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Preparation and characterization of PDMS-D2EHPA extraction gel membrane for metal ions extraction and stability enhancement

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ABSTRACT

A novel extraction gel membrane (EGM) was prepared via gelation technique by forming polydimethylsiloxane-di (2-ethylhexyl) phosphoric acid (PDMS-D2EHPA) extraction gel layer on the outer surface of PVDF ultrafiltration hollow fibers. This special design aims to achieve both efficient mass transfer within the thin extraction gel layer and improvement in operating stability by preventing the extractant (D2EHPA) loss from EGM. The physical and chemical properties of the prepared EGM were studied via a series of characterization techniques, and the fixed-site jumping carrier mechanism for EGM was confirmed. The influences of the EGM preparation parameters on its performance in nickel separation were investigated systematically. The optimal extraction efficiency and stability of EGM were achieved by the EGM prepared from the ratio of 10:8.0:0.2 for PDMS / TEOS / DBTL, 24 wt% PDMS concentration, 40 min-coating and a low level (15–25%) of relative humidity. Using EGM prepared from these conditions, long-term operating stability was tested and the flux results were compared to that of the conventional supported liquid membrane (SLM) process. It was shown that the flux attenuation of the EGM was only 34.11% within 120 h, while that of the conventional SLM was 100% within 45 h. Simultaneously, the initial flux of EGM was as high as 2436.30 mg m^{-2} h^{-1} which was 7.1 times of that of the conventional SLM. The results of this study indicate evident advantages of the novel EGM process over the traditional SLM by showing higher flux and operating stability.

1. Introduction

Supported liquid membrane (SLM) is a technique combining the conventional liquid extraction and membrane separation processes. It is prepared by imbedding the liquid membrane phase (i.e. organic extracting phase) in small pores of a polymer support by capillary forces [1,2]. Combined with conventional extraction techniques, the advantages of SLM include convenient operation, higher separation factors, smaller dosage of organic phase and lower operating cost. Therefore, SLM technique has application potentials in separation and recovery of heavy metals, fine chemicals and pharmaceutical ingredients, etc. However, the major challenge impeding large scale application of SLM is the insufficient membrane stability caused by the liquid membrane phase loss during operations [3]. This problem has significant impacts on both flux and service life of SLM.

An effective approach to enhance the stability of SLM was to create a protective layer by interfacial polymerization reactions. Kemperman et al. [4] selected the piperazine and trimesoyl chloride as monomers to modify SLM for transport of nitrate ions. Wang et al. [5] developed a composite membrane by interfacial polymerization top layers on the surface of the polysulfone membrane support to separate Cr(VI) using SLM process. Unfortunately, the adhesion of interfacial polymerization layer to the substrate was not strong in some cases and it resulted in poor mechanical stability. Besides, the coating layer would offer the additional mass transfer resistance [6]. Yang et al. [7] suppressed the loss of liquid membrane phase by plasma polymerization surface coating, which evidently improved the stabilization of SLM. However, the size of the membrane surface pores could be reduced due to the application of this technique, resulting in a decreased mass transfer of SLM system [8]. Efforts have also been made to improve the stability of the SLMs via regenerating the SLM system through continuous re-impregnation of the support with liquid membrane phase [9,10]. This method was efficient but that could not essentially inhibit the loss of membrane liquid. In addition, this process would cause the feed and/or strip solutions pollution by the membrane liquid [6,8]. Therefore, the technique for enhancing the stability of SLM is still limited and worth exploring.

Gelation is a specific dispersion system in which the polymers

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formed a spatial network structure by cross-linking with each other. This structure may fulfill the functions of locking the liquid membrane phase and improving the stability of SLM. In 1990, Neplenbroek et al. [11] firstly combined SLMs with gel technology. The polyvinyl chloride (PVC) gelled supported liquid membranes were prepared that effectively suppressed SLM-degradation and had no negative influence on the flux. However, this effect was not successfully verified by later researchers [12]. Ho et al. [13] developed a supported polymeric liquid membranes (SPLMs) to remove organics from aqueous streams. The stability of SLMs was improved by the p-nitrophenol- polypropylene glycols (PNP-PPG) cross-linking structure inside the pores of the support. Unfortunately, the cross-linked PPG material was susceptible to hydrolytic, enzymatic and biological degradation under unfavorable conditions [14]. Kumar et al. [15] used polymethylmeth acrylate alcohol (PMMA) as the gelator to prepare a homogeneous gel network on the surface of SLM for purifying phenol . It was found that the stability was maintained for at least 165 h with 0.2% (w/w) PMMA in the coating. Whereas, mass transfer of the target solute was hindered by PMMA gel network structure, which reflected in the reductions of flux compared with the uncoated membrane.

Recently, ionic liquids (ILs) have conquered a prominent position in the field of gelled SLMs technology due to the advantages in good thermal stability, extremely low volatility and ability to dissolve a large range of organic molecules [16]. Izák et al. [17] used a very stable polydimethylsiloxane (PDMS) gel system supported ionic liquid polymer membrane (SILM) for separation of ternary mixtures butan-1-ol-acetone-water. It was reported that no changes in stability of the SILM were observed after five months. Jansen and Friess [18,19] developed polymerized ionic liquids gel membrane. The ionic liquid [EMIM][TFSI] acted as a plasticiser for the polyvinylidene fluoride-hexafluoro propylene (PVDF-HFP) copolymer by avoiding the ionic liquid loss from the polymer network. Voss et al. [20] prepared 12-hydroxyoctadecanoic acid/[C6mim][Tf2N] supported ionic liquid membrane. The loss of ionic liquid was effectively suppressed by gelled membranes and, CO_2 gas transport was enhanced. Plaza et al. [21] used supported gelled ionic liquid membranes based on [bmim][PF6] in order to separate butanol from the aqueous solution. The SILM prepared with a low concentration gelator showed a permeability comparable to traditional membrane evaporation and better selectivity. Theoretically, due to the possibility of synthesizing suitable ionic liquids for different processes, SILMs may have wide application potentials in separation and purification field. In addition, the instability of the SLMs may be solved to some extent by the application of the ionic liquids. However, the ionic liquids technology was restricted by unknown toxicity, high cost and complication in synthesis [22,23]. In addition, the high viscosity of many ionic liquids made the filling of the porous support quite difficult [24,25]. Therefore, although with some attractive findings, it is still challenging to construct a SLM consisting both ideal stability and high mass transfer via a universal process.

In this work, innovative extraction gel membrane (EGM) was designed for metal ion extraction. EGM was prepared by embedding the extractant di(2-ethylhexyl) phosphoric acid (D2EHPA) in a thin layer of polydimethylsiloxane-tetraethyl orthosilicate (PDMS-TEOS) cross-linking network formed on the outer surface of a hydrophilic PVDF support. Based on this design, both the efficient mass transfer within the thin extraction gel layer and the extractant locking effect of the gel layer were expected due to the structure and the physical and chemical characters of the EGM. Consequently, an improved operating stability can be achieved by inhibiting extractant loss. Firstly, the surface and cross-section properties of the prepared EGM were studied via a series of characterization techniques, and the mechanism of mass transfer facilitation by the EGM was analyzed. Secondly, using Ni(II) as a representative metal ion, the effects of various preparation parameters such as crosslinking agent content, PDMS concentration, coating time and environmental relative humidity on extraction efficiency were investigated by simultaneous extraction and stripping experiments. Finally, the performance of EGM prepared at the optimal conditions in both flux and long-time operating stability were tested and compared with the conventional SLM process.

Table 1
Properties of the hollow fibers used for the modules of EGM and SLM.

Hollow fibers (the support of EGM)		Hollow fibers (the support of SLM)	
Material	PVDF	Material	PVDF
Hydrophilicity	Hydrophilic	Hydrophilicity	Hydrophobic
Inner diameter (μm)	600	Inner diameter (μm)	800
Outer diameter (μm)	900	Outer diameter (μm)	1200
Effective surface area of the fibers (m^2)	5.9×10^{-4}	Effective surface area of the fibers (m^2)	7.5×10^{-4}
Nominal pore size (μm)	0.1	Nominal pore size (μm)	0.2
Porosity (%)	82	Porosity (%)	84
Effective length of the fibers (cm)	20	Effective length of the fibers (cm)	20
water flux ($kg\,m^{-2}\,h^{-1}$)	424.3	water flux (ethyl alcohol wetted) ($kg\,m^{-2}\,h^{-1}$)	84.2

2. Experimental

2.1. Chemicals and materials

The chemicals used in the crosslinking reaction including PDMS (M.W. 4200), TEOS, hexane, and dibutyltin dilaurate (DBTL) were all analytical grade. Organic solvents including sulfonated kerosene and D2EHPA were industrial grade. The properties of the laboratory made hollow fibers used as the support of the EGM and the SLM (for comparison) are illustrated in Table 1.

2.2. EGM preparation

In the experiments, the predetermined amount of PDMS was dissolved in hexane at room temperature and magnetic stirred for at least 1 h. TEOS and DBTL were then added and thereafter, the crosslinking reaction happened. The schematic of the crosslinking reaction between PDMS and TEOS is shown in Fig. 1. Under the action of the catalyst DBTL, hydroxyl-terminated PDMS was induced to undergo dealcoholization reaction with the ethoxy group in TEOS, which resulted in initial formation of the gel network. After 1 h, D2EHPA was added into the polymer solution under magnetic stirring and a homogeneous solution was obtained in another 1 h. The hollow fibers were immersed in the polymer solution for specified time. Thereafter, the hollow fibers with the extraction gel layer precursor were taken out from the polymer solution and placed on the non-woven fabrics for 12 h for thoroughly volatilization of hexane. The hollow fibers were further heated at 35 °C for 24 h to guarantee the complete formation of the extraction gel membrane.

2.3. Membrane characterization

2.3.1. Membrane morphology

The morphology of surface and cross-section of the prepared membranes were observed with a field emission scanning electron microscope (SEM, S4800, Hitachi Limited, Japan). A piece of membrane sample was attached on the sample holder by the conductive adhesive sheet and dried under vacuum for at least 24 h. The cross-section photos of the hollow fibers were obtained by immersing the fibers in liquid nitrogen and fractured carefully. Then the sample was sputtered with a conductive metal (Gold > 99.8%) under vacuum using Bal-Tec SCD 005 sputter coater. SEM images were then taken at randomly selected locations and at suitable magnifications.

2.3.2. Membrane surface roughness and hydrophobicity

The surface roughness of EGM was analyzed by atomic force