EXCLUSION OF LETHAL METAL ION BY MEANS OF POLY M-PHENYLENE (ISOPHTHALAMIDE) ULTRAFILTRATION MEMBRANES

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Abstract
Poly m-phenylene (Isophthalamide) (PMIA) Ultrafiltration were synthesized by Non-solvent induced phase inversion technique using Lithium Chloride (LiCl) with various compositions of Poly ethylene glycol (PEG-600) and N-methyl pyrrolidone (NMP) solvent. The effects of compositions of PEG-600, pure water flux and percentage water content of the membranes were studied. The application of PMIA membranes in separation of toxic heavy metal ions from solutions was also attempted and the results were discussed.

Keywords: Poly m-phenylene (Isophthalamide), Ultrafiltration and heavy metal separation.

1. Introduction

With the development of membrane technology, separation, concentration and purification have become feasible operation with modern compact modules. Flux and rejection of membrane process are mainly influenced by size and charge of the molecule to be separated and membrane pore size. Surface properties of a membrane also play a vital role. It is because the major drawback of membrane separation process is fouling, induced by adsorption of particulate matter onto the membrane surface or deposition into the pores, and is mainly controlled by surface properties.

The majority of the polymeric ultrafiltration membranes are prepared by phase inversion technique [1]. In Nonsolvent Induced Phase Inversion process, a homogeneous polymer solution is cast as a thin film in a coagulation bath. The exchange of nonsolvent and solvent induces the phase separation phenomena in the polymer solution, which usually leads to the formation of an anisotropic (asymmetric) structure with a relatively thin skin supported on a much thicker porous substrate in the resulting membrane. Membranes prepared by this process usually contains large elongated voids (macro voids) in their sub layer structure.

Poly m-phenylene (Isophthalamide) (PMIA) is the aromatic polyamides having high thermal stability and excellent mechanical properties [2]. PMIA fibers are very resistant to solvent dissolution. The chemical structure of PMIA is shown in Fig. 1.Removal of toxic metal ion such as Cu, Zn, Hg, Cd, Pb and Ni from industrial waste waters is required for meeting the present need for water reuse. The presence of lead in drinking water will cause serious health problems leading to death in extreme exposure case [3].

In the present study, attempts were made to develop new PMIA Ultrafiltration membranes with LiCl in the presence of different compositions of PEG-600 using NMP solvent and studied for removal of lead (Pb) from water.
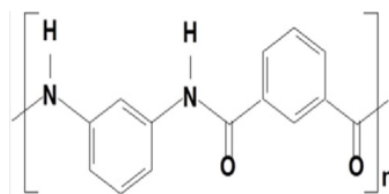

Fig.1.Chemical structure of Poly m-phenylene (Isophthalamide) (PMIA).

2.1 Materials

Commercial grade poly m-phenylene (Isophthalamide) (PMIA) (Mw = 36.8KDa), (T_g = 274°C); was purchased from Sigma Aldrich, India. All the polymers were dried in a vacuum for 8 h prior to use for membrane preparation. Polyethylene glycol 600 (PEG 600) was obtained from Merck (I) Ltd., and was used as non solvent additive for the ultrafiltration membrane preparation. Analar grade N-methyl-2-Pyrrolidone (NMP) from SRL Chemicals, India Ltd. was sieved through molecular sieves (Type – 5A°) to remove moisture and stored in dry conditions prior to use. Dextrans with molecular weights 19, 40, 70, and 150 KDa were procured from Sigma – Aldrich Co. (Milwaukee, WI) and stored at a suitable temperature before use. Anhydrous Lithium Chloride (LiCl) was purchased from Loba Chemie Pvt. Ltd. and used as such as the inorganic additive. Analytical grade Lead Nitrate was procured from Hi-media Laboratories Ltd., India, used for the preparation of metal ion solution. Hydrochloric acid and sodium hydroxide were procured from SRL Chemicals Ltd., India and used for pH adjustment.

2.2 Ultrafiltration setup

The membrane characterization was studied in a dead end Ultrafiltration (UF cell-S76-400-Model, Spectrum, USA) with a diameter of 76 mm, fitted with Teflon coated magnetic paddle. This cell was connected to a compressor with pressure control valve and gauge through a feed reservoir. The schematic representation of dead end UF cell is given in Fig. 2.
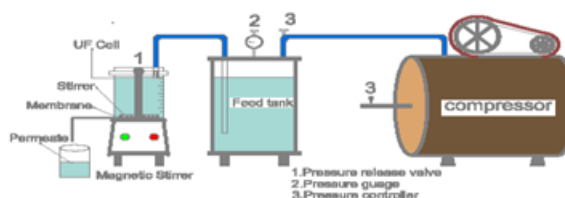

Fig.2. Schematic representation of dead end UF cell.

The membranes were placed in UF cell and compacted with deionized water at 414KPa for initial 15 min. Then the pure water flux (J_{w1}) of the membranes was membranes measured at 345KPa for 5 min in a regular interval of 1 hr till it reaches the steady state flux as follows [4].

$$J_w = \frac{Q}{A\Delta t} \qquad \text{--- (2)}$$

Where Q - The quantity of permeate collected (L), Δt - The sampling time (h) and A - The membrane area (m^2).

The membrane hydraulic resistance (Rm) (Eqn.2.) of the membranes was measured at a different trans membrane pressure (ΔP) of 69,138,207,276 and345KPa [5]. Water uptake of the membrane was measured by soaking them in water for 24 h and wet weight (m_1) was measured after wiping with blotting paper. Later on, these wet membranes were placed in vacuum oven at 45 °C for 24 h and the dry weight (m_2) was determined (Eqn.3) [6]. Porosity of the membrane was determined using gravimetric method (Eqn. 4.) [7]. MWCO was found using dextrans of different molecular weight (198, 20, 70 and 150 KDa). The percentage rejection was calculated using the formula as given below (Eqn. 5) [8].

$$Rm = \frac{\Delta P}{J_w} \text{ --- (1)}$$

$$\% \ water \ uptake = \frac{m_1 - m_2}{m_1} \times 100 \qquad --- (2)$$

$$\varepsilon = \frac{m_1 - m_2}{\rho w A L} \ --- (3)$$

$$SR(\%) = \frac{(1 - C_p)}{C_f} \times 100 \ --- (4)$$

Where,

ρ_w -Density of water; A - Effective area of the membrane and L - Membrane thickness.

C_p and C_f are the concentrations of permeate and feed solutions respectively.

2.3 Heavy metal (Pb) rejection

Aqueous solution of Pb^{2+} with an approximately 1000ppm concentration was prepared using PEI in deionized water. The ph of the solution was adjusted to 6.25 using 0.1 HCl or 0.1M NaOH. These aqueous solution or metal chelates were thoroughly mixed and left standing for 5 days for complete binding. The concentration of each metal ion in feed and permeate after passing through the membrane in UF setup was measured using Atomic Absorption Spectrophotometer Perkin Elmer 2380. The % metal ion rejection was evaluated using equation 4.

3. Results and Discussions

3.1 Membrane Preparation

The PMIA membranes were prepared by dissolving PMIA polymer of 10 wt% with 4 wt% of LiCl and different compositions of PEG-600 in NMP solvent by thoroughly mixing it for 6 h at 90°C. The prepared dope solution was kept for deareation and then cast on a glass plate, allowed to evaporate for 30sec followed by immersion of glass plate with casting solution in a non- solvent water bath.

Table 1: Preparation of casting solution for membrane formation.

Membrane Code	PMIA wt%	LiCl wt%	PEG wt%	NMP wt%
M0	10	4	0.5	86
M1	10	4	1	85
M2	10	4	1.5	84.5
M3	10	4	2	84

3.2 Permeability analysis

UF is a pressure driven process and hence the pure water flux of the membrane increases with time and pressure.

The PMIA membrane has macro voids and hydrophilic in nature thereby has good water permeability which is shown in Fig. 3. When the additive amount increased in the casting solution the rate of exchange of solvents increased inside the coagulation bath which facilitates the formation of membrane with larger pores. Hence the pure water flux of the membrane increases significantly from 214 $Lm^{-2}h^{-1}$(M1) to 276 $Lm^{-2}h^{-1}$(M4) as the additive amount increased. Fig. 4 shows that Water content (%) of the membranes increases from 52.54% (M1), 71.76% (M2), 75.34% (M3) to 83.11% (M4) and the porosity measurements were 19.61 (M1), 23.07 (M2), 41.97 (M3) and 48.85 (M4).
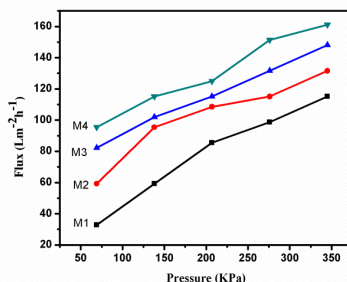

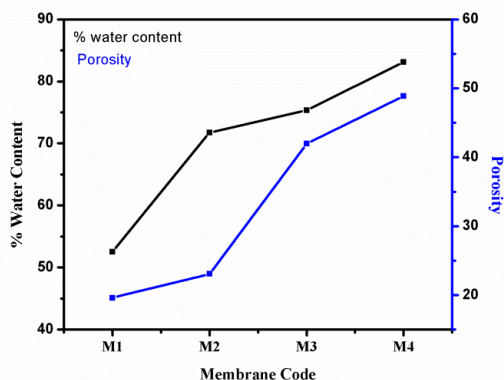**Fig. 3 Effect of pressure for PMIA membranes**

Fig. 4 Water content (%) and Porosity of PMIA membranes

MWCO of composite LiCl-PEG doped PMIA membranes was determined using detrans of different molecular weights of 19, 40, 70 and 150KDa by solute transport method which corresponds to a solute rejection than 80% [9, 10] was chosen as its cut off.

Table 2: MWCO, Porosity, Mean pore size and Thickness of PMIA membranes

Membranes	Membrane hydraulic resistance (R_m) $(KPa\ L^{-1}m^2h)$	MWCO (KDa)	Porosity (%)	Mean pore size (nm)
M1	9.02	40	19.61	18
M2	5.76	40	23.07	27
M3	5.5	70	41.97	28
M4	2.51	70	48.85	30

3.3 Role of PMIA membranes on metal-ion rejection

UF processes cannot be directly applied for ionic level rejections due to the large pore size of the membranes. Polyethyleneimine (PEl) a water soluble chelating polymer used to form complex with metal ions such as Cu(II), Cd(II), Ni(II) and Zn (II), by doing so the size of the metal ion increases. When the pore size of the membrane increases, separation efficiency decreases (larger voids). The membrane without additives shows larger separation efficiency than the blended membranes.

The rejection of Pb^{2+} using PMIA membranes were carried out individually for all the membranes and the results were shown in Fig.5. In the absence of PEI it was observed that all metal ions were completely passing through the membranes over the acidic range of pH. Beyond pH 7, all the metal ions precipitated as insoluble hydroxides. Hence the pH was kept exactly at 6.25 and the rejection was carried out in the presence of PEI because at this pH strong protonation of metal chelates with stretching of complex takes place [11].From the Fig.5 it was observed that the rejection of Pb^{2+} decreases as the PEG concentration increases in the dope solution for membrane preparation.

4. Conclusion

Ultrafiltration membranes were widely used in industries for the removal of toxic metal ions from solution. The prepared PMIA membranes with Lithium Chloride and various composition of PEG-600 using NMP solvent were asymmetric with large macro voids. Hence they have good water permeability, water content and porosity. The pore size increased with the increase in concentration of PEG-600 so the removal of Pb2+ from the aqueous solution is maximum for PMIA membrane M1 with 0.5 wt% of PEG-600 in the dope solution.

5. Refrences

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