Separation and Purification Technology 136 (2014) 250–257

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Facile and cost effective PVA based hybrid membrane fabrication for acid recovery

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ARTICLE INFO

Article history:
Received 9 August 2014
Received in revised form 14 September 2014
Accepted 15 September 2014
Available online 1 October 2014

Keywords:
Anion exchange membrane
Hybrid membrane
Diffusion dialysis
Acid recovery
PVA

ABSTRACT

A new route for a hybrid anion exchange membrane was proposed for diffusion dialysis (DD) using polyvinyl alcohol (PVA) and glycidyl trimethyl ammonium chloride (EPTAC) as starting materials and aminopropyltriethoxysilane (KH550) as crosslinking agent. A series of membranes were prepared by varying the content of EPTAC. The obtained membranes were characterized with ion exchange capacity (IEC), water uptake (W_R), linear expansion ratio (LER), tensile strength (TS), elongation at break (E_b), thermal decomposition temperature (Td) and initial decomposition temperature (IDT), etc. Their diffusion dialysis (DD) performance was conducted with a simulated feed containing 0.81 M HCl + 0.18 M $FeCl_2$. The results show that the membranes not only have good chemical/thermal stability, but possess high DD performance. The dialysis coefficients (U_H) are in the range of 0.011–0.018 m/h and the separation factors (S) are in the range of 18.5–21 at 25 °C, both are higher than those of the commercial DF-120 membrane (0.009 m/h for U_H, 18.5 for S) determined at the same conditions. Considering its low cost and easy fabrication, the route for hybrid anion exchange membranes provides better candidates in DD process for acid recovery.

1. Introduction

Pickling of metal fine mines with inorganic acids is one of the key steps in manufacturing metal or its related products [1–3]. Inorganic acids are also used in metals etching in hydrological industries, steel industry, electronics industries, etc [4–9] During these processes, large quantities of aqueous waste which contains metal ions and acids of high concentration will be produced. The accumulation of metal ions in the waste will result in decreased efficiency of the picking/etching agent. Dumping these wastes posed severe environment pollution. In the meantime, recovering acids from these wastes for reuse can be cost effective. The above mentioned facts prompted the related industries to give serious consideration in treating these wastes.

To date, methods to treat such wastes include: neutralization [10], extraction [11], evaporation [12], electrodialysis [13], diffusion dialysis [14], etc. Most methods are limited by the high energy cost, high capital investment and thus are not economically feasible. For example, evaporating sulfuric acid-contained wastes for the recovery of the acid involves concentrating the free acid, removing the sulfate and decomposing the sulfate [15]. In comparison, diffusion dialysis based an anion exchange membrane provides an attractive method to treat such wastes, which can make the recycle of the acid in addition to the recovery of metal ions and water and thus has been considered to be a cleaner, energy-efficient and low cost technology.[16]. Till now, it has been widely used in the recovery of inorganic acids including hydrochloric acid (HCl) [17], sulfuric acid (H_2SO_4) [18], and nitric acid (HNO_3) [19] and some organic acids [20,21], etc. As shown in Fig. 1, there has been an increased interest in associated studies over the years.

Besides on the sorption of the individual components on membrane, diffusion dialysis relies mainly on the difference in the diffusivity between acids and salts in the membrane. The anion exchange membrane is critical for the purpose. The anion exchange membrane for diffusion dialysis differs from that for electrodialysis and it should be stable in acid medium with good diffusivity toward protons, while good rejection to other cations, relatively high water content but poor water permeability. Stachera et al. reported a dialytic membrane prepared by photo-initiated polymerization of 4-vinyl-pyridine with varying amounts of DVB in the pores of PP substrate [22]. Surface modified and pore-filled anion exchange membranes were also prepared for diffusion

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http://dx.doi.org/10.1016/j.seppur.2014.09.013
1383-5866/

Nomenclature

PVA	polyvinyl alcohol	TS	tensile strength
EPTAC	glycidyl trimethyl ammonium chloride	E_b	elongation at break
KH550	aminopropyltriethoxysilane	IDT	initial decomposition temperature
DI	deionized	Td	thermal degradation temperature
DD	diffusion dialysis	SEM	scanning electron microscopy
IEC	ion exchange capacity	U_H	dialysis coefficient of HCl
W_R	water uptake	U_{Fe}	dialysis coefficient of $FeCl_2$
LER	linear expansion ratio	S	separation factor

dialysis [23,24]. Commercial membranes are available for this use, such as strong-base anion exchange membrane AFN, AFX produced from Astorm Co. Ltd. [25]. Additionally, domestic commercial membrane S_{203} manufactured by Ningbo environmental protection equipments factory (China) [9] is prepared from linear plastic polysulfone (PSF) followed by chlomethylization and quaternary amination. Nevertheless, this membrane is in cessation of production due to environmental contamination from chloromethyl ether. To avoid the use of chloromethyl ether, a new route was developed for AEM from poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) [26] via bromination followed by quateramination. The membranes can be serially developed via the bromination position (aryl and benzyl position) and content as well as the crosslinking stage and a very famous commercial membrane DF120 from it is now manufactured by Tianwei Membrane Co. Ltd.(China) and widely used in processes industries [27,28]. Recently, to increase the thermal stability, organic–inorganic hybrid ion exchange membranes have been developed via the incorporation of silica into polyethylene oxide (PEO) [29], poly (methyl acrylate) (PMA) [30,31]. Especially, multisilica crosslinking agents were developed and widely used for preparation of diffusion dialysis membranes from polyvinyl alcohol (PVA) in our lab [32–35]. To enrich the types of anion exchange membrane, an efficient and facile method was proposed to prepare hybrid anion exchange membrane based on PVA and glycidyl trimethyl ammonium chloride (EPTAC) in this paper. PVA was firstly grafted to EPTAC and mixed with aminopropyltriethoxysilane (KH550) to obtain a homogeneous solution, then through sol–gel reaction to fabricate PVA based hybrid membrane. Both reactions were conducted at mild conditions, high efficiency and good yield. The route not only avoids the complicated synthesis and the use of expensive solvents or hazardous chemicals but also endower the membrane with crosslinking structure via the reaction of KH550 with EPTAC. The effect of membrane preparation conditions such as the amount of EPTAC on membrane structure and intrinsic properties will be investigated. Furthermore, diffusion dialysis experiments were conducted for $FeCl_2$/HCl aqueous mixture to demonstrate the separation performance of the prepared membranes.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA,99%) is supplied by Shanghai Yuanli Chemical Co (Shanghai, China). The average degree of polymerization was 1750 ± 50 (corresponding a molecular weight of 77,000 ± 2200). Glycidyl trimethyl ammonium chloride (EPTAC,95%) is obtained from Sinopharm Chemical Reagent Co., Ltd (China). Other reagents are of analytical grade and from domestic chemical reagents company. Deionized water (DI water) was used throughout.

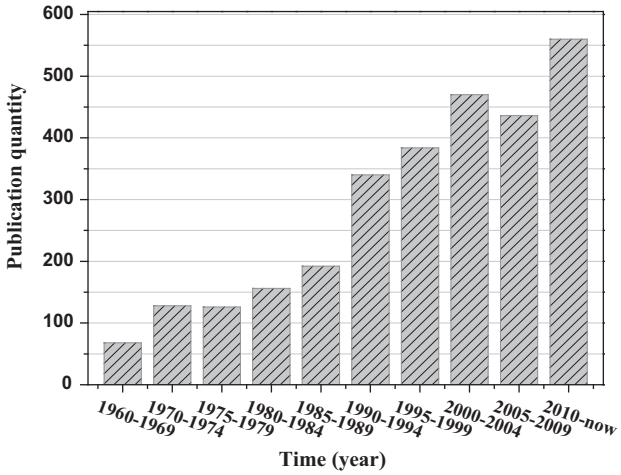

Fig. 1. Chronology of diffusion dialysis documents. *Source:* www.scopus.com [search settings: Abstract-Title-Keywords (diffusion dialysis). Search date: August 4. 2014].

2.2. Preparation of anion exchange membranes

PVA(5 g) is immersed in DI water(95 g) at room temperature for 1 day, then heated to 102 °C at the rate of 10 °C/h and kept at 102 °C for 2.5 h. The homogeneous solution is cooled to 60 °C before use.

A certain amount of EPTAC was added to the PVA aqueous solution (100 g) in a round bottomed flask equipped with mechanical stirrer and thermometer. The pH value of the reaction solution was adjusted to 11–12 by adding 0.5 mol/L KOH aqueous solution. After keeping the reaction at 90 °C for 6 h, the solution was cooled to room temperature. The grafting degrees of PVA-g-EPTAC polymers were controlled by changing the amount of EPTAC according to Table 1. Then KH550 (1 g) was added into the above PVA-g-EPTAC solutions. The mixture was stirred at 60 °C for 24 h and then cast onto glass plates which were dried at room temperature under ventilated circumstances for 72 h. After peeling off from the glass plate, the prepared films were dried at 130 °C for 4 h. The films

Table 1
The main composition of the PVA grafted EPTAC membranes.

Number	PVA solution (5.0wt%)	EPTAC
A	100 g	1.5 g
B	100 g	2.5 g
C	100 g	3.5 g
D	100 g	4.5 g
E	100 g	5.5 g