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Comparison of Commercial Anion-Exchange Membranes for Pickle Waste Treatment by Electro-Electrodialysis

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Abstract: This study deals with recovery conditions of acids from the pickle waste of leather industry by applying of electro-electrodialysis process. The pickle waste consists of NaCl, HCOOH, H_2SO_4, and organic dirt. The four commercial anion exchange membranes (Neosepta AFN, ACM, AMH, and Polysulfone SB-6407) have been used and the necessary specific energies for recovering conditions as well as the most appropriate membranes were determined. In the laboratory-scale experiments, AMH anion-exchange membrane has the best combination of electrochemical, mechanical properties and high ion permselectivity. On the contrary, AFN membrane showed good performance with respect to other membranes used and it has the lowest necessary specific energy. In this method, HCl was also produced from its salt during the recovering process.

Keywords: Acid recovery, electro-electrodialysis, anion-exchange membranes, leather pickle waste

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INTRODUCTION

Many industrial processes generate low-grade acidic waste streams. In the leather industry, low-grade acidic waste streams are produced from the pickle, tanning, and dyeing process. Particularly, the properties of waste streams in the leather industry depend on the technology and chemical treatment processes (1). The pickle process treatment with acid and salt is to protect the tanning as required. H_2SO_4 is the most used acid, and generally it is used together with HCOOH when the pickle is necessary to adjust at high pH values.

A conventional and popular method for treating the waste acid solution is neutralization process for direct discharge (2). But, the process generates a large amount of sludge, which causes serious disposal problem. With environmental legislation, tighter technology is required for current and developing processes to meet new legislative targets.

The efficient treatment technology used for treatment of acidic waste effluents in the past few decades is electrodialysis (ED) process (3–9). The other process is diffusion dialysis (DD), which is used for recovering acids from waste effluents, particularly for regaining inorganic acids from exhausted galvanization baths. DD has advantages, particularly from the point of energy consumption during its application. In the process, the external force is not required to promote separation, only the energy is necessary to pump the feed and receiver solutions into the compartments (10–13). Electro-electrodialysis (EED) (14–17) is an electromembrane process that consists of a pair of electrodes for every unit of cells. However, this combination causes higher capital cost due to the increase in the number of electrodes in the cell. In spite of the higher capital cost, EED has been shown to be capable of achieving higher acid concentrations than ED. This is due to the higher water flux in ED through both the anion- and cation-exchange membranes (2).

Before EED experiments, the applicability of DD and ED with three compartment cells for recovering of acids from leather pickle waste effluents was examined. However, successful results were not obtained by the DD method and ED with three compartment cells, because of high salt concentration and organic dirt in the pickle sample. When they were used, either the recovered acid was very low or organic dirt solution was obtained. Therefore, among these methods, the EED method was chosen. The commercial anion exchange membranes (polysulfone SB-6407, Neosepta AFN, AMH, ACM) have been used and the necessary specific energies were determined in both the clean solutions and the pickle samples taken from private leather industry.

EXPERIMENTAL

Chemicals and Membranes

All chemicals were reagent grade purchased from Merck Co. and used as received. SB-6407 anion-exchange membrane was obtained from Gelman

Science, and Neosepta AMH, ACM, AFN anion-exchange membranes produced by the Japanese firm Tokuyama Soda Co. Ltd. were kindly supplied by Eurodia Ltd. Both SB-6407 and Neosepta membranes contain quaternary ammonium bases $N(CH_3)_3^+$ as ionic groups (10, 18). The main characteristics of the anion-exchange membranes are presented in Table 1.

Electro-Electrodialysis Experiments

The schematic illustration for EED experiments is shown in Fig. 1. There was a graphite anode and a noncorrosive steel cathode in the side compartments of the electro-electrodialysis. The anolyte and catholyte solutions were 300 mL. The circulation of the solutions through the electro-electrodialysis cell was performed by a peristaltic pump and flow rates of the solutions were $1.2 \times 10^{-6}\,m^3\,s^{-1}$ in the course of EED. The color of the waste solution was turbid yellow. Before the experiments, the solid particulars in the waste were filtered. Overall acid concentrations of the anolyte and the catholyte were measured periodically by titrations with a sample 1 mL. The composition of the acid mixtures was determined with potentiotitrimetry method in nonaqueous media, and methanol was used as solvent (19). According to paper (20) the observation of the inflection point was possible within 5–10% water content in the sample, particularly; it wasn't possible to determine when the sample contained 25% water content. For this reason, the titration experiment was performed with 1 mL sample and diluted to 20 mL with methanol; 0.05 N NaOH in methanol was used as titrant. The Cl^- content was determined by argentometry. All experiments were carried out at room temperature.

Table 1. The properties of the ion-exchange membranes used in this study

Membrane	AFN	ACM	AMH	SB-6407
Thickness (mm)	0.15–0.20	0.11–0.13	0.26–0.28	0.152
Exchange capacity (meq/g · dry membrane)	2.0–3.5	1.4–1.7	1.3–1.5	2.15
Electric resistance (ohm/cm^2)	0.4–1.5	4.0–5.0	11.0–13.0	0.3–1.2[a]
Water content (%)	40–55	13–18	17–22	50–55[a]
Characteristic	Resistant against organic fouling	Low H$^+$ transport	High mechanical chemical strength	—
Burst strength (kg/cm^2)	2–3.5	2–3	12	—

[a] Determined at laboratory.

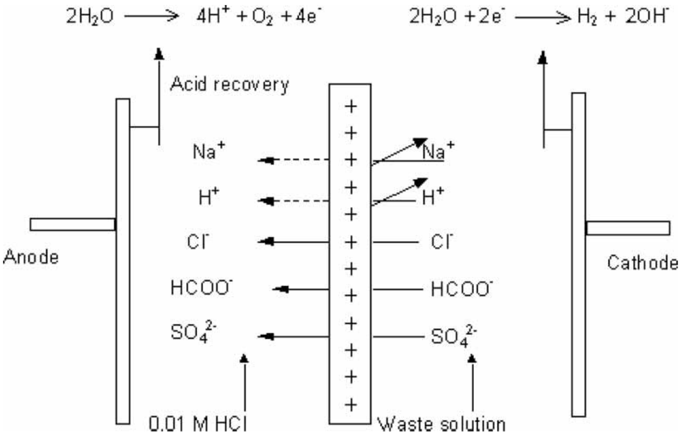

Figure 1. The schematic illustration of the cell used in EED experiments.

Determination of the HCOOH in Samples

Gas chromatography (ATI Unicam 610 series gas chromatography, C-R 7A Plus [Shimadzu] chromatopac Integrator system) was used in order to investigate whether formic acid in the pickle sample decomposed or not. Formic acid in samples was esterified before measuring by gas chromatography. The experimental equipment and conditions were listed as follows:

Technique: GC-capillary

Column: CP-Sil 5 CB fused silica WCOT, 25 m × 0,15 mm, df = 2 μm, Cat. No. 7692

Temperature: 65°C (4 min.) 200°C, 50°C/min.

Carrier gas: N_2, 10 psi, Make up (N_2): 15 psi

Injector: Split, T: 250°C

Detector: FID, T: 250°C

Sample size: 0.5 μL

Conc. range: 1%

Solvent: toluene

Courtesy: 1. Dijkstra, Solvay Pharmaceuticals, Weesp, The Netherlands.

RESULTS AND DISCUSSION

Composition of the Leather Pickle Waste

Two different kinds of pickle waste effluents, which are the cattle and sheep pickle from private leather industry, were used. The composition of cattle pickle waste was approximately 2 M NaCl, 0.15 M HCOOH, and 0.07 M H_2SO_4 and the sheep pickle waste was approximately 1.8 M NaCl and 0.1 M H_2SO_4. The amount of formic acid in the cattle pickle waste was found to be 13–18% by GC. The amount of H_2SO_4 was determined with potentiometric titration in nonaqueous media. The first inflection point was corresponding to H_2SO_4 and the second was for HCOOH. Amounts of Na were determined by flame photometry.

Results of Experiments Made with Clean Solutions Similar to Waste Pickle

Electro-electrodialysis experiments was made with clean solutions similar to the cattle pickle waste samples for four different anion-exchange membranes at current density of 5 mA/cm^2. The similar pickle waste solution was a mixture of 0.6 M NaCl, 0.1 M HCOOH, 0.015 M H_2SO_4 and does not contain any organic dirt. The variations of overall acid concentration with time for the studied membranes are shown in Fig. 2, in which the highest recovered acid was obtained with AFN membrane. The amount of Na^+ in recovered acid mixture was obtained as 184 ppm for AMH membrane, 7978 ppm for SB-6407 membrane, 200 ppm for AFN membrane, and 10247 ppm for ACM, respectively. It is seen that the lowest Na^+ in recovered acid was obtained with AMH membrane. When current density was increased to 15 mA/cm^2, the overall solution was passed through SB-6407 polysulfone anion-exchange membrane from catholyte to anolyte in a 1 h period. This indicates that electro-osmotic water flux was at high current density for

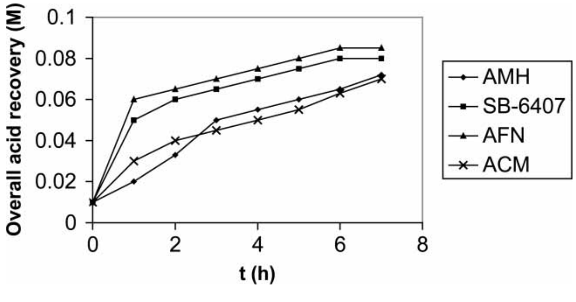

Figure 2. Results of EED performed with the clean solution (0,6 M NaCl, 0.1 M HCOOH, 0.015 M H_2SO_4) at 5 mA/cm^2.

Table 2. Analysis of the solution in anolyte compartment after 7 h EED time for the sheep pickle waste at current density of 5 and 10 mA/cm^2, respectively

	Na^+ (ppm)		Cl^- (M)		Overall H^+ (M)	
Membranes	5 mA/cm^2	10 mA/cm^2	5 mA/cm^2	10 mA/cm^2	5 mA/cm^2	10 mA/cm^2
AFN	82	103	0.04	0.05	0.050	0.11
SB-6407	738	1,850	0.12	0.17	0.035	0.075
AMH	32	58	0.035	0.06	0.055	0.09
ACM	357	857	0.055	0.085	0.040	0.08

SB-6407 membrane. Concentration of obtained acid didn't vary when AFN and AMH membranes were used in current density with 15 mA/cm^2. In other words, the higher current density is not suitable for these membranes.

Results EED Made with the Sheep Pickle Waste

The sheep pickle sample waste contains approximately 1.8 M NaCl and 0.1 M H_2SO_4 mixture except HCOOH and its pH was around 1. Analysis of recovered acid mixture in anolyte compartment was listed in Table 2, in which EED was applied with 7 h time at the current density with 5 and 10 mA/cm^2. The highest Na^+ content in recovered acid mixture was obtained with SB-6407 membrane. Figure 3 shows the variation of overall acid concentration recovered through tested AEMs with time at 5 and 10 mA/cm^2 current density. It can be seen that, the amount of recovered acid was higher at 10 mA/cm^2 for all membranes. During experiments, the anolyte volume was increased for ACM and SB-6407 membrane as a result of electro-osmotic water flux, so the recovered acid solution with these membranes was cloudy due to also the dragging of organic particular with electro-osmosis.

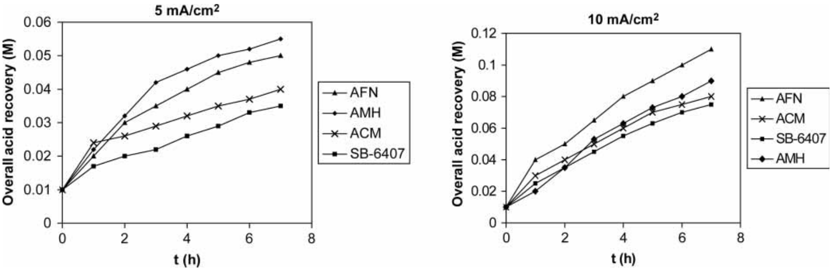

Figure 3. The variation of overall acid concentration with time at 5 and 10 mA/cm^2 current density tested on AEMs for the sheep pickle waste sample.

Results of EED Experiment with the Cattle Pickle Waste

In Fig. 4, the time variation of overall acid concentration in anolyte compartment was given at 5 mA/cm^2 current density for 12 h. It can be seen that the overall acid concentration increases to the maximum level with AFN membrane. The current density should be limited on the cathode for avoiding metal deposition during EED. When the current density was lifted to 10 mA/cm^2, the formation of the metal deposition was observed on the cathode.

The lowest Na$^+$ ion was passed to anolyte compartment for AMH membrane as shown in Table 4. In case of SB-6407 membrane, the highest Na$^+$ quantity was determined. Moreover, it was shown that the color of anolyte samples was clear for AMH and AFN membranes; on the contrary, the anolyte samples was turbid for ACM and SB-6407 membranes. The chemical analysis of the solution in anolyte compartment after EED experiment (12 h) with AMH membrane on 15 mA/cm^2 current density is listed in Table 4. On the basis of these results, it may be concluded that ACM and SB-6407 membranes are not suitable for acid recovery with EED from leather pickle waste.

The hydrated ion radii and molar ionic conductivities of counter ions that were presented in Table 3 show that Cl$^-$ ion has lowest ionic radius and highest molar ionic conductivity. In separation processes such as electrodialysis when multiple counter-ions are competing through an ion-exchange membrane, a lower molecule size and higher ionic equivalent conductivity are beneficial for the transport of a counter-ion through the ion-exchange membrane (21, 22). From this point, it is expected that Cl$^-$ ions should be highest transport. In an parallel of this assumption the highest transport was observed for Cl$^-$ ion as presented in Table 4. In an other point, the transport

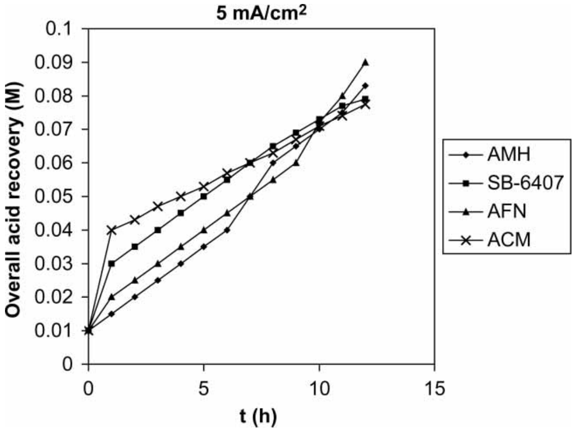

Figure 4. The variation of the overall acid concentration with time in anolyte compartment at 5 mA/cm^2 current density for the cattle pickle waste sample.

Table 3. The hydrated ionic radius and molar ionic conductivities of counter ions at 25°C

Ions	Molar ionic conductivites ($\times 10^{-4}$ S m^2 mol^{-1})	Ionic radius (pm)
H^+	349.8	900
Na^+	50.1	450
Cl^-	160.0	300
SO_4^{2-}	76.3	400
$HCOO^-$	54.6	350

of formic acid could happen with less than other ions at the end of the EED experiment. It can be seen that the highest transported Cl^- ion was obtained with SB-6407 membrane. AFN membrane has a low amount of cross-linking agent and a large concentration of ionogenic groups (18). For ACM membrane, the presence of a modified layer on the surface which increases its electrical resistance may be at the origin of additional heating at the solution-membrane interface (18). Generally, the transport of anion through anion-exchange membranes is related with their permselectivity properties.

The Estimation of the Necessary Specific Energy for Acid Recovery

The necessary specific energy for acid recovery from 1 L effluent is estimated by the following equation (17)

$$E = \frac{I}{V}\int_{to}^{t} V(t) \cdot dt$$

where E is the required specific energy (JL^{-1}), I, the total current during the separation (A), v is the initial volume of the catholyte (L), V is the cell voltage

Table 4. (a) Analysis of the solution in anolyte compartment at 5 mA/cm^2 current density after 12 h EED time of cattle pickle waste and for each membrane required specific energies in the same conditions (b) Analysis of the solution in anolyte compartment after 12 h EED time for AMH membrane at 15 mA/cm^2 of cattle pickle waste

Membranes	Na^+ (ppm)	Cl^- (M)	HCOOH (M)	H^+ (M)	$E \cdot 10^4 (J.L^{-1})$
SB-6407	5,633	0.1375	0.045	0.07	1.62
ACM	1,091	0.0575	0.020	0.07	2.59
AMH	48	0.050	0.007	0.07	1.63
AFN	323	0.040	0.020	0.08	1.56
AMH^b	230	0.115	0.014	0.15	8.06

at time t during the separation (V), t_o the initial time (s), t, time. The required specific energies for used membranes are listed in Table 4. It was found that the required lowest energy has AFN membrane. These results indicate that proton leakage through the AFN membrane under the experimental conditions is lower than that of others because the energy necessary combines the effects of total cell voltage and proton leakage through the anionic membrane (17). It was established that the best membrane suitable for the reconcentration of H_2SO_4 by electrodialysis are those in which the sorption of acid and diffusion of protons are minimized (21) since any proton being electrolytically reduced is replaced by a proton migrating through the membrane (17). In addition, a good anionic membrane optimally combines low proton leakage, high limiting current density, low membrane voltage, and high mechanical resistance. In our previous works, the sorption of HCOOH, H_2SO_4, and HCl on the studied membranes and their specific electrical conductivity as well as current-voltage plots were investigated and the transport of formic acid through these membranes with diffusion dialysis and electro-electrodialysis was examined (23, 24).

CONCLUSIONS

Among the membrane processes for recovering of acids from the pickle waste effluents, EED method was found to be the most appropriate. In this method, the most appropriate membranes have been determined as AMH and AFN membranes due to the low water transports, low acid sorptions, high ion permselectivity, and low proton leakage. AFN membrane requires the least specific energy, on the contrary, AMH membrane has somewhat higher specific energy but shows high mechanical and chemical strength properties. In all experiments, the amount of Na^+ in recovered acid was obtained in the following order, AMH $<$ AFN $<$ ACM $<$ SB-6407, respectively. Therefore, the highest selectivity for all the studied conditions was observed by AMH membrane. Furthermore, the recovered acid solution was obtained as cloudy for SB-6407 and ACM membranes. The anionic transport order are $HCOO^- < SO_4^{2-} < Cl^-$ for all the studied membranes, respectively. This means that the recovering of formic acid can be obtained after the other acids in this medium.

When the amount of recovered acid with respect to studied clean, sheep and cattle pickle waste solutions for all membranes was compared at $5\,mA/cm^2$ current density after 7 h EED experiments, the highest recovery was obtained with AFN membrane for clean solution medium. In addition, the amount of recovered acid was decreased about 40% decrease at the same current density and the same electrolysis. In the case of AMH membrane, the amount of recovered acid was decreased as 15% for sheep and cattle pickle wastes with respect to clean solution. No difference between cattle pickle and clean solution was obtained for recovered acids with ACM and SB-6407 membranes; on the contrary about 40% difference was decreased for sheep pickle.

When the current density or the electrolysis time was increased, the amount of recovered acid was increased about 50% for all membranes, the highest one was obtained with AFN membrane. The decreasing of recovered acid for sheep and cattle pickle samples with respect to clean solution expected results in terms of the pickle waste dirt at the same current density. Moreover, it was not affecting the recovered acid, either sheep or cattle pickle solution, used for AFN and AMH membranes. In other words, the presence of formic acid in the medium made no difference in observation. However, the difference for sheep pickle waste was the same as for ACM and SB-6407 membranes while the difference for cattle waste was not observed with respect to clean solution. This case can be considered due to increasing of electro-osmotic water flux by formic acid transport.

Moreover, with the applied method in this study, HCl was also produced from NaCl solution while recovering of HCOOH and H_2SO_4. But the detailed study is still necessary to separate the acid mixture produced. Anion-exchange membranes having higher permselective properties need to be found for application of recovery purposes. In addition, the necessary specific energy found for AFN membranes is less than about 10^3 times than for removing of H_2SO_4 from decontamination effluents (17).

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