thermal techniques such as distillation, evaporation and pyrolysis, which are economic processes only for large volumes of effluents. These methods are being replaced by membrane techniques such as dialysis, electro dialysis (ED), and electro hydrolysis (EHD) [5–9]. Among the membrane techniques, EHD is an attractive technique for treating waste. This technique has the advantage of allowing recycling of the acid and also the production of lower amounts of salt effluents or sludge. In addition to these advantages it 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 [10–12]. Salt splitting is a new technology dependent on the availability of membranes and EHD process. The process of salt splitting is a potentially important use for electrochemical technology [13–16]. It is a process that utilizes cation and/or anion exchange membranes (CEM/ AEM). It combines selective ion transport through membranes with electrochemical reactions at electrodes. The dissociation of water results in hydrogen ion and hydroxide ion formation at the two electrodes [17]. The anodic oxidation of water generates protons and oxygen.

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (1)$$

The cathode reaction generates hydroxyl ions and hydrogen from water.

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2 \quad (2)$$

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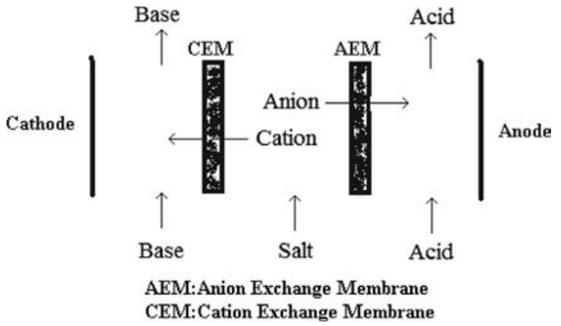

Fig. 1. The schematic diagram of the cell used for EHD experiments.

Fig. 1 shows a diagram of the apparatus for our EHD experiments that is made from polyamide and designed with IEMs [18,19]. The detailed explanation about this apparatus is given in the experimental section. As the general meaning, according to the potential applied to the EHD cell, sodium ions from the middle chamber of the cell migrate through the CEM towards the catholyte where they combine with the hydroxyl ions to form NaOH. The uncomplexed anions separated from sodium in the middle chamber migrate to the anode chamber through the AEM, where they combine with the protons and form acid anodically. The electrolysis of sodium sulfate into sulfuric acid by EHD can be represented by the general reaction:

$$Na_2SO_4 + 2H_2O \rightarrow H_2SO_4 + 2NaOH \quad (3)$$

The same process and reaction can occur in the presence of potassium ion.

The aim of this paper is to study the EHD process for the recovery of bases with three types of commercial AEMs and CEMs as a function of current, the type of ion-exchange membranes, the nature and the concentration of the solutions. The results were evaluated statistically with the analysis of variance (ANOVA) in order to test for the significant differences between two different ions (sodium and potassium) in this membrane process.

## 2. Experimental

### 2.1. Apparatus, membranes and solutions

The apparatus for EHD experiments is made from polyamide designed with an IEM (AEM and CEM) in between according to the well-established procedure reported elsewhere (Fig. 1) [18,19]. Three chambers were attached by means of inserting two screws on their flanges with IEMs in between. The membranes were cut as a circle with a diameter of 30 mm and glued into the inner mounting wall of each of the three chambers with silicone rubber sealant to prevent any leakage between the chambers. A stainless steel and Pt were used as a cathode and anode, respectively, and their active dimensions were 30 mm. The electrodes were fitted in the inner wall of apparatus and were symmetrically separated about 65 mm from the membrane surface. The flow of solutions was performed by peristaltic pump (913 Mity Flex, double-way). The power supply used in electrolysis experiments was capable of supplying a potential of up to 32 V and a direct current of up to 2 A. The AEMs (AHA, ACM, AMH) and CEMs (CMB, CMS, CMX) selected in this study were kindly supplied from Eurodia Co. The main characteristics of the AEMs and CEMs are listed in Tables 1 and 2, respectively. To ensure that the IEMs were initially in a suitable form for this application, the following steps were conducted for all membrane samples (7.065 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 each to remove inorganic impurities. The resulting membranes were finally immersed in 1.0 M HCl solutions to transform membranes to their hydrogen form for 24 h. On the other hand all AEM samples (7.065 cm$^2$) 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 each to remove inorganic impurities. The resulting membranes were finally immersed in 1.0 M NaCl solutions to transform membranes to their chloride form for 24 h. Analytical grade reagents KOH, $K_2SO_4$, $KNO_3$, KCl, NaOH, $Na_2SO_4$, $NaNO_3$, NaCl, $H_2SO_4$, $HNO_3$ and HCl were obtained from Merck Co.

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 (meq/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 |

### 2.2. Experimental procedure and chemical analysis

Each experiment was duplicated under identical conditions for two hours. Samples were taken at time intervals (for fifteen minutes) from the cathode chamber to determine the base regeneration. The concentration of base was determined with suitable acid solutions in the presence of suitable indicators volumetrically.

### 2.3. Evaluation of the results

The results were obtained with the titration of samples which were taken from the catholyte solution within the fixed time intervals. The results were evaluated individually, however it was thought that it would be better if the results of both sodium and potassium were evaluated with some statistic programs. For this reason, the results of the experiments were analyzed with the statistical package for social sciences (SPSS) program and ANOVA method. In our study, ANOVA method provided us a statistical test of whether or not the means of several groups are all equal in the point of different ions (sodium and potassium).

## 3. Results and discussion

### 3.1. Effect of current on EHD

The various experiments were performed in the conditions of 0.01 M NaOH/CMB/0.02 M $Na_2SO_4$/ACM/0.01 M $H_2SO_4$ and also for potassium ion as 0.01 M KOH/CMB/0.02 M $K_2SO_4$/ACM/0.01 M $H_2SO_4$. In these experiments, currents such as 15, 30 and 45 mA were applied to the cell of EHD. The concentration of acid and base occurred in the anode and cathode chambers increased with increasing the current 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 gives a more concentrated solution as acid and base.

These experiments were performed with three different currents in eight different time sections using two different metal ions. Hence it was thought that not only current but also time and the nature of metals could have an effect in the base formation in the chambers. For this reason Two Way ANOVA was applied to the values with applying of 45 mA current. The results are given in Tables 3 and 4. In Table 3, it can be easily seen that group averages are different from each other since the probability value (p-value) is smaller than the selected significance level ($p = 0.001 < \alpha = 0.05$) in terms of nature of metals. It means that according to the nature of metals, group averages are different from each other statistically. If the values are examined in terms of time, the same comments are valid. The p-value in terms of time is smaller than the selected significance level ($p = 0.012 < \alpha = 0.05$). Hence, group averages due to 15, 30, 45, 60, 75, 90, 105 and 120 min are accepted different from each other. In order to determine differences between the metal types, among the multiple comparison tests, least significant difference (LSD) test was used. As a result of this test, it was seen that the differences between the averages of these obtained values via usage of sodium or potassium ion ($p = 0.001 < \alpha = 0.05$) were found statistically significant and the multiple comparison table is given in Table 4.

Table 3
ANOVA table current (45 mA) effect: tests of between-subjects effects

| Source | Type III sum of squares | df | Mean square | F | Sig. (p) |
|---|---|---|---|---|---|
| Corrected model | 85.260[a] | 8 | 10.658 | 9.782 | .003 |
| Intercept | 214.404 | 1 | 214.404 | 196.784 | .000 |
| Time | 49.619 | 7 | 7.088 | 6.506 | .012 |
| Cell | 35.641 | 1 | 35.641 | 32.712 | .001 |
| Error | 7.627 | 7 | 1.090 | | |
| Total | 307.291 | 16 | | | |
| Corrected total | 92.887 | 15 | | | |

Dependent variable: current density, 45 mA.

[a] R squared = .918 (Adjusted R Squared = .824).

Table 4
Multiple comparison table of current (45 mA) effect: pairwise comparisons

| I(Cell) | J(Cell) | Mean difference (I–J) | Std. error | Sig[a] | 95% Confidence interval for difference[a] | |
|---|---|---|---|---|---|---|
| | | | | | Lower Bound | Upper Bound |
| K | Na | 2.895* | .522 | .001 | 1.751 | 4.219 |
| Na | K | –2.895* | .522 | .001 | –4.219 | -1.751 |

Dependent variable: current, 45 mA
Based on estimated marginal means
* The mean difference is significant at the .05 level.
[a] Adjustment for multiple comparisons: Least Significant Difference (equivalent to no adjustments).

### 3.2. *Effect of membrane types on EHD*

The experiments were performed in order to determine the effect of CEM type. 0.01 M NaOH/CEM/0.02 M $Na_2SO_4$/ACM/0.01 M $H_2SO_4$ and also for potassium ion as 0.01 M KOH/CEM/0.02 M $K_2SO_4$/ACM/0.01 M $H_2SO_4$ were chosen as a testing condition and 45 mA were applied to the EHD cell. The CEMs selected in this study were CMB, CMS and CMX. The results obtained from these experiments showed differences from one membrane type to another one. The differences on the experiments' results about the types of membranes could be explained with the structure of the membranes. The ion exchange capacity of membranes increased CMB > CMS > CMX. For this reason, metal ion migration through the CEM increased in the same order.

On the other hand in order to determine the effect of the type of the AEM to the amount of acid and base that would be recovered, the experiments were repeated in the optimum conditions with the best type of the CEM. 0.01 M NaOH/CMB/0.02 M $Na_2SO_4$/AEM/0.01 M $H_2SO_4$ were chosen as a testing condition and 45 mA were applied to the EHD cell and also the same conditions were performed for the recovery of KOH from potassium salt. The AEMs selected in this study were ACM, AMH and AHA. The differences on experiments' results about the types of membranes were explained with the structure of the membranes. The ion exchange capacity of membranes increased ACM > AMH > AHA. The sulfate ion migration through the AEM also increased in this order.

Two Way ANOVA was applied to the values with the use of ACM (as a common and optimum condition membrane for both metals). The results are given in Table 5. In this table, it can be easily seen that group averages are not different from each other since the p-value is higher than the selected significance level ($p = 0.283 > \alpha = 0.05$) in terms of metal types. It means that according to the metal types, group averages are not different from each other statistically. If the values are investigated in terms of time, p-value in terms of time is smaller than the selected significance level ($p = 0.001 < \alpha = 0.05$). For this reason, the group averages due to 15, 30, 45, 60, 75, 90, 105 and 120 min are accepted different from each other with the same significance level.

### 3.3. *Effect of the composition of salt solution on EHD*

In order to investigate the effect of different anions for EHD process, the experiments were performed by using NaCl, $NaNO_3$ and $Na_2SO_4$ as a salt solution in the middle chamber of the cell. In these experiments, 0.01 M NaOH/

Table 5
ANOVA Table of Membrane (ACM) effect:tests of between-subjects effects

| Source | Type III sum of squares | df | mean square | F | Sig. (p) |
|---|---|---|---|---|---|
| Corrected model | 84.891[a] | 8 | 10.611 | 16.432 | .001 |
| Intercept | 222.248 | 1 | 222.248 | 344.162 | .000 |
| Time | 84.020 | 7 | 12.003 | 18.587 | .001 |
| Cell | .871 | 1 | .871 | 1.349 | .283 |
| Error | 4.520 | 7 | .646 | | |
| Total | 311.659 | 16 | | | |
| Corrected total | 89.412 | 15 | | | |

Dependent variable: type of AEM, ACM.
[a] R squared = .949 (adjusted R squared = .892)

CMB/0.02 N salt solution/ACM/0.01 M acid solution were chosen and 45 mA were applied to the system. The same conditions were applied for base recovery from salts of potassium. Sodium and potassium transport order from the middle chamber to the cathode chamber through the CEM with respect to different anolyte solutions was obtained as $MNO_3 > MCl > M_2SO_4$ when the concentration of catholyte and anolyte solutions were 0.01 M. In the experiments, it was observed that the recovery values of base show variations which depend on the solubility of the salt forms of the metal and on the anion/cation radius. The results of these experiments were also evaluated statistically. The statistical results are given in Table 6 for nitrate. In this table, it can be easily seen that group averages are not different from each other since the p-value is higher than the selected significance level ($p = 0.219 > \alpha = 0.05$) in terms of metal types. It means that according to the metal types as sodium or potassium, group averages are not different from each other statistically. If the values are investigated in terms of time, the p-value in terms of time is smaller than the selected significance level ($p = 0.000 < \alpha = 0.05$) because of this group averages due to 15, 30, 45, 60, 75, 90, 105 and 120 min are accepted different from each other with the same significance level.

### 3.4. *Effect of the concentration of salt solution on EHD*

In order to discuss the effect of the concentration of the salt solution, the experiments were performed using 0.01 M base/CMB/X M salt solution/ACM/0.01 M acid. $1.10^{-2}$, $2.10^{-2}$ and $5.10^{-3}$ M salt solutions were used for each metal and 45 mA was applied to the system. It is clearly understood that the transport of ion increased with increase of the initial concentration of the salt solution. Because during the EHD process, an ion exchange took place between ions presented in both chambers resulting from a difference in electrochemical potentials under the driving force of not only a direct current but also the metal ions which increased in the cathode chamber. Note that metal ions were being reduced with time in the middle chamber and nonetheless the formation of base was rising. The order of the concentration was found like that: $2.10^{-2} > 1.10^{-2} > 5.10^{-3}$ M for both of

Table 6
ANOVA table of salt composition ($NO_3^-$) effect:tests of between-subjects effects

| Source | Type III Sum of squares | df | Mean square | F | Sig. (p) |
|---|---|---|---|---|---|
| Corrected model | 207.546[a] | 8 | 25.943 | 21.632 | .000 |
| Intercept | 543.094 | 1 | 543.094 | 452.842 | .000 |
| Time | 205.360 | 7 | 29.337 | 24.462 | .000 |
| Cell | 2.187 | 1 | 2.187 | 1.823 | .219 |
| Error | 8.395 | 7 | 1.199 | | |
| Total | 759.035 | 16 | | | |
| Corrected total | 215.941 | 15 | | | |

Dependent variable: type of salt solution, nitrate.
[a] R squared = .961 (adjusted R squared = .917)

Table 7
ANOVA table of salt concentration (0.02 N) effect: tests of between-subjects effects

| Source | Type III Sum of Squares | df | Mean Square | F | Sig.(p) |
|---|---|---|---|---|---|
| Corrected Model | 84.891[a] | 8 | 10.611 | 16.432 | .001 |
| Intercept | 222.248 | 1 | 222.248 | 344.162 | .000 |
| Time | 84.020 | 7 | 12.003 | 18.587 | .001 |
| Cell | 0.871 | 1 | .871 | 1.349 | .283 |
| Error | 4.520 | 7 | .646 | | |
| Total | 311.659 | 16 | | | |
| Corrected total | 89.411 | 15 | | | |

Dependent Variable: Concentration of salt solution, 0.02 N
[a] R Squared = .949 (Adjusted R Squared = .892)

the metal ions. Although the best recovery from both of the metal types were obtained via the use of 0.02 N salt concentrations, data did not give us any differences. The statistical results are given in Table 7 for 0.02 N salt concentrations. It can be easily seen that group averages are not different from each other since p-value is found higher than the selected significance level ($p = 0.283 > \alpha = 0.05$) in terms of metal types. It means that according to the metal types, group averages are not different from each other statistically. If the values are investigated in terms of time, p-value in terms of time is smaller than the selected significance level ($p = 0.001 < \alpha = 0.05$) because of this group averages due to 15, 30, 45, 60, 75, 90, 105 and 120 min are different from each other statistically.

## 4. Conclusions

This research has demonstrated the EHD of sodium/potassium sulfate, nitrate and chloride in a three compartment cell using commercial AEMs and CEMs. The results show that while CEMs allow the transfer of sodium/potassium, particularly the CMB which is the most efficient than CMS and CMX membrane, this order can be given as ACM > AMH > AHA for the sulfate/nitrate/chloride transport. On the other hand, it was determined that the current was important because of transport of the ions from one cell to the other through the membrane and the best results were obtained when the current was applied as 45 mA. For this reason, in the other experiments CMB and ACM membrane were used as CEM and AEM, respectively and 45 mA was applied to the cell as current. By use of CMB membrane and increasing the concentration of salt solution, maximum degree of sodium/potassium transport is determined and it is seen that these affect not only the transport of sodium/potassium but also the formation of acids in the anode chamber due to the transport of sulfate/nitrate/chloride. In addition to these results, the type of the salt forms of sodium/potassium also influences the transfer of sodium/potassium and the order of the formation amount of acid in the anolyte solution, that increased in the order of $HNO_3 > HCl > H_2SO_4$.

A three compartment cell, using commercial anion and cation exchange membranes, has been used for the recovery of base from the salts of metals. Recovery is greater at higher current and higher salt concentration. This performance improvement must be balanced against the increase in cost associated with separation of sodium/potassium salt and the higher energy cost associated with the higher voltage in the three compartment cell.

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