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Study on adsorption phenomenon of diffusion dialysis for acid recovery

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ABSTRACT

Diffusion dialysis (DD) is widely used to recover acid from waste water. This study examined the acid adsorption phenomenon from the non-steady state to dynamic equilibrium in a continuous dialyzer, and obtains the breakthrough curves at different acid concentrations and for different acid species (HNO_3, H_2SO_4, H_3PO_4). Then the dynamic adsorption capacities (Q_{ads}) were calculated from breakthrough curves via the integration method, and they were identical to the Freundlich equilibrium isotherm. Finally, the operating conditions, such as the volumetric liquid flow rate of the feed, flow ratio and temperature were optimized on the basis of the adsorption and diffusion phenomenon in the DD process.

1. Introduction

A technological process in membrane separation, diffusion dialysis (DD) with anion-exchange membrane, has attracted considerable interest in acid recovery because it is characterized by high proton permeability, strong salt rejection, low energy consumption and easy operation during processing [1].

Recovery by DD of HCl, H_2SO_4, and HNO_3 from waste solutions has been studied [1–3], and the membrane mass transfer coefficient and diffusivity of those acids in the membrane have been quantified [4]. The general approach has been to use the first assumption of the solution-diffusion model that was used to describe the DD process. This is the simplest application of the model because only concentration gradients are involved [5]. However, the force and process of acid through the membrane from the dialysate cell to the diffusate cell have never been investigated in detail. Therefore, it has been a widely accepted research objective to establish the model of the DD process, especially the relationship between the characteristics of the membrane and the transport process in the field of acid recovery [6,7].

Recently, researchers have reported the dynamic adsorption process through cation exchange membranes [8] and membrane chromatography [9,10]. In the membrane chromatography process, the ion-exchange membrane is used as an alternative to conventional resin-based adsorption columns to purify molecules. Membrane chromatography operates in convective mode, which can significantly reduce diffusion limitations commonly encountered in column separation processes [11]. Although it is much simpler than DD, it provides a possible way to relate the adsorption phenomenon to the DD transport process.

The aim of the present study is to examine the acid adsorption phenomenon of anion-exchange from the non-steady state until dynamic equilibrium is obtained in the DD process. The study on mechanism will be beneficial to optimization of operational parameters of the DD process for acid recovery.

2. Experimental procedure

2.1. Materials and analysis

All the acid solution used for diffusion dialysis experiment was prepared with analytically pure chemicals (HNO_3, H_2SO_4, H_3PO_4) and de-ionized water (conductivity <10 μS/cm). The acid concentration was determined by titration using 0.1 mol/L NaOH with phenolphthalein as an indicator.

2.2. Apparatus

The anion exchange membranes were Selemion DSV type (Asahi Glass Co., Ltd., Japan) and a 0-Type diffusion dialyzer was used for diffusion dialysis. The dialyzer was separated by nine sheets of anion exchange membranes (0.25 × 0.16 m) into five dialysate and five diffusate cells (each cell was 0.18 × 0.002 × 0.10 m in volume). The effective membrane area was 0.162 m^2

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Table 1
Characteristics of the Selemion DSV type anion exchange membrane.

Item	Specifications
Thickness	100 μm
Burst Strength	0.14 MPa
Resistance	1.1 Ω cm^2 (0.5 M/L NaCl)
IEC[12]	4.5–5.5 meq/g

(9 × 0.18 m × 0.10 m). Table 1 shows the ion exchange membrane's characteristics [12] (www.selemion.com).

In order to avoid the influence of different acid ions, the membranes are saturated with about 1.0 mol/L acid used in the following experiment for 3 h, then rinsed and washed with de-ionized water repeatedly (3–4 times) every three hours before the experiment until water conductivity in the cells was the same as in the de-ionized water. All the experiments were conducted at an ambient temperature around 20 ± 1 °C. Fig. 1 shows the experimental apparatus and the DD principles.

2.3. Experiment and calculations

In order to displace air from all the cells, two feed-in techniques were used. Feed-in condition 1, dialysate cells were filled with feed and diffusate cells were filled with de-ionized water. Feed-in condition 2, all the cells were filled with de-ionized water. Then, the following steps were the same. As the complete displacement of air required 2–3 min, the beginning of each experiment was adjusted to this point. During the displacement, the acid concentration in the feed decreased. In both the cases, the solutions were pumped by two peristaltic pumps YZ1515x (Baoding Longer Precission Pump Co., Ltd,). The acid concentrations in the residual and recovery solutions were determined at various times until the dynamic equilibrium was reached.

In order to simplify calculations, all the equations were based on a series of assumptions: (1) the concentration profile in each cell in the direction of the flow is linear at equilibrium, (2) no flux of the solvent through the membrane, and (3) a uniform component concentration over the cross section of the compartment.

Based on material balance, the total acid capacities (Q_{total}) in the continuous dialyzer at equilibration time can be expressed as follow:

Feed-in condition 1:

$$Q_{total} = C_F V_{dia} + \int_0^{t_{eq}} (C_F \cdot V_F + C_W \cdot V_W - C_{D,t} \cdot V_D - C_{R,t} \cdot V_R)dt \quad (1)$$

Feed-in condition 2:

$$Q_{total} = \int_0^{t_{eq}} (C_F \cdot V_F + C_W \cdot V_W - C_{D,t} \cdot V_D - C_{R,t} \cdot V_R)dt \quad (2)$$

where t_{eq} is the initial time point when the concentrations of recovery solution and residual solution reach a stable values in dynamic DD process.

C_F and C_w are the acid concentrations of feed solution and de-ionized water respectively, $C_W = 0$ mol/L. $C_{D,t}$ and $C_{R,t}$ are the concentrations of residual solution and recovery solution at time t, respectively. $C_R^{t_{eq}}$ and $C_D^{t_{eq}}$ are the acid concentrations of recovery solution and residual solution at time of t_{eq}, respectively.

V_D, V_F, V_W and V_R are the volumetric liquid flow rates of the residual solution, the feed solution, de-ionized water and recovery solution, respectively. v_{dia} and v_{dif} are the total volumes of the dialysate cells and diffusate cells, respectively, $v_{dia} = v_{dif} = 0.18$ L.

The total acid capacities are including two parts: the amount adsorpted in the ion exchange membrane (Q_{ads}) and accumulated in the solution of the cells ($Q_{solution}$).

$$Q_{total} = Q_{ads} + Q_{solution}. \quad (3)$$

According to the above assume, $Q_{solution}$ can be expressed as follow:

$$Q_{solution} = \frac{1}{2}(C_F + C_D^{t_{eq}})V_{dia} + \frac{1}{2}(C_W + C_R^{t_{eq}})V_{dif}. \quad (4)$$

Eqs. (5) and (6) can be obtained, describing the amounts adsorpted in the ion exchange membrane (Q_{ads}) under the different Feed-in conditions by combining the Eqs.(1)–(4).

Feed-in condition 1:

$$Q_{ads} = \int_0^{t_{eq}} (C_F \cdot V_F - C_{D,t} \cdot V_D - C_{R,t} \cdot V_R)dt + \frac{1}{2}(C_F - C_D^{t_{eq}})V_{dia} - \frac{1}{2}C_R^{t_{eq}}V_{dif} \quad (5)$$

Feed-in condition 2:

$$Q_{ads} = \int_0^{t_{eq}} (C_F \cdot V_F - C_{D,t} \cdot V_D - C_{R,t} \cdot V_R)dt - \frac{1}{2}(C_F + C_D^{t_{eq}})V_{dia} - \frac{1}{2}C_R^{t_{eq}}V_{dif}. \quad (6)$$

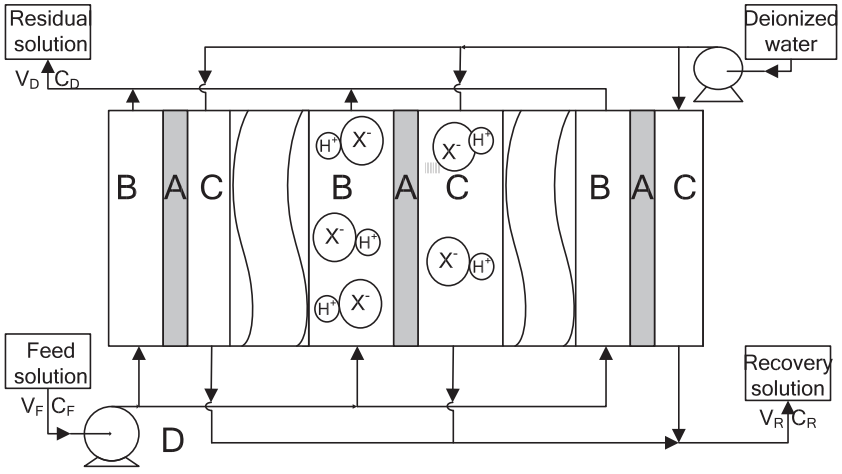

Fig. 1. The experimental apparatus and DD principles (A – Anion-exchange membrane, B – Dialysate cell, C – Diffusate cell, D – Peristaltic pump).