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Anion exchange membranes used in diffusion dialysis for acid recovery from erosive and organic solutions

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ABSTRACT

Diffusion dialysis (DD) is a process that the solutes pass through the ion exchange membrane from the feed side to water side. Some solutes such as $HCl–FeCl_2$ may be erosive on membrane structure during practical DD process. The erosion effects are investigated by four anion exchange membranes, including commercial membranes DF-120 and 9010, and our previous membranes based on quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) and polyvinyl alcohol (PVA). Besides, the membranes are also used to separate organic solution containing HCl and glyphosate, which is produced largely during the preparation of glyphosate pesticide.

The membrane structures are damaged and their performances are reduced after the erosion of $HCl–FeCl_2$, which are mainly attributed to the loss of $–N^+(CH_3)_3Br^-$ and –OH groups. The weight loss percent is in the range of 10–21%, the ion exchange capacity decreases but the swelling degree increases. The dialysis coefficient of HCl ($U_{H\text{-}1}$) and separation factor (S_1) reduce to 0.006–0.010 m h^{-1} and 13.9–15.5 for commercial membranes, and 0.016–0.024 m h^{-1} and 33.2–47.6 for QPPO/PVA membranes, correspondingly. Besides, the membranes without erosion are used to separate organic solution containing HCl and glyphosate. The $U_{H\text{-}2}$ is in the range of 0.0040–0.0062 m h^{-1} for commercial membranes, and 0.0094–0.0104 m h^{-1} for QPPO/PVA membranes. The $U_{H\text{-}2}$ values are generally stable within 10 h, and the acid concentration in the feed side decreases from 5.82 to 3.16 mol L^{-1}. Hence, the QPPO/PVA membranes can be potentially applied in DD process to recover acid from organic solution containing HCl and glyphosate.

1. Introduction

Diffusion dialysis (DD) using anion exchange membrane is an effective separation process for acid recovery [1]. During DD process, the membrane is fixed in a two-compartment cell. One compartment is filled with waste solution such as $HCl/FeCl_2$ [2–4], which is signed as dialysate side or feed side [4]. The other compartment is filled with water, which is signed as diffusate side, or water side in this paper for convenience of comparison. The membrane, as a key factor during DD process, can be equipped in two types of DD dialyzers including batch and continuous dialyzers, as illustrated in Scheme 1. The batch dialyzer is used mainly in laboratory [5]. The concentration in feed side is homogenous but decreases with the time, and the concentration in water side is also homogenous but increases with the time. The continuous dialyzer can be used for practical separation [1,3,6]. The concentration is generally stable in either feed side or water side with respect to the time. However, the concentration in feed side decreases, and the concentration in water side increases along the flowing direction.

The continuous DD running has two characters which are often insignificant or even neglected for batch DD running. Commercial membrane DF-120, which contains fibers as support and is produced by Tianwei Membrane Co. Ltd., Shandong of China, is taken as an example to separate $HCl/FeCl_2$. Firstly, one part of the membrane contacting with pure water (concentration of 0% in Scheme 1) tends to become red and soft after several months, and even falls off from its fibers support. Secondly, long-term DD running is needed to obtain high concentration in water side (recovered acid), and low concentration in feed side (depleted solution) [7]. The recovered acid can be reused [1], and the depleted solution may be further extracted.

The continuous dialyzer needs dozens of membrane sheets with large area. For example, forty membrane sheets, with total area of 3.2 m^2, need to be equipped in the continuous dialyzer [1,3]. Hence, usually only commercial membranes can be used for the continuous DD running. The commercial membranes sometimes have insufficient DD performances due to their imperfect structures. For example, the continuous dialyzer using commercial

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Nomenclature

QPPO	quaternized poly(2,6-dimethyl-1,4-phenylene oxide), which contains $-N^+(CH_3)_3Br^-$ groups	$U_{H\text{-}2}$	dialysis coefficient of HCl for HCl/glyphosate waste solution
PVA	polyvinyl alcohol	DMF	dimethyl formamide
EPh	monophenyl triethoxysilane	IEC	ion exchange capacity
TEOS	tetraethoxysilane	W_R	water uptake
DD	diffusion dialysis	M	mol L^{-1}
$U_{H\text{-}0}$	dialysis coefficient of HCl for HCl/$FeCl_2$ solution	SEM	scanning electron microscopy
S_0	separation factor for HCl/$FeCl_2$ solution	EDS	energy dispersive spectrometer
$U_{H\text{-}1}$	dialysis coefficient of HCl after the erosion of HCl–$FeCl_2$	C_f	the acid concentration in feed side
S_1	separation factor after the erosion of HCl–$FeCl_2$	C_d	the acid concentration in water side

DF-120 membrane with area 500 m^2 can only treat the waste solution of 6 $m^3\,d^{-1}$ [8]. Hence, membranes with superior structures need to be developed further. Recently, new commercial membrane 9010 has been developed in Tianwei Membrane Co. Ltd. Besides, we have also developed anion exchange hybrid membranes based on quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) and polyvinyl alcohol (PVA) [9]. The QPPO/PVA membranes contain both $-N^+(CH_3)_3Br^-$ and –OH groups, as shown in Scheme 2. The –OH groups can accelerate the transport of H^+ ions and thus enhance the DD performance (0.021–0.049 m h^{-1}, 26–39), which are much higher than those of commercial DF-120 membrane (0.009 m h^{-1}, 18.5). The high batch DD performance indicates that the QPPO/PVA membranes may be potentially applied in continuous DD running.

Fortunately, the characters of continuous DD running can also be simulated with smaller membrane sample according to the DD mechanisms. The possible reason for the HCl–$FeCl_2$ erosion is that the $FeCl_2$ component can be hydrolyzed in water side. Part of the $FeCl_2$ may be changed into $Fe(OH)_2$, and then become Fe_2O_3 within the membrane matrix near the water side. The emergence of $Fe(OH)_2$ and Fe_2O_3 damages membranes matrix, which will be simulated in this work. Besides, the long-term running can also be simulated through batch DD process. Here waste solution containing HCl and glyphosate (Scheme 2) will be used. The waste solution is produced largely during the preparation of glyphosate pesticide [10–12]. The solution also contains other organic components such as triethylamine and trimethyl phosphate but without much water. After the DD process, the recovered HCl can be reused, and the glyphosate can also be recrystallized within the depleted solution.

Hence, this work is to investigate the erosion effect of HCl–$FeCl_2$ and the long-term DD running of HCl/glyphosate solution. The erosion effect and long-term running will be compared among four membranes including commercial DF-120 and 9010, and previous QPPO/PVA membranes [9]. The erosion effects on membrane properties are evaluated by the weight loss percent, water uptake (W_R), ion exchange capacity (IEC) and DD performance. Finally, the membranes without erosion will be used to separate organic solution containing HCl and glyphosate for 10 h.

2. Experimentals

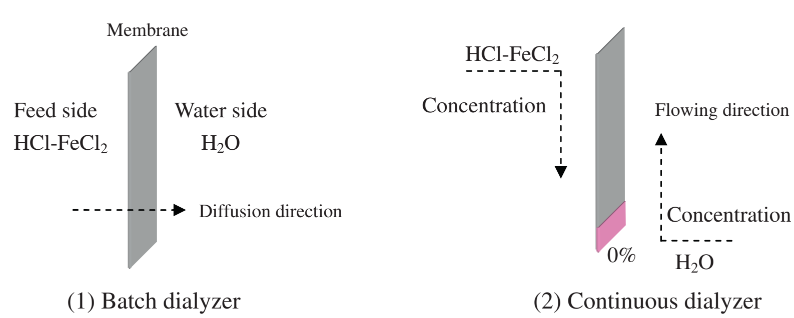
2.1. Materials

Quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) solution was prepared from brominated poly(2,6-dimethyl-1,4-phenylene oxide) through quaternization. The procedures were similar to those of our previous reports but without the hydrolysis process [4]. PVA was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. (China). The average degree of polymerization was 1750 ± 50. Monophenyl triethoxysilane (EPh), tetraethoxysilane (TEOS) and other regents were from domestic chemical reagents company and of analytical grade. Distilled water was used.

2.2. Four types of anion exchange membranes

Two commercial and two QPPO/PVA membranes were used in this research. The membrane properties and batch DD performances were listed in Table 1.

(1) Commercial membrane DF-120 was used as a reference. DF-120 membrane was based on QPPO and was widely used in China for acid recovery [1,3,4,8,13]. DF-120 membrane had the thickness of 320 μm in wet state, water uptake ($W_{R\text{-}0}$) of 42%, ion exchange capacity (IEC_0) of 1.96 mmol/g in dry state, dialysis coefficient of HCl ($U_{H\text{-}0}$) of 0.009 m h^{-1} and separation factor (S_0) of 18.5.
(2) Commercial membrane 9010 was used as a reference. 9010 membrane was a new mode produced by Shandong Tianwei Membrane Technology Corporation of China. The membrane



Scheme 1. Schematic structures of the DD devices: (1) the solution concentration in batch dialyzer changes with the time, while (2) in continuous dialyzer changes with the flowing direction.