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Optimization of composite nanofiltration membrane through pH control: Application in $CuSO_4$ removal

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Abstract

An approach to optimize the membrane performance by controlling the acidity or basicity of the diamine solution containing bifunctional piperazine, trifunctional 3,5-diaminobenzoic acid and acidic/basic additive is introduced. It was found that with the addition of sulphuric acid (H_2SO_4), pore radius becomes bigger and the skin layer becomes thinner. On the other hand, the membrane thickness was found to increase with the addition of triethylamine (TEA) whereas the pore radius was not affected by the addition of TEA. The membrane flux increased when the membrane was prepared under acidic condition, however, the mechanical strength of the membrane pores was poor and subjected to severe compaction problem. $CuSO_4$ rejection under different pore radius was simulated using Donnan steric pore model (DSPM). The simulation result shows that the optimum pore radius to separate $CuSO_4$ should be as close as possible to the size of hydrated Cu^{2+} ion which is around 0.53 nm. The experimental rejections for membrane with different pore radius were compared to the simulated result. It was found that the trend of rejection agreed well with the simulated data which indicated that optimized $CuSO_4$ removal could be achieved using membrane prepared with the addition of 0.5% sulphuric acid.

Keywords: pH control; Optimization; Copper sulfate; Rejection; Flux; Nanofiltration

1. Introduction

There are many parameters to be considered in fabricating an interfacial polymerized composite membrane. The composition and morphology of composite membranes prepared by interfacial polymerization (IP) method depends on several variables, such as concentration of reactants, partition coefficients of the reactants, reactivity ratios where blends of reactants are employed, solubility of nascent polymer in the solvent phase, the overall kinetics and diffusion rates of the reactants, presence of by-products, hydrolysis, cross linking and post treatment [1]. Although, a number of patents have thoroughly discussed these techniques, however, these parameters were seldom disclosed in the literature.

Among the membrane fabrication parameters, pH control is one of the parameters that researchers pay less attention. It has been a general practice to add acid acceptor in the aqueous solution to get membrane with better rejection and improved reproducibility especially when the required membrane is a reverse osmosis. However, this phenomenon is not the rule of thumb in the case of nanofiltration. For nanofiltration membrane, high selectivity of divalence ion towards monovalence ion is crucial to enable the separation process to be carried out at lowest possible operating pressure yet having high water flux.

The application of acid acceptor in controlling the membrane performance is well discussed in the literature [2–5]. It is commonly known that at the beginning of the reaction, the pH is relatively high due to the presence of diamine in the aqueous phase. However, as the reaction continues, diamine is consumed which leads to a decrease of pH. Moreover, the decreased in pH is also favored by the release of HCl produced during the polycondensation reaction [6]. In the absence of an acid acceptor, the diamine itself will become the acceptor and caused a drop in polymer yield [7]. Kim et al. [8] prepared an active layer by the interfacial polymerization of a mixed aqueous solution of polyhydric phenol and an aromatic

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Nomenclature

$c_{i,m}$, $c_{j,m}$	solute concentration inside membrane (mol/m^3)
$C_{i,p}$, $C_{j,p}$	concentration of component i and j at permeate (mol/m^3)
$C_{i,w}$, $C_{j,w}$	concentration of component i and j at feed wall side (mol/m^3)
$D_{i,p}$	hindered diffusivity of component i (m^2/s)
$D_{i,}$	bulk diffusivity of component i (m^2/s)
F	Faraday constant (C/mol)
j_i	solute flux component i (mol/m^2/s)
j_v	volume flux (based on membrane area) (mol/m^2/s)
k	mass transfer coefficient (m/s)
$K_{i,\mathrm{c}}$	hindrance factor for convection
$K_{i,\mathrm{d}}$	hindrance factor for diffusion
r_p	pore radius (m)
r_r	radius of stirrer (m)
r_s	ion stokes radius (m)
R	gas constant (J/mol/K)
R_i	observed rejection
T	temperature (K)
x	film thickness or axial direction (m)
$\Delta x/A_\mathrm{k}$	effective thickness/porosity
X_d	effective volume charge density (mol/m^3)
z_i	charge of component i (−)

Greek letters

γ_i^o	activity coefficient of component i in the bulk solution
γ_i	activity coefficient of component i in membrane
ξ	ratio of fixed charge density/feed concentration
λ	ratio of stokes radius of component i to pore radius
υ	kinematic viscosity (m^2/s)
ω	stirring speed (s^{-1})
Φ_i, Φ_j	steric partition term at membrane interface
ψ_m	electrostatic potential (V)
$\Delta\psi_\mathrm{D}$	Donnan potential difference at interface (V)

Subscripts

i	cations
j	anions

amine with a solution of aromatic acyl halide dissolved in an organic solvent. The pH of the mixed aqueous solution is adjusted to 8–13 where the optimum performance of membrane was found. The role of basic additive is not limited to the elimination of hydrochloric acid. In fact, it can influence the polycondensation rate by controlling the state of diamine dissociation. The dissociation of the diamine will influence the transfer rate of the reactant into the organic phase and becomes the rate-controlling step of the reaction [6].

On top of it, the nature and the amount of strong alkaline play an important role in both yield and viscosity of polyamides. It has been shown that an excess of strong acceptors beyond the ratio of 2:1 (acid acceptors, diamine) causes a decrease of both yield and viscosity of polyamides from ethylenediamine and hexamethylenediamine due to the hydrolysis of acid chlorides [6]. Konagaya et al. [9] carried out the polymerization involving hydrophilic additive to produce the copolyamides from *iso*/terephthaloyl chloride, 4,4′-diaminodiphenylsulfone, and 2,4-diaminobenzenesulfonic acid using acid acceptors, such as pyridine or triethylamine (TEA). They found that the copolyamides with high reduced viscosity could not be obtained, even if acid acceptor such as pyridine or TEA was added.

Our previous research revealed that for the formulation consisting hydrophilic additive, it is advisable that the polymerization time should be as low as possible to get a defect free thin skin layer [10]. However, to carry reaction at such low short time (<5 s) is technically restricted. Therefore, it is a need to source for other method to control the rate and extent of the polymerization. The objective of this paper therefore is to study the acidity/basicity (pH) of diamine solution as a new mechanism to control the morphology (pore, thickness) of the effective skin layer and at the same time tailor fabricates the membrane with optimum properties for copper sulfate removal.

2. Experimental

2.1. Material

The polysulfone Udel P-1700 (Mn: 17,000) was purchased from Solvay Advanced Polymers, L.L.C. Piperazine, 3,5-diaminobenzoic acid, *n*-hexane, sodium chloride, sulphuric acid (96%) and glucose were supplied by Merck Company, Germany. *N*-methylpyrrolidone, triethylamine (TEA) and trimesoyl chloride were purchased from Fluka and polyvinylpyrrolidone from Sigma–Aldrich Co. The tightly woven polyester, style 0715 Dacron Fabric was supplied by Texlon Corporation (USA).

2.2. Preparation of polysulfone support layer

The polysulfone support was prepared by dissolving 15% Udel P-1700 polysulfone (supplied by Solvay Advanced Polymers, L.L.C.) in *N*-methylpyrrolidone (NMP, Fluka) with 18% polyvinylpyrrolidone (PVP-10, Sigma, MW: 10,000) as the pore-former. The solution was cast onto a tightly woven polyester fabric with a nominal thickness of 100 μm using a lab-developed auto-casting machine. The entire casting machine was kept in an air-conditioned room and the temperature was maintained between 24 and 26 °C with a relative humidity of 59–61% during the casting