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Acidic Recovery from Wastewater of Automotive Battery Plant Using Membrane Technology

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Abstract

Diffusion dialysis (DD) equipped with anion exchange membranes (AEMs) is used as an effective tool to recover acid from various types of waste acid solutions. The aim of this study was to investigate the possibility of using the DD process to recover sulfuric acid (H_sSO_4) from the acidic wastewater from an automotive battery plant. A numbers of experimental runs was conducted to optimize the equipment's operating conditions, particularly variations in feed flow and flow rate ratios. The results showed that H_2SO_4 permeated well through the AEM, while metal ions were efficiently rejected. The recovery of H_2SO_4 increased as flow rate decreased. Approximately 84.5% of H_2SO_4 could be recovered at 9.38×10^{-5} m^3 h^{-1} m^{-2}. Pb^{2+} rejection was 69.5%. In addition, recovery efficiency could be improved by increasing the flow rate ratio. At the highest flow rate ratio, DD could recover up to 90% of H_2SO_4 while the lowest rejection of Pb^{2+} (61%) was obtained. Also, the investigation of the effect of variation of flow rate ratio on recovery efficiency revealed that the optimum flow rate ratio should be controlled at around 1 to 1.2.

Keywords: Acid recovery; Anionic exchange membrane; Battery plant; Metal ions rejection; Synthetic wastewater

Introduction

Typically, the production process of automotive battery involves grid casting, lead oxide and paste sheets. These processes create large amount of acidic wastewater and heavy metals such as lead (Pb^{2+}) and iron (Fe^{2+}). Due to industrial effluent standards, lead-bearing wastewater requires special treatment before being discharged. Conventionally, acidic wastewater is treated by a neutralization process using NaOH,

$Ca(OH)_2$ or NH_3-H_2O [1,2]. However, this method produces large quantity of chemical sludge which requires further chemical treatment before being disposed to secure landfill.

Technologies to recover inorganic acids have been extensively studied, including ion exchange, distillation, electrohydrolysis, solvent extraction and pressure driven-membrane separation [3-7]. Diffusion dialysis (DD) is an alternative method that can be effectively used for acid recovery. In principle, DD is a membrane separation process equipped with an Anion Exchange Membrane (AEM) which allows selective passage of H^+ and anionic species. The main driving force is governed by a concentration difference across an AEM, which follows the Donnan criteria of co-ion rejection and preserves charge balance. Among other compatible acid recovery techniques, DD is a relatively environment-friendly technology due to its high acid recovery yields and high metal rejection efficiency, minimal chemical usage, low energy consumption, and operational simplicity [8-10]. In addition, recent research has investigated the utility of an anion exchange membrane (AEM) to recover acid and reject metal ions [11-16].

In this study, we aimed to explore the potential of DD-AEM to recover H_2SO_4 from acidic wastewater from an automotive battery production plant, and to determine the optimum operating conditions.

Experimental

1) Chemicals and wastewater

All chemicals used in this study were analytical grade, including; 98% concentrated H_2SO_4 (Merck, Germany), $Pb(NO_3)_2$ reagents (Applichem, Germany), NaOH (Fisher Chemical, Belgium), phenolpthalein (Labchem, Australia) and ICP multi-element standard solution (Perkin Elmer, USA).

The actual acidic wastewater was taken from the final sedimentation tank of an automotive battery plant in Samut Prakarn, Thailand. The chemical characteristics of this wastewater are shown in Table 1.

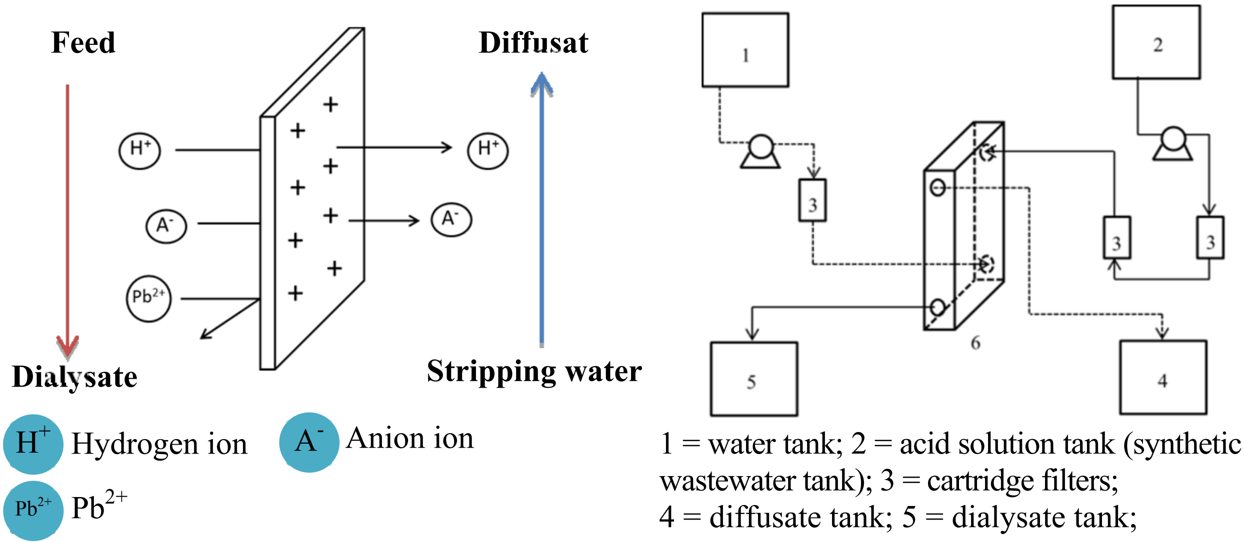
The synthetic wastewater in this study was prepared from analytical grade H_2SO_4 and $Pb(NO_3)_2$ reagents to resemble the chemical characteristics of the acidic wastewater, as shown in Table 1. The free H^+ concentration was around 0.03 mol L^{-1}, and the concentration of $Pb(NO_3)_2$ in the solution was 6 mg L^{-1}.

Table 1 Chemical composition of acidic wastewater taken from the final sedimentation tank from an automotive battery production plant

Parameters	**Concentration (mg L^{-1})**		
	Acidic	**Tap water**	**Deionized water**
TDS	9.07×10^3	163	1.02
H^+ (mol L^{-1})	0.03	2.5×10^{-8}	3.1×10^{-6}
Pb	5.693	ND	ND
Fe	3.439	ND	ND
Zn	0.261	0.16	0.09
Cr	0.05	ND	ND
Mn	0.014	ND	ND
SO_4^{2-}	2888.67	18	ND
NO^{3-}	0.33	2.29	0.45
Cl^-	21.19	12	ND

2) Experimental setup

In this study, a laboratory-scale DD was set up to recover H_2SO_4 from the acidic wastewater from the automotive battery plant. The DD principle and the experimental schematic for this study are illustrated in Figure 1 (a) and 1(b), respectively. The dialyzer stack was separated by 40 sheets of AEM (DF 120, Shandong China), with each AEM sheet measuring 0.2 m width × 0.4 m in length. The total membrane area was 3.2 m^2.The characteristics of the AEM used in this study are shown in Table 2 [8]. In order to achieve high diffusion efficiency, the flow pattern of the feed and stripping water (i.e. tap water) were counter-current due to the low linear flow velocity in the dialyzer stack [17]. As shown in Figure 1, both synthetic wastewater and tap water were passed through a cartridge filter (PTFE, 50 µm) to remove suspended particles before entering the dialyzer. Before the start of each experiment, the dialyzer stack was fed with the synthetic wastewater (feed side) and tap water (water side) before closing the valves. The AEM was soaked for 2 h to equilibrate the ionic condition between both sides [18]. Then, each experimental run was started, and samples were taken after each run had reached its steady state condition. The steady state was predetermined by running the system with the following opera- ting conditions: feed flow rate 9.38×10^{-5} $m^3\ h^{-1}\ m^{-2}$, flow rate ratio 1 to 1, as shown in section 3.1 selecting the stripping water. Therefore, for all runs, a steady state was attained after 5 h of operation.



1 = water tank; 2 = acid solution tank (synthetic wastewater tank); 3 = cartridge filters;
4 = diffusate tank; 5 = dialysate tank;
6 = diffusion dialyzer

(a) (b)

Figure 1 The Diffusion Dialysis (DD): (a) Principe of DD
(b) The experimental schematic of DD process used in this study

Table 2 Properties and specification of AEM

Item	Specifications
Material	BPPO amination and crosslinking
Water content (%)	42.34
Thickness (mm)	0.2-0.23
Transference number of ions in membrane	0.981
Membrane area resistance (Ω cm^2)	3.5-4.0
Ion exchange capacity (mmol g^{-1})	1.7-1.9
Burst strength (MPa)	> 0.9

Figure 2 illustrates the sources of wastewater from each production unit and the DD process. It was found that pH of this wastewater was around 1.44, with total lead concentrations exceeding the permissible discharge limit (Industrial Effluent Standard in Thailand).

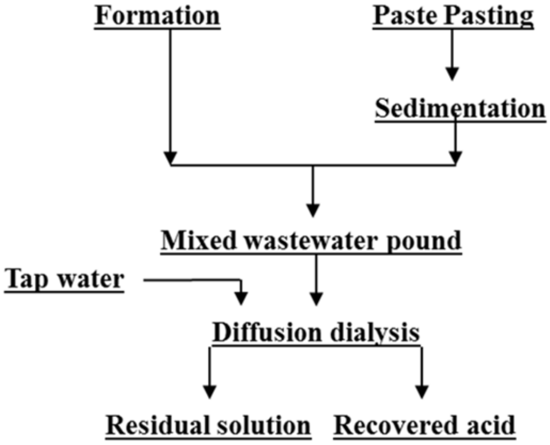


Figure 2 Production process and wastewater treatment using DD process flow sheet

3) Method and calculations

Concentration of H_2SO_4 was determined by titration, using 0.05 mol L^{-1} of NaOH as titrant with phenolphthalein as an indicator [9]. The concentrations of Pb^{2+} in the feed and diffusate were analysed using ICP-OES (Perkin Elmer, Optima 8000, USA). Total acid recovery percentage (%R) was calculated using the following equation [19].

$$\%R = \left(\frac{Q_d C_d^H}{Q_{feed} C_f^H}\right) \times 100 \tag{1}$$

Where Q_d is the flow rate of diffusate (L h^{-1}), Q_{feed} is the flow rate of feed (L h^{-1}), C_d^H and C_f^H are concentrations of H_2SO_4 in diffusate and feed (mol L^{-1}), respectively.

The percentage of Pb^{2+} rejection (%r) was calculated by the following equation.

$$\%r = 1 - \left(\frac{Q_d C_d^M}{Q_{feed} C_f^M}\right) \times 100 \tag{2}$$

Where C_d^M and C_f^M are the concentrations of Pb^{2+} in diffusate and feed (mol L^{-1}), respectively.

Results and discussion

1) Selecting the stripping water

To investigate the possible influence of the conductivity of the stripping the water on the performance of the DD, two experiments were set up to investigate the performance of DD using different type of stripping water (tap water and DI water). Synthetic wastewater containing 0.03 mol L^{-1} of H^+ was used in this study. The operating conditions used in this test were flow rate ratio (stripping flow rate/feed flow rate) of 1 to 1 (feed flow rate and stripping water flow rate was 9.38×10^{-5} m^3 h^{-1} m^{-2}).

Figure 3 shows that a higher %R was achieved using tap water as stripping water. After the system had reached equilibrium, %R obtained from the test run with tap water and DI water were 84.24% and 60.25%, respectively. The difference can be explained by the level of H^+ concentration in the stripping water. Since pH of DI water was relatively lower than that of the tap water, this resulted in a higher H^+ concentration in the DI water. This result confirms the theoretical consensus among researchers that concentration gradient is the major driving mechanism of the diffusion of H^+ from the feed side to the diffusate [20]. Also, with respect to the conductivity of stripping water, it can be said that the amount of ionic species in the stripping water has less effect of the DD performance concerning the %R. As a result of this clear finding, tap water was subsequently used as stripping water for the later experiments.

2) Effect of feed flow rate on the diffusion dialysis performance

In order to investigate the effect of feed flow rate on the DD performance, five experimental runs were conducted by varying the feed flow rate as follows: 9.38×10^{-5}, 15.63×10^{-5}, 21.88

$\times 10^{-5}$, 28.13×10^{-5} and 34.38×10^{-5} m^3 h^{-1} m^{-2}. Other variables were kept constant, i.e. flow rate ratio was 1 to 1. The operating time to reach equilibrium for each run was 5 h.

Figure 4 showed the effect of feed flow rate on %R and %r after 5 h of operation. It was found that increasing feed flow rate led to reduced %R. The highest acid recovery (up to 85%) was obtained at the lowest feed flow rate (9.38×10^{-5} m^3 h^{-1} m^{-2}). In addition, lowest acid recovery (67%) was observed when the feed flow rate raised to 34.38×10^{-5} m^3 h^{-1} m^{-2}. In contrast to the results of %R, the %r increased when the feed flow rate had increased. Increasing the feed flow rate to 28.13×10^{-5} m^3 h^{-1} m^{-2} caused a maximum %r of 81%. However increasing the feed flow rate beyond 28.13×10^{-5} m^3 h^{-1} m^{-2}, an unchanged in %r was observed.

At higher feed flow rates, the diffusion layer at the surface of AEM is relatively thinner while the turbulence in the bulk solution is rather greater than for the lower feed flow rate. These conditions would hinder transportation of H$^+$ across the membrane. Since the AEM is able to repel the cationic species (M^{2+}) and prevent them from moving across the membrane, the possible causes of these cations to pass through the membrane would depend on the degree to which these ions can form complexes with anionic species in the bulk solution. Hence, a higher feed flow rate would shorten the retention time for Pb^{2+} to form complex ions (i.e. $[PbCl_3]^-$, $[Pb(OH)_3]^-$). Such a condition would reduce the opportunity for Pb^{2+} to diffuse across the membrane [21, 22].

3) Effect of flow rate ratio on diffusion dialysis performance

To investigate the effect of flow rate ratio, five experimental runs were conducted. During each run, the system was fed with the acidic wastewater at a fixed flow rate 15.63×10^{-5} m^3 h^{-1} m^{-2}. Five variables of stripping water flow rate were adjusted to acquire the designated flow rate ratio: 0.4, 0.8, 1.0, 1.2 and 1.6. Figure 5 shows the plots of H$^+$ concentration in the diffusate and %R against flow rate ratio.

It was found that raising the flow rate ratio from 0.4 to 1.6 caused an increase in %R, but reduced the concentration of H$^+$ in the diffusate. The %R varied from 37.43 to 96% while the concentration of H$^+$ in the diffusate varied from 0.018 to 0.028 mol L^{-1}.

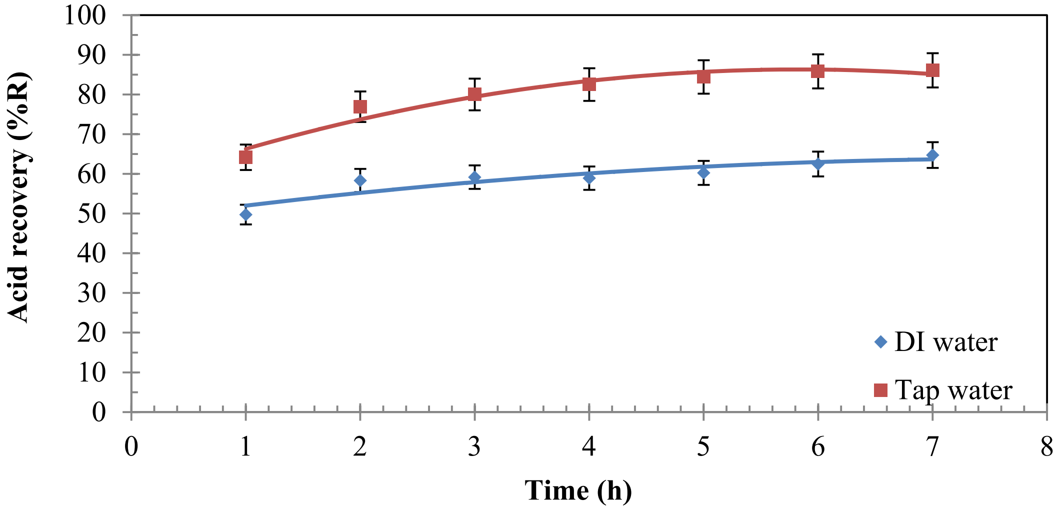


Figure 3 %R against time at different type of stripping water
[Operating conditions: feed flow rate 9.38×10^{-5} m^3 h^{-1} m^{-2}, flow rate ratio 1 to 1]

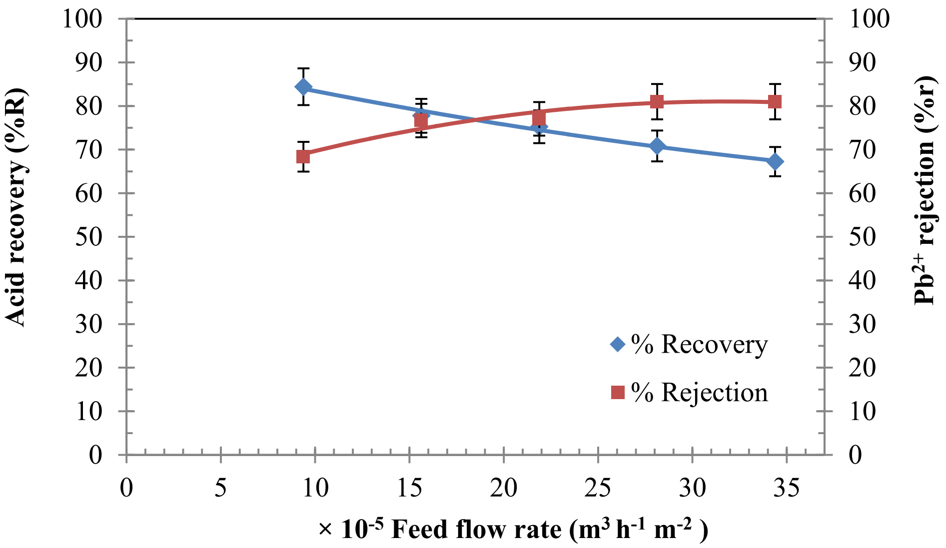


Figure 4 Effect of feed flow rate on %R and % r [Operating conditions: flow rate ratio of 1 to 1]

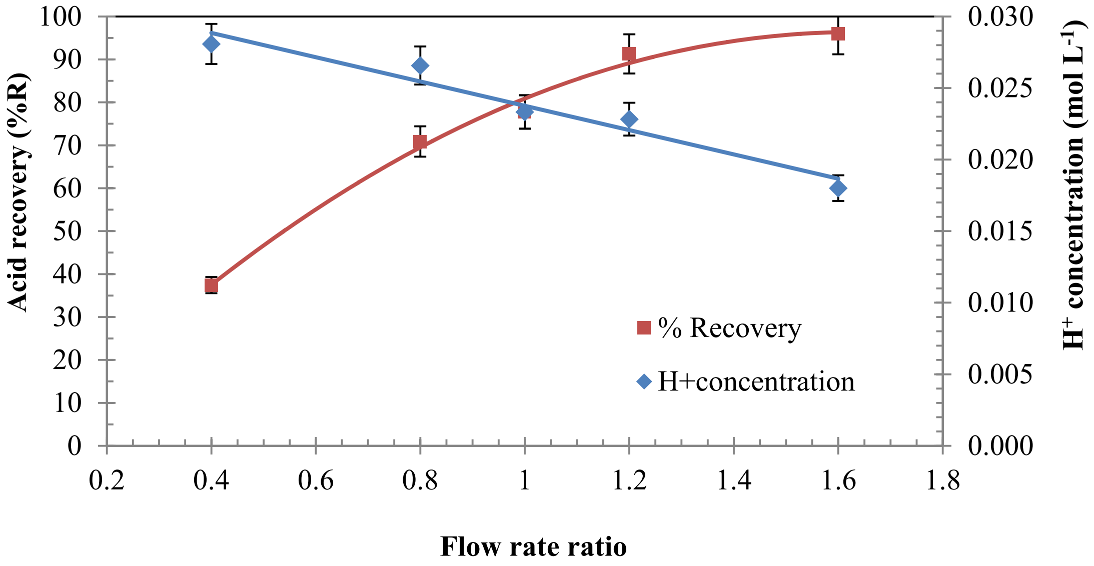


Figure 5 Effect of flow rate on H^+ concentration and %R in the diffusate

These results revealed that the performance of the DD process depends strongly on concentration gradient. Since a higher flow rate ratio allows more stripping water to enter the system, the concentration differences between the feed side and diffusate side was larger at higher water to feed ratios. Hence, a higher %R was obtained at higher flow rate ratios [1, 10, 23, 24].

Considering Pb^{2+} rejection, it was found that the %r had decreased from 86% to 61% when the flow rate ratio increased from 0.4 to 1.6, as shown in Figure 6. From the result, Pb^{2+} tends to diffuse through the membrane at higher flow rate ratios. This is probably caused by a high stripping rate at higher flow rate ratios. Hence, the complex form of Pb^{2+} was stripped away at a faster rate than that under a lower flow rate ratio.

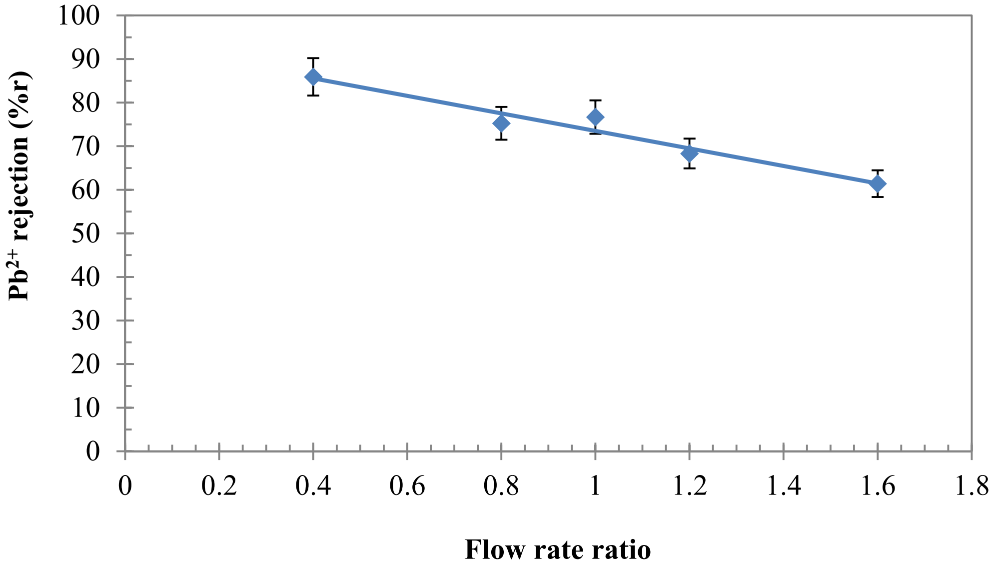


Figure 6 Effect of flow rate ratio on metal ions rejection

Results of %R and %r at variable flow rate ratio are summarized in Table 3. As expected, highest acid recovery (96.33%) was obtained at highest flow rate ratio (1.6 to 1) due to the effect of higher concentration gradient, while the lowest Pb^{2+} rejection (61.44%) and molarity of H^+ in diffusate (0.0187 mol L^{-1}) was also obtained. In contrast, a lower flow rate ratio would cause higher Pb^{2+} rejection and molarity of H^+ but lower %R. From these results, the optimum flow rate ratio could be sensibly determined by weight up %R and %r with the molarity of H^+ in diffusate. Based on previous studies, it was recommended that the flow rate ratio should be controlled in range 1.0 - 1.2 [1, 19]. In this study, the flow rate ratio was controlled at 1.

Table 3 Summary of % R and %r at variable flow rate ratio.

Flow rate ratio	Acid recovery (%R)	H^+ concentration in diffusate (mol L^{-1})	Pb^{2+} rejection (%r)
0.8	55.05	0.0289	77.53
1.0	80.87	0.0238	73.51
1.2	89.13	0.0221	69.49
1.6	96.33	0.0187	61.44

Conclusions

The performance of a continuous process using the AEM-equipped DD to recover acid from acidic wastewater from an automotive battery plant was evaluated. The results point to the following conclusions:

1) Concentration gradient is the major driving mechanism for the diffusion of H^+ through the AEM.

2) %R is dependent on the concentration difference of H^+ between the feed and stripping water.

3) %R tends to increase at lower feed flow rate, while in contrast, Pb^{2+} tends to move faster across the membrane at lower feed flow rates.

4) %R tends to increase as the flow rate ratio increases. In contrast, %r and H^+ concen-

trations decreased with increasing flow rate ratios.

5) For further study, the optimum operating conditions was as follows: feed flow rate 15.63 × 10^{-5} m^3 h^{-1} m^{-2} and flow rate ratio between 1.0 to 1.2.

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