

PERFORMANCE OF DIFFUSION DIALYSIS FOR PICKLING EFFLUENT OPERATING UNDER A HIGH FLOW RATE

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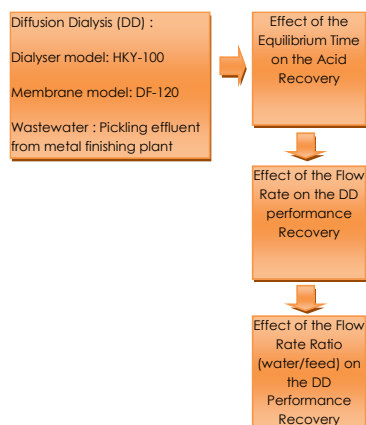
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Graphical abstract



Abstract

Diffusion dialysis (DD) is a membrane separation process. The major driving mechanism is an ionic concentration gradient. An anion-exchange membrane (AEM) equipped with DD is efficiently used for purifying waste acid and metal ion separation. The goal of this laboratory-scale study is to investigate the efficiency of a diffusion dialyser (model HKY-001), which was equipped with an AEM (model DF120), to purify waste acid solution (sulphuric acid). This study was conducted with actual waste acid from a pickling bath of an electroplating manufacturer in Samut Prakarn Province. In the experimental tests, the operating parameters, such as time to reach equilibrium, feed flowrate, water to feed ($Q_{\text{water}}/Q_{\text{feed}}$) and type of stripping water, were varied. To examine the performance of this treatment unit, the concentration of H^+ (mol.L^{-1}), acid recovery (% as H^+) and metal ion rejection (%) were monitored regularly. In conclusion, increasing the feed flow rate will likely decrease the H^+ recovery (%). The rejection (%) of Zn, Mn and Pb is likely to increase with increases in the feed flow rate. A higher metal ion rejection (%) can be achieved at a lower water-to-feed ratio.

Keywords: Diffusion dialysis, DF-120, high flow rate; pickling effluent, sulphuric acid recovery

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1.0 INTRODUCTION

Over recent years, there has been an explosive growth in Thailand, one of the most important sources of acid usage and waste is from metal finishing industries, where pickling is one of the major steps performed. In this step, pickling agents, such as H_2SO_4 and HCl , are used to treat metal surfaces (Agrawal and Sahu 2009; Rosocka 2010; Luo *et al.* 2011(a)). The treatment and disposal of waste acid solution typically involves neutralisation/precipitation with chemicals, such as NaOH or CaO . However, this method is chemical intensive and results in a large amount of chemical sludge. Moreover, the beneficial values of residual free acids that can be recovered from the waste stream during this process for reuse are also ignored (Wei *et al.* 2010; Li *et al.* 2012). Many researchers have developed technologies to recover inorganic acids from other types of wastewater processing, including distillation,

evaporation, ion exchange or solvent extraction, as well as distillation and pressure-driven membrane separation processes (Luo *et al.* 2011(a); Li *et al.* 2012; Luo *et al.* 2013). Among these methods, diffusion dialysis (DD) has become a more attractive technology for acid recovery because it can provide high acid recovery (%) with minimum energy consumption, environmental friendliness, cost effectiveness, high compatibility and operation simplicity (Oh *et al.* 2000; Luo *et al.* 2011(a); Luo *et al.* 2011 (b); Luo *et al.* 2015).

DD is a membrane-separation process. Anion exchange membrane allows a selective passage of H^+ and anionic species. Major driving force is governed by a concentration difference across an AEM, which follows the Donnan criteria of co-ion rejection and preserves charge balance (Luo *et al.* 2011(a); Li *et al.* 2012).

A number of researchers have reported promising results of the DD technique recovering acids and alkalis

from various waste discharges, including herbicide production, steel production, metal refinement and electroplating (Ersoz *et al.* 2001; Negro *et al.* 2001; Palařy and Źáková 2001; Tongwen and Weihua 2004; Luo *et al.* 2013; Wang *et al.* 2015). DD can also be used to separate sulphuric acid from other salts in their solutions by providing high percentage of H⁺ recovery and metal elimination (Palařy and Źáková 2004; Li *et al.* 2012).

In this study, a DD unit coupled with an AEM (model DF-120) was used to recover sulphuric acid from a waste acid solution, which was taken from a pickling tank of a metal finishing manufacturer. An investigation of the suitable operating parameters was examined. The membrane allows H⁺ to permeate, while rejecting metal ions. The recovery of H₂SO₄ from the waste acid solution is shown in Figure 1. With the difference of concentration between both sides of the membrane, the H₂SO₄ in the feed side (waste acid) tend to pass through the membrane to the water side (recovered acid). The SO₄²⁻ ions are allowed to diffuse, whereas the metal ions cannot move across the AEM. Regarding the H⁺ ions, these ions have a greater diffusion competition than that of the metal ions and can pass through the positively charged membrane due to their smaller size, lower valence state and higher mobility. Therefore, H⁺ ions can diffuse together with the SO₄²⁻ to preserve electrical neutrality in the solution. (Li *et al.* 2011(a))

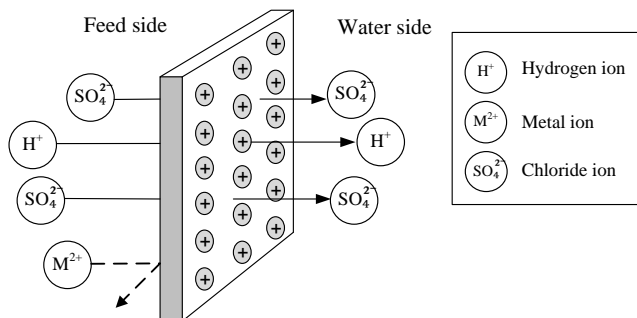


Figure 1 Diagram of H₂SO₄ recovery by DD-AEM

2.0 EXPERIMENTAL

This study was conducted using a laboratory-scale system. The experimental set up of the DD unit used in this study is shown in Figure 2.

2.1 Experimental set-up

This study was conducted using a laboratory-scale system. The schematic diagram of the experimental set up of the DD unit used in this study is shown in Figure 2. A diffusion dialyser was equipped with 40 sheets of AEMs (dialyser model: HKY-100, membrane model: DF-120, Shandong, China), which contained 40 diffusate cells and 40 dialysate cells, through which the flow pattern of the feed and water was counter current. The ion exchange capacity of this model is 100 L.day⁻¹. The effective dimensions of each membrane for mass transfer are 200 x 400 mm, and the total membrane area is 3.2 m². The properties and specifications of the membrane are provided in Table 1.

2.2 Materials

This study used actual waste acid from a pickling tank of a metal finishing company. Physical and chemical characterizations of the actual waste acid (taken from pickling tank); de-ionised water (DI) and tap water are shown in Table 2. The waste acid was filtered through a cartridge filter to avoid clogging in the membranes. Each experimental run was conducted at room temperature, which was below 40°C. At the end of each run, tap water was pumped into the device until the concentrations of H⁺ of diffusate and dialysis were equilibrated.

2.3 Calculations

The H⁺ concentration was determined by titration the samples with 0.1 M NaOH. The metal contents in the acid solutions were analysed using an inductive couple plasma mass spectrometry (ICP-MS) from Perkin Elmer.

The percentage of total acid recovery was calculated by the following equation:

$$\begin{aligned} \text{Recovery (\%)} &= (Q_r C_r^{H^+} / Q_f C_f^{H^+}) \times 100 \quad (1) \\ &= Q_r C_r^{H^+} / (Q_r C_r^{H^+} + Q_d C_d^{H^+}) \times 100 \quad (2) \end{aligned}$$

Where, $C_d^{H^+}$, $C_r^{H^+}$ and $C_f^{H^+}$ are the concentration of H⁺ (mol.L⁻¹) in the dialysate, recovered acid and feed, respectively. Q_d , Q_r and Q_f are the flowrate of the dialysate, recovered acid (m³.h⁻¹) and feed (m³.h⁻¹), respectively.

Table 1 Physical characteristics of the DF-120 AEM used in the study

Properties and specifications	Values
Materials	BPPO amination
Standard thickness (mm)	0.25
Electrical resistance (ohm/cm ²)	≤ 4.0 (20°C)
Total ion exchange capacity (mol/kg)	1.4 ~ 1.5
Mullen burst test strength (MPa)	> 0.9
Thermal stability (°C)	< 45°C
Moisture content (%)	45
Permselectivity (%)	≥ 95
Transference number of ions	≥ 97

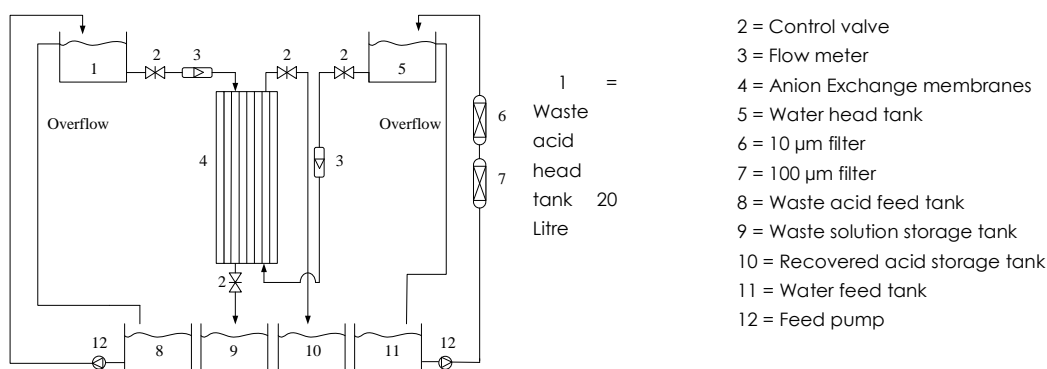


Figure 2 Experimental set up for DD

Table 2 Physical and chemical characterizations of the waste acid (taken from pickling tank); de-ionised water (DI) and tap water

Parameters	Units	Used Acid	De-ionised water (DI)	Tap water
pH	at 25°C	0.5	6.9	7.8
Turbidity	NTU	0.3	0.19	0.29
TDS	mg/L	472	17	382
Fe	mg/L	0.5	0	0
Mn	mg/L	9.219	0	0
Zn	mg/L	7.821	0.087	0.163
Pb	mg/L	2.94	0	0
Sulphate	mg/L	112,614	0	18
Nitrate	mg/L	230	0.45	2.29

The metal leaching ratio was calculated as follows:

$$\text{Leaching (\%)} = \frac{(Q_r C_r^M / Q_f C_f^M) \times 100}{(Q_r C_r^M / (Q_r C_r^M + Q_d C_d^M)) \times 100} \quad (3)$$

$$= \frac{(Q_r C_r^M / (Q_r C_r^M + Q_d C_d^M)) \times 100}{(Q_r C_r^M / (Q_r C_r^M + Q_d C_d^M)) \times 100} \quad (4)$$

Where, C_f^M , C_d^M and C_r^M are the concentrations of the metal ions (mol.L⁻¹) in the feed, dialysate, and recovered acid, respectively.

And, metal rejection was calculated by the following equation:

$$\text{Rejection (\%)} = 100 - \text{Leaching (\%)} \quad (5)$$

3.0 RESULTS AND DISCUSSION

3.1 Effect of the Equilibrium Time on the Acid Recovery

At first, the effect of time to reach the dynamic equilibrium state was investigated. The DD was fed with actual waste acid, which contained $1.1 \text{ mol } [\text{H}^+].\text{L}^{-1}$, and a water to feed ratio (water/feed) was controlled at 1 to 1. Stripping water was tap water, and water temperature was approximately 30°C . Relatively high flowrates of 0.5 , 1.0 and 1.5 L.h^{-1} (or 0.16 , 0.31 and $0.47 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$, respectively) were chosen to examine the system performances. After the diffusion process had reached steady state, the concentrations in recovered acid and dialysate were determined.

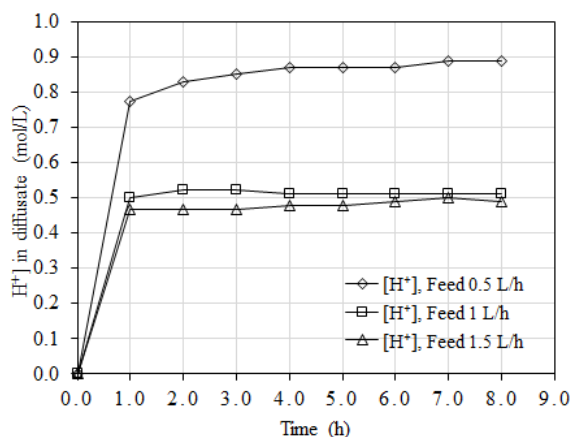


Figure 3 Effect of the equilibrium time on the H^+ Recovery

Figure 3 shows the effect of the equilibrium time on the H^+ Recovery. At a low flow rate of 0.5 L.h^{-1} , a steady state for acid recovery was achieved after 3 h. At a higher flow rate, the steady state was reached faster than the low flow rate. However, for all the three flowrates, the system seems to reach equilibrium after 3 h of operation.

This result corresponds to the results from a previous study, which reported that the steady state for acid recovery was typically achieved after 2 to 3 h. (Oh *et al.*, 2000; Wei *et al.*, 2010) According to this result, the liquid samples of the recovered acid and residual solution from all experimental runs were taken after 3 h of operation to effectively determine the optimum condition of the DD system.

3.2 Variation of the Feed Flow Rate

To examine the effect of feed flowrate on the system performance, variation of flowrate were conducted with waste acid solutions, taken from a pickling tank of a metal finishing manufacturer.

Each of the experimental runs was conducted at room temperature (30°C). The system was operated at a relatively high flow rate. The designated flow rate used for this study ranged from 0.16 to $1.25 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$. The initial concentration of H^+ in the feed was

kept at $1.09 \text{ mol } [\text{H}^+].\text{L}^{-1}$. For each experimental run, a water to feed ratio (water/feed) was controlled at 1 to 1.

Figure 4 shows the acid recovery for different flow rates. The acid recovery (%), when stripped with tap and DI water, decreased as the feed flowrate increased from 0.16×10^{-3} to $1.25 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$. The same pattern of decreasing in concentration of H^+ in the recovered acid was also observed. Based on these results, it can be said that for a membrane with a constant surface area, the protons (H^+) likely have limited time to permeate across the AEM.

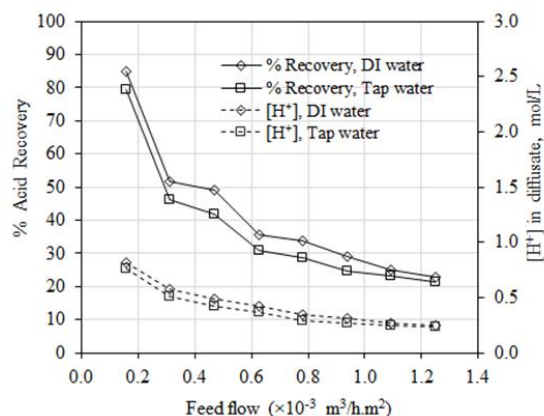


Figure 4 Concentration of $[\text{H}^+]$ and H^+ recovery (%) at various feed flow

From this study, acid recoveries (%) up to 80% and 85% were achieved at the minimum flow rate of $0.16 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$ when stripped with tap and DI water, respectively. These results are consistent with the values reported in previous studies. According to Wei *et al.* (2010) and Li *et al.* (2012), the optimum flow rate for this model (DF-120) ranged between 0.18 and $0.22 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$ and the maximum acid recovery (%) was approximately 80% at $0.21 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$.

The metal rejection (%) was also monitored to examine the DD performance. Figure 5 shows metal rejection (%) at various feed flowrates. During this study, the system was operated with water to feed ratio (water/feed) equal 1 to 1. The initial concentrations of $[\text{Mn}^{2+}]$, $[\text{Zn}^{2+}]$ and $[\text{Pb}^{2+}]$ in the feed solution were 10, 6 and 3 mg/L, respectively. As seen in Figure 7, at a minimum flow rate of $0.16 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$, the Mn, Zn and Pb ion rejections (%) were approximately 87.4%, 77.3% and 82.3%, respectively. The rejection (%) of Mn ions remained largely unchanged when the flow rate was more than $0.3 \times 10^{-3} \text{ m}^3.\text{h}^{-1}.\text{m}^{-2}$. This pattern was similar to the rejection of Zn and Pb ions.

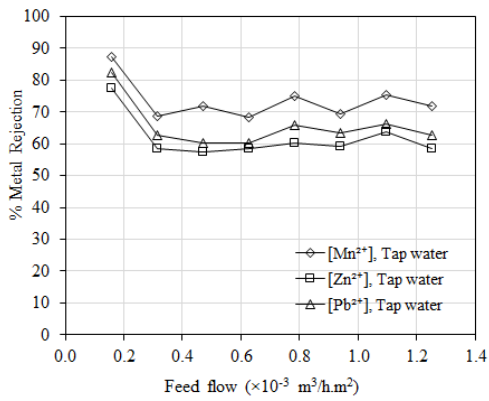


Figure 5 Metal ion rejection (%) at various feed flow

3.3 Variation of Water to Feed Ratio

The influence of water to feed ratio on the DD performance was also examined. The feed of waste acid was controlled at $0.16 \times 10^{-3} \text{ m}^3 \cdot \text{h}^{-1} \cdot \text{m}^{-2}$, and the stripping flowrate was varied to obtain water/feed ratios of 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4.

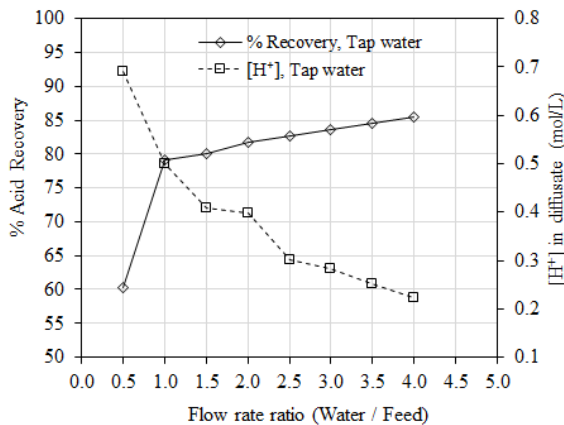


Figure 6 Concentration of [H⁺] and H⁺ recovery (%) at various water to feed ratio (water/feed)

Figure 6 shows that the H⁺ recovery (%) increased markedly with rises in the stripping water. Increasing water to feed ratio from 0.5 to 4 caused an increase in H⁺ recovery (%) from 60% to 85%, whereas the concentration of H⁺ in the recovered acid decreased from 0.7 to 0.2 mol.L⁻¹. Because increasing the water stripping rate had escalated the concentration difference between the residual solution or "dialysate" and the recovered acid or "diffusate", thus increasing the driving force for H⁺ diffusion, more H⁺ permeated through the AEM and ended up in the "diffusate". Furthermore, a gradual rise in H⁺ recovery was observed when the water to feed ratio exceeded 1.

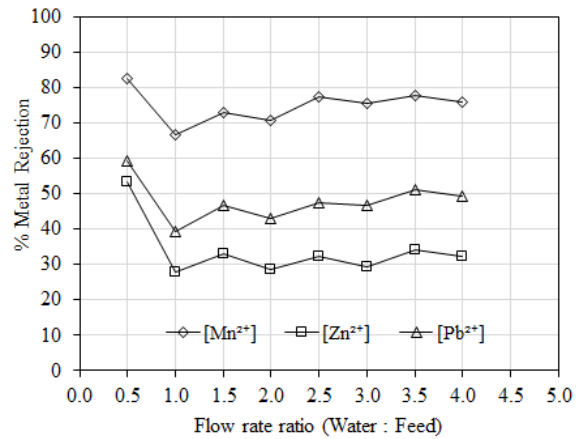


Figure 7 Metal rejections (%) at various water to feed ratio

Considering metal ion rejection (%), varying the flow rate ratio decreased the metal ion rejection (%). Figure 7 illustrates that the ability of AEM to reject Mn, Pb and Pb ions was in the following order: [Mn] > [Zn] > [Pb]. It was also found that highest metal rejection (%) was observed at lower water to feed (0.5:1). This result also corresponds with the previous work of Li *et al.* (2012), which found that "increasing the water/feed ratio decreases the metal rejection". However, increasing the ratio to more than 1 resulted in relatively unchanged percentage rejections of Mn, Zn and Pb ions. From these results, it can be said that the optimal operating conditions should be weighted upon the H⁺ recovery (%) in the diffusate (permeate or recovered acid) and rejection (%) of the concern metal ions.

4.0 CONCLUSION

In conclusion, diffusion dialysis equipped with an AEM (model DF120) is able to purify sulphuric acid from waste acid which was taken from a pickling tank of a metal finishing manufacturer. Increasing the feed flow rate decreases H⁺ recovery (%). Although the system was operating at relatively high flow rate, the major driving mechanism is governed by the concentration gradients between "diffusate" and "dialysate". Increasing the feed acid has hindered the transport of the protons (H⁺) to permeate through the AEM. A higher metal ion rejection (%) can be achieved at a lower ratio of water to feed. Approximately 85% of the H₂SO₄ was recovered under the selected operating conditions. DF-120 was able to reject metal species of interest, Mn, Zn and Pb in the waste acid, whereas the rejection of Zn ions was relatively low. The series of metal rejection by DF-120 is of the following: Mn > Zn > Pb. The results of this study give valuable suggestions for further study on the possibility of using DD for acid recovery from wastewater of battery manufacturing plant, in which the wasted acid contains high concentrations of Pb.

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