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Design of novel ultrafiltration systems based on robust polyphenylsulfone hollow fiber membranes for treatment of contaminated surface water

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HIGHLIGHTS

- Synthesis and characterization of novel polyphenylsulfone (PPSu) hollow fiber membranes dry-wet spinning method.
- PPSu fibers exhibited 91% turbidity rejection and 5 log E-Coliform reduction at a pressure of 1 bar with 73 L m^{-2} h^{-1} flux.
- A household water treatment device and a hand pump operated submerged UF membrane system were designed and fabricated.

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ABSTRACT

This work focuses on development of robust but economical hollow fiber ultrafiltration systems that could be operated with or without electric power to treat polluted surface water. A diverse experimental study was carried out to synthesize novel hollow fiber membranes based on polyphenylsulfone (PPSu) and polyvinylidenefluoride (PVDF) fibers for surface water treatment. A manual hollow fiber spinning machine incorporated with an inexpensive spinneret was designed to fabricate hollow fibers from dope compositions of 20 wt% PVDF in DMAc and 20 wt% PPSu in NMP by phase inversion technique. Isothermal ternary phase diagrams of PVDF or PPSu/solvent/non-solvent systems were established using three different solvents such as *N,N*-dimethylacetamide (DMAc), 1-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylformamide (DMF) with water being the non-solvent. The indigenous fibers had an approximate outer diameter of 1.5 mm and the wall thickness of 0.25 mm and were housed in inexpensive PVC and UPVC tubes using epoxy resin and nylon end connectors. PVDF hollow fibers (HF) exhibited 94.8% turbidity rejection, whereas PPSu fibers exhibited 91% rejection with 5 log E-Coliform reduction from surface water at a low hydraulic pressure of 1 bar with high flux values of 125 L m^{-2} h^{-1} and 73 L m^{-2} h^{-1}, respectively at a substantial water recovery of 80%. A water purification device capable of generating 25 L h^{-1} purified water flow at an overhead tank pressure of 0.5 bar was designed and fabricated for households along with a hand pump operated submerged ultrafiltration (UF) system for treatment of surface water in flood prone regions. Detailed economic estimation of the indigenously designed water purification device for household purpose is presented which shows a low operating cost of 0.02 US $ per liter of purified water obtained.

1. Introduction

The reliability and ease of operation of membrane-based water filtration systems have led to their increasing use in water and wastewater treatment. In particular, low-pressure membrane techniques such as microfiltration (MF) and ultrafiltration (UF) have attracted a considerable amount of attention for surface water clarification and disinfection by size exclusion and usually produce a filtrate free of turbidity and microbes from river, lake and pond water resources [1–4]. A number of module designs such as plate and frame, spiral-wound, tubular and hollow fiber are available. Among these, hollow fibers (HF) have emerged one of the most important membrane geometries, mainly due to superior membrane surface area per unit of module volume, good flexibility in operation and self-supporting structure [5–7]. Global market for

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low-pressure membranes has grown at an impressive rate during the last 10 years and 60% of applications are for drinking water [8].

Among hydrophobic polymers, polyphenylsulfone (PPSu) and polyvinylidenefluoride (PVDF) are thermally stable, possess good chemical resistance, high mechanical strength and are resistant to several organic compounds [9–11]. Extensive research has been carried out by investigators on development of PVDF HF membranes for various applications such as membrane distillation, gas separation and ultrafiltration. A great deal of attention was devoted to study the effect of different parameters during preparation of PVDF HF membrane. However, till date, research on synthesis and characterization of PPSu HF membranes has rarely been discussed in the literature. This may be due to the fact that the preparation of PPSu HF membranes is a complicated process involving many parameters such as polymer solution composition and viscosity, length of air gap, polymer extrusion rate, winding motor speed, nature of internal and external coagulant mediums. While the polymer type and properties are critical for membrane fabrication, the selection of appropriate solvents is another significant consideration in dope preparation [12,13]. Commonly, dimethylformamide (DMF), dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) polar aprotic solvents are used for the preparation of PVDF and PPSu dope solutions. The suitable solvents for preparing polymer dope solutions are selected from the ternary phase diagrams which are plotted by determining fractional concentration of each component by titration [14].

The present work involves synthesis and testing of robust PPSu hollow fiber membranes which has not been reported in literature especially for treatment of surface water. The membranes were characterized by porosity and pore size measurements, scanning electron microscopy (SEM), pure water permeation and bovine serum albumin (BSA) rejection studies. Influence of various spinning parameters on structural dimensions of HF membranes is described in detail. Further, design and development of ultrafiltration system based on both PPSu and PVDF hollow fiber membranes are presented as novel economical alternative for treatment of surface water in households. The economy involving fabrication of such a device and its low operating cost on account of operation by utilizing static water head pressure instead of a pump is another interesting feature of this manuscript. Design and performance of hand pump operated ultrafiltration system capable of implementation in the absence of electrical power is described. Other prospects of this research could be treatment of industrial effluents besides process intensification through design of membrane bioreactors which eliminate secondary clarifiers, bring down capital investment and operating cost with enhanced process safety and lower environmental pollution for effective treatment of municipal wastewater.

2. Experimental

2.1. Materials

Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) procured from s.d fine chemicals. Polyvinylidenefluoride (PVDF) and polyphenylsulfone (PPSu) polymers were supplied by Kynar and Solvay, USA. Deionized water and tap water were used as bore fluid and in gelation bath, respectively.

2.2. Phase diagram

The turbidity change of polymer solution in different solvents like NMP, DMAc and DMF was visually observed and precipitation point lines were plotted. 20 wt% PVDF and PPSu solutions were prepared and taken in a sealed container with magnetic stirrer. Water was added drop wise with a syringe until the solution became turbid. The cloud point was marked when turbidity of solution persisted for at least a few minutes. If demixing with pure water and formation of persistent particles were too rapid, then water was added to a small extent in the solvent. Subsequently the solvent was added to dilute the solution and make it clear again. The weight of container was regularly monitored and recorded after each change in composition. Ternary phase diagram was plotted by calculating fractional concentration of components by titration method [14].

2.3. Hollow fiber membrane spinning process

Hollow fiber membranes were spun at room temperature (25–30 °C) employing the solution extrusion and phase inversion technique. The spinning solutions were prepared from 20 wt% PVDF and PPSu in DMAc and NMP, respectively. The polymers were dissolved in solvents and stirred at approximately 60 °C for about 12–15 h to ensure complete dissolution of the polymer. The prepared polymer dopes were transparent and homogenous at room temperature and the mixtures were then degassed overnight. In this process, the polymer solution was loaded into a reservoir and forced into the spinneret using pressurized nitrogen. The dope solution and the internal coagulant liquid were forced through a tube-in-orifice spinneret, in such a manner, that the polymer solution flowed through a ring nozzle while the coagulating fluid was fed through the inner tube [15]. Fig. 1 shows the process of hollow fiber spinning method. The polymer solution was directly extruded into a coagulation bath at an air gap of 13 cm. In this work, the bore liquid and the coagulation medium were distilled and tap water, respectively. Spinning conditions were kept constant as follows. The pressure applied on the spinning solution was about 4 bar and bore liquid flow rate was kept at 6.0 mL min^{-1}. After spinning, the hollow fibers were drawn out from coagulation bath by pulling motor at a speed of 30 revolutions per second (rps). The fibers were collected in a take-up drum and immersed in ethanol solution for approximately 24 h to replace water in membrane pores by ethanol that possesses lower surface tension [16,17]. Dimensions of the annular spinneret opening, the polymer to bore volumetric flow rate ratio and the draw ratio are the primary factors that affect final fiber size. The membrane structure, pore size and pore size distribution are determined by many factors including air gap length, quench air temperature and type of solvent used [18].

2.4. Characterization of HF membranes

2.4.1. Scanning electron microscopy (SEM)

SEM is a powerful technique for analyzing the structure of the membranes. The cross-section and surface of the PVDF and PPSu HF membranes prepared were examined by software controlled digital SEM-JEOL Model JSM-5410, Japan.

2.4.2. Porosity and pore size measurement

The overall porosity of membrane (ε) was estimated using a method based on density measurements [19]. It was calculated based on Eq. (1).

$$\varepsilon = \left[1 - \frac{\rho_{\text{membrane}}}{\rho_{\text{raw polymer}}}\right] \quad (1)$$

where ρ_{membrane} and $\rho_{\text{raw polymer}}$ are the densities of the membrane and raw polymer powder used for membrane synthesis respectively. The volume was calculated according to the inner/outer diameters and the length of the fiber sample. The weight of the membrane was determined by an analytical balance (Contech, CA-224, 0.1 mg). The density of intrinsic PVDF is taken as 1.77 gm cm^{-3} [20] and PPSu as 1.29 gm cm^{-3} [21].