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Synthesis and characterization of poly 3-methyl 2-vinyl pyridinium nitrate incorporated polyvinylidine fluoride ultrafiltration membrane for metal ion removal

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ABSTRACT

Poly 3-methyl 2-vinyl pyridinium nitrate (P3M2VPN) was successfully synthesized from 2, 3-lutidine. The structure of the compound was characterized by IR, NMR and mass spectral analysis. The P3M2VPN incorporated polyvinylidine fluoride ultrafiltration membrane (PVDF/P3M2VPN) was prepared by the phase inversion through wet process and the membranes were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), atomic force microscopy, water content, hydraulic resistance, contact angle, pure water flux, membrane, porosity and molecular weight cut-off were investigated for the influence of P3M2VPN. The intermolecular interactions between the blend membranes were established by ATR-FTIR. The membranes showed an increase in overall porosity, hydrophilicity and decrease in mean surface-pore size, with the increase of P3M2VPN content. Surface parameters of the membrane such as surface free energy, interfacial free energy, work of adhesion and spreading coefficient were calculated. The removal of heavy metal ions such as copper, lead and cadmium using modified PVDF membranes from aqueous solutions has been systematically investigated. The modified membranes exhibit excellent separation properties with high permeabilities at low trans-membrane pressures. The removal of dissolved metal ions is more by P3M2VPN enhanced structure than PVDF membrane.

1. Introduction

Pyridinium refers to the cationic form of pyridine. This can either be due to protonation of the ring nitrogen or because of addition of a substituent to the ring nitrogen, typically via alkylation. The pyridine attracts much attention, mainly because of the presence of the nucleophilic nitrogen atom, which makes possible a variety of reactions, e.g., protonation, quaternization or complexation of metals. In consequence, vinylpyridinium derivatives have found many applications as polyelectrolytes [1,2], polysoaps, interpolyelectrolyte complexes with synthetic and natural polyanions, corrosion inhibition [3,4], electrolyte for lithium batteries [5], dye removal from waste water [6], drug delivery [7], membrane preparation [8,9], microbial activity [10], etc. The poly 3-methyl 2-vinyl pyridinium nitrate is a type of cationic polyelectrolyte. Polyelectrolytes are mostly hydrophilic; many studies have been carried out for surface modification of membranes with polyelectrolytes to enhance hydrophilicity and antifouling properties. Malaisamy and Bruening have prepared high flux nanofiltration membrane by adsorption of multilayer polyelectrolyte membranes on polymer supports [11]. The poly 4-vinyl pyridinium compounds are very effective in removing bivalent cations from an aqueous feed, showing performances (flux:rejection) which are comparable to the best commercial nanofiltration membranes [12].

Polyvinylidine fluoride (PVDF) is an important material in the field of polymeric membranes because of its mechanical, thermal and chemical stability as well as its excellent film-forming property and applicability in wide pH range (1–11). However, PVDF is hydrophobic in nature, and this results in the adsorption and deposition of hydrophobic solutes on the membrane surface [13]. This kind of adsorption and deposition can cause severe membrane fouling by forming a thick gel layer and blocking of the pores resulting in flux decline and a short life of the membrane. Much effort has been devoted to alter the hydrophobicity of PVDF by blending with hydrophilic materials. The chemical modification method could be employed to improve the hydrophilicity of the

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membrane, but the main chain of the PVDF molecule would be changed and the advantages of the PVDF membrane might be decreased [14]. Additionally, besides the amphiphilic copolymers, inorganic particles such as Al_2O_3, SiO_2, TiO_2, ZrO_2, Fe_3O_4, $LiOCl_4$ and CdS were also introduced in the PVDF solutions in fabricating organic–inorganic hybrid membranes. It has also been demonstrated that the addition of inorganic fillers has led to an increase in the membrane hydrophilicity, pure water flux, rejection, antifouling mechanical strength and effective control of the membrane surface performance [15–19].

The synthesis and characterization of poly 3-methyl 2-vinyl pyridinium nitrate (P3M2VPN) and the effect of P3M2VPN concentration on PVDF membranes performance with respect to the pure water flux (PWF), water content (WC), contact angle, compaction, membrane hydraulic resistance, porosity and molecular weight cut-off (MWCO) are reported in the present investigation. The intermolecular interaction of the membrane is determined by ATR-FTIR technique, and hydrophilic nature of the membrane is investigated by the contact angle technique. The surface morphology of the blend membrane is studied by SEM and AFM. Further, the effect of the P3M2VPN on the rejection and permeate flux of toxic heavy metal ions such as Cu^{2+}, Pb^{2+} and Cd^{2+} has been investigated.

2. Materials and methods

2.1. Materials

2,6-Lutidine (SPECTROCHEM), sulfuric acid, Polyvinylidene fluoride (Kynar grade 760, Mw 444,000), potassium persulfate (MERCK), t-butyl catechol (SPECTROCHEM) and sodium hydroxide were used as such without further purification. Analar grade N-methyl-2-pyrrolidone (NMP) from SRL Chemicals Ltd., India. The solvents such as diethyl ether, acetone, ethanol and methanol were purified according to literature method.

2.2. Methods

IR spectra were recorded with KBr pellets using Perkin Elmer RXI FTIR spectrometer. ^{1}H NMR spectra were obtained on a BRUKER-300 NMR spectrometer. Molecular weight of the pyridinium monomers were obtained on a JOEL GC EI + Mass spectrometer. The zeta potential of the polyelectrolyte was determined by Malvern Zetasizer Nano-ZS ZEN3600 using double distilled water with a concentration of 1 mg/mL. FTIR spectra of PVDF and polyelectrolyte incorporated PVDF membranes were recorded using Attenuated Total Reflectance (ATR) technique on a BRUKER ALPHA FTIR-ATR spectrometer in the range 4000–500 cm^{-1}. The cross sectional images of the membranes have been captured by HITACHI SU6600 field emission scanning electron microscope. The contact angle measurements of water on the wet membrane surfaces were carried out by the Sessile drop method at ambient temperature using a Goniometer (contact angle meter, HO-IAD-CAM-01, HOLLMARC).

2.3. Synthesis of 3-methyl 2-pyridineethanol

100 g (0.9334 mol) of 2,3-lutidine and 28.02 g (0.9334 mol) of paraformaldehyde were heated in an autoclave at 220 °C for about 3 h in presence of 1.1396 g (0.0042 mol) of potassium persulfate in ethanol. t-butyl catechol in traces was used as an inhibitor [20]. The product was separated by vacuum distillation. The boiling point of 6-methyl 2-pyridine ethanol is 120 °C at 12 mm Hg, yield: 38.36 g (30%).

2.4. Synthesis of 3-methyl 2-vinylpyridine (3M2VP)

The dehydration of 3-methyl 2-pyridineethanol was carried out by the addition of 3.75 g (0.094 mol) of powdered NaOH and trace amounts of t-butyl catechol to 25 g (0.165 mol) of 6-methyl 2-pyridine ethanol. The mixture was stirred and refluxed for 45 min at 120 °C under vacuum [21]. The product was dissolved in 300 mL of water (pH 9) and extracted thrice with ether. It was dried over anhydrous Na_2SO_4 overnight. The product was collected by vacuum distillation after the removal of Na_2SO_4 by filtration. The boiling point of 6-methyl 2-vinyl pyridine is 64–65 °C (3 mm Hg), Yield: 11.38 g (58%).

2.5. Synthesis of 3-methyl 2-vinylpyridinium nitrate (3M2VPN)

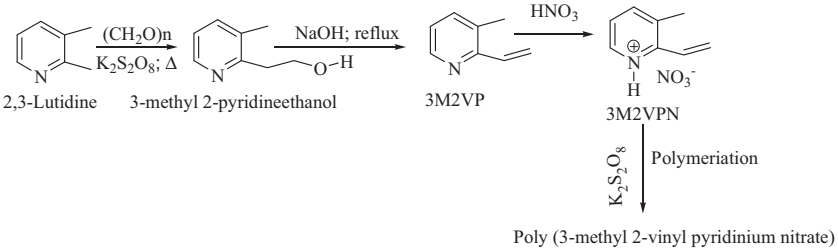
1 g (0.0084 mol) of freshly distilled 3-methyl 2-vinyl pyridine was dissolved in 15 mL of diethyl ether at −10 °C under nitrogen atmosphere. To the above solution 0.6 mL of HNO_3 and 10 mL of diethyl ether were added drop wise with continuous stirring at −10 °C and the resultant solid was filtered after 30 min, washed with diethyl ether and dried under vacuum to obtain yellow solid. Yield: 1.4982 g (98%); mp 114 °C.

2.6. Polymerization of 3-methyl 2-vinyl pyridinium nitrate (P3M2VPN)

5 mmol of 3-methyl 2-vinyl pyridinium nitrate was dissolved in appropriate amount of distilled water and the solution was first flushed with N_2 for 10 min. Later 0.37 mmol of potassium persulfate was (dissolved in 2 mL of distilled water) added and stirred, heated under vacuum at 90 °C for about 4 h. The viscous product was precipitated using acetone and purified by re-precipitation from methanol by ether. The synthetic route for the preparation of poly 3-methyl 2-vinyl pyridinium nitrate is presented in Scheme 1.

2.7. Membrane preparation

Polymeric membranes were prepared by phase inversion method, using PVDF and P3M2VPN. Different ratios of PVDF/P3M2VPN/NMP solutions were prepared and their compositions are listed in Table 1. The homogeneous solution was prepared by dissolving 15 wt.% of polymer in the presence of NMP under constant mechanical stirring in a round bottom flask for 6 h at 80 °C.



Scheme 1. Synthetic route of poly 3-methyl 2-vinylpyridinium nitrate