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Polyvinylidene fluoride (PVDF) hollow fibre membranes for ammonia removal from water

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Abstract

Polyvinylidene fluoride (PVDF) hollow fibre membranes with asymmetric structures and good hydrophobicity have been prepared by a phase-inversion method and have been applied to removal of ammonia from water. Aqueous solution containing sulfuric acid was used as stripping solution to accelerate the removal of ammonia. A mathematical model was presented to simulate the ammonia removal in PVDF hollow fibre modules. Experimental results indicate that the post-treatment with ethanol is useful to improve both the hydrophobility and the effective surface porosity of the resulting PVDF hollow fibre membranes, and thus favors the ammonia removal. Increasing the pH value of water is capable of promoting the removal of ammonia. The initial concentration of ammonia and the feed velocity of the acid stripping solution have negligible effects on the ammonia removal. The ammonia stripping rate increases as the feed velocity is increased up to 0.59 m/s or $Re > 0.32$, after which the feed velocity shows no effect. All the experimental data are in excellent agreement with the modeling results.

Keywords: Ammonia removal; Hollow fibre membrane; Polyvinylidene fluoride (PVDF)

1. Introduction

Ammonia is a common and undesirable contaminant in wastewater and biomass cultivation medium [1,2]. The accumulation of ammonia in water results in eutrophication and depletion of oxygen due to nitrification and thus harms the water-borne organisms such as fish. On the other hand, ammonia produced from protein catabolism in cell culture medium, which ranges from 50 to 300 mg/L in total ammonia concentration, is very harmful to the cell culture [3]. Such adverse effects of ammonia have promoted developing various techniques for its removal such as biological nitrification–denitrification, breakpoint chlorination, air stripping and selective ion exchange, etc. [4–9]. Although biological nitrification–denitrification methods have been used in reducing ammonia–nitrogen content in sewage effluent to an acceptable level, the effectiveness of this process is restricted by slow bioconversion and unfavorable environmental factors. Chlorination and ion-exchange process have also occasionally been applied to industrial wastewaters containing high levels of ammonia. However, most of these methods suffer from disadvantages of high cost and difficult maintenance due to chemicals used in oxidation and regeneration.

Development in hollow fibre membrane contactors provides an attractive alternative for the removal of various volatile contaminants including ammonia [10,11]. In such operations, the hollow fibre membrane provides a barrier between gas and liquid, and the gas components diffuse through membrane pores or dense membrane matrix into the liquid phase. Compared to conventional absorption or

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stripping processes such as bubble columns and packed beds, the membrane processes provide many advantages including larger interfacial area per unit volume, independent control of gas and liquid flow rates without any flooding, loading, foaming, and known gas–liquid interfacial area, etc. Recognition of these advantages is reflected by a number of investigations on the use of membrane modules for gas absorption and stripping reported in the literature [12–17]. Furthermore, due to the tangential nature of the flow in membrane contactors, the gas stripping process does not require operation at a high-pressure drop. This also contributes to lower capital cost and ease of operation.

Membranes used for removal of dissolved volatile species from water usually are hydrophobic in nature so as to provide less mass transfer resistances. Polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes are the ideal candidates because of their good hydrophobicity [18–20]. However, the commercial PP and PTFE membranes are limited to their symmetric structures, restricted pore size range and porosity. Alternatively, polyvinylidene fluoride (PVDF) has become a new membrane material in recent years due to its both good hydrophobicity and feasibility to form asymmetric membranes via phase inversion methods [21–25]. The asymmetric membranes give much less mass transfer resistance compared to symmetric membranes [26,27]. Therefore, in this work, PVDF hollow fibre membranes with different morphological structures have been prepared and tailored for ammonia removal from water. Performances of the PVDF hollow fibre membrane modules for ammonia removal at various operating conditions have been investigated both experimentally and theoretically.

2. Experimental

2.1. Fabrication of PVDF hollow fibre membranes

PVDF hollow fibre membranes were prepared by spinning polymer dopes consisting of K-760 PVDF polymer (Elf Atochem, USA), *N*,*N*-dimethylacetamide (DMAc, MERCK) as the solvent, and water and lithium chloride (LiCl, MERCK) as additives. Tap water was used as both internal and external coagulants. Experimental apparatus and detail procedures were described elsewhere [22–25]. Dope compositions and spinning conditions for preparing the hollow fibre membranes are summarized in Table 1. Post-treatment of immersion for some of the fibres in ethanol was carried out for 5 min before drying in ambient conditions.

2.2. Characterization of the hollow fibre membranes

Gas permeation test was performed to determine the microstructure parameters of the resulting membranes. The wet hollow fibres were dried at the ambient condition (25 ± 1 °C and RH = 60–65%). A test module containing 2–10 fibres with its length of about 6 cm was made using a stainless steel cylinder. The upstream pressure was in the range from 34.48 to 206.85 kPa, which was measured by the pressure transducer (Basingstoke, England). Pure nitrogen gas was used as a test gas and the permeation flux was measured at 25 ± 1 °C and atmosphere using a soap-bubble flow meter. The gas permeation data obtained at different operating pressures were analyzed using a method developed by Kong and Li [26] and Li et al. [27].

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations were carried out to examine the cross-sectional structure and the surface morphology of the membranes, respectively.

In the wetability test, water was fed into the lumen side of a hollow fibre membrane. The operating pressure was increased stepwise at 0.5×10^5 Pa (0.5 bar) interval. At each pressure, it was maintained for at least 1 h to check whether any water appeared in the outer surface of the fibre. The critical water entry pressure (P_c) is taken as the pressure for the first appearance of water droplet in the outer surface of the hollow fibre membrane. The hydrophobicity was further supported by the contact angle measurement using Tensiometer K14 (Kruss, USA) for the fibres. In general, the greater the critical water entry pressure and the contact angle, the more hydrophobic the membrane would be. The properties of the membranes and the membrane module are reported in Tables 2 and 3, respectively.

2.3. Ammonia removal in the PVDF hollow fibre membrane module

A membrane module was prepared for ammonia stripping from water. The membrane with the batch number of PVDF-2A was used because it possesses the best hydrophobicity and the highest effective surface porosity. The experimental set-up for the removal of ammonia from wastewater is schemat-

Table 1
Preparation conditions of the PVDF hollow fibre membranes

	Dope composition (PVDF/DMAc/LiCl/H_2O) (%, w/w)	Internal coagulant flow rate (cm^3/min)	Fibre take-up velocity (m/min)	Post-treatment with ethanol
PVDF-1	15/77.87/5.22/1.95	1.3	3.62	No
PVDF-2	14/76.87/5.22/1.95	1.3	3.62	No
PVDF-2A	14/76.87/5.22/1.95	1.3	3.62	Yes
PVDF-3	14/76.87/5.22/1.95	1.5	4.03	No
PVDF-3A	14/76.87/5.22/1.95	1.5	4.03	Yes