

Fabrication and Characterization of Polysulfone-Zeolite ZSM-5 Mixed Matrix Membrane for Heavy Metal Ion Removal Application

G. P. Syed Ibrahim¹, Arun M. Isloor^{1*}, Amir Al Ahmed², B. Lakshmi³

¹Membrane Technology Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575 025, India

²Center of Research Excellence in Renewable Energy (CORE-RE), King Fahd University of Petroleum & Minerals, Saudi Arabia

³Department of Chemistry, Reva University, Bangalore 560054, Karnataka, India

ABSTRACT

Mixed matrix membranes (MMMs) of Polysulfone (PSf)-Zeolite ZSM-5 (ZZSM-5) were prepared by phase inversion method with a dose ranging from 1.0 to 4.0 Wt. % with polyvinylpyrrolidone (PVP) as the fore forming agent. The prepared mixed matrix membranes were scrutinized for their permeation, hydrophilicity and anti-fouling nature. Characterization of the membrane was carried out by Electrokinetic analyzer. The heavy metal ions rejection experiment has been carried out and the results manifested that, the PZM-4 membrane exhibits higher pure water flux of 348.88 L/m² h, contact angle of 72.7° and the heavy metals rejection of Pb²⁺ (98.54%) and of Cd²⁺ (95.32%) ions. Taken as a whole, the modified PSf-ZZSM-5 ultrafiltration membranes are the attractive candidate for the water treatment.

Keywords: Polymers, Zeolite ZSM-5, Polysulfone, Membranes, Heavy metal rejection, Hydrophilic additive

1.0 INTRODUCTION

The most omnipresent problem distressing human across the globe is insufficient potable water. Adopting these glitches calls out for the water purification. In the forthcoming decades, there will be an intensification of potable water demand even in the water abundant regions [1]. Water scarcity hails from prompt development and industrialization. Contaminant such as heavy metal ions have led to severe environmental concerns [2]. Membrane filtration is one of the ways out to get rid of water contamination since it encompasses low energy consumption, no phase change, easy scale-up and maintenance [3, 4].

Membrane properties are flexible and pore size can be adaptable according to their applications [5]. Membrane technology is broadly pertinent in many areas such as dye removal, desalination and heavy metal rejection [6, 7, 8].

Detrimental heavy metal such as cadmium, nickel, zinc, copper, mercury, chromium, and lead contamination of the environment is a weighty universal glitch [9]. Principally, lead (Pb) poisoning i.e. plumbism is one of the major issues as it affects the human body segments such as heart, bones, intestines, kidneys, and reproductive and nervous systems. The entry of lead into the human body can cause symptoms like abdominal pain, confusion, headache,

* Corresponding to: Arun M. Isloor (email: isloor@yahoo.com)

anemia, irritability, and in severe cases seizures, coma, and death [10]. Recently FDA warns of Pb poisoning risk from cosmetic clay. Moreover, lead has no known useful role in living organism [11]. World Health Organization (WHO) has established the maximum contaminant level (MCL) of Pb in drinking water at 15 μ g/L [12]. In addition, cadmium (Cd) has been recognized as very toxic and it has been merged in “Big Three” category of heavy metals [13]. Symptoms of acute poisoning include headaches, nausea, vomiting, weakness, pulmonary edema and diarrhea and a disease called “Itai–Itai” in Japan is specifically associated with cadmium poisoning [14]. From the above fallouts, it is much exculpated that we need a confiscated system to get rid of heavy metal toxicity. Mixed matrix membranes would be the spot-on alternative to fulfill the above-mentioned requirements with the uniform distribution of zeolite ZSM-5 throughout the membrane matrix. They furnish better separation properties to membranes because of their adapted worthy permeability, selectivity, mechanical strength, thermal stability and chemical resistance [15]. Polysulfone (PSf) based membranes are rummage-sale as ultrafiltration and microfiltration system most extensively for its outstanding heat resistance, chemical compatibility and durable over a wide range of pH [16]. The major drawback of these PSf membranes is that they are hydrophobic in nature. However the water purification membranes necessitate substantial hydrophilicity in order to cope up with productivity issues. Similarly, membranes suffer from fouling and hence lead to low membrane lifetime [17]. The low permeability and fouling are predominantly due to low surface

hydrophilicity and low porosity. So, all over the globe, researchers are looking for a membrane with finely-balanced characteristics. As per the literature is concerned, adding the hydrophilic additive to PSf membrane can increase the hydrophilicity, permeability and antifouling property [18]. Kumar *et al.* investigated the effect of adding N-succinyl chitosan as an additive to PSf membrane. The modified PSf membrane exhibited enhanced hydrophilicity and permeation fluxes with flux recovery ratio of 70% compared to the pristine PSf membrane [19]. Moideen *et al.* reported the effect of adding poly (ethylene glycol) 1,000 (PEG) on the morphology and membrane properties. The results have shown that permeability, hydrophilicity, and antifouling property have been augmented. Also, the tailored membrane has shown flux recovery ratio of 72.84% and the heavy metal such as Pb²⁺ and Cd²⁺ rejection of 99.48 and 95.5% [20]. Ana *et al.* studied the effect of polyvinylpyrrolidone on the morphology and membrane properties. The improved pore density and membrane permeability were observed for the modified membrane than the virgin membrane [21]. Kumar *et al.* investigated more extensively the influence of poly (N-vinylcaprolactam-co-acrylic acid) as an additive to PSf membrane. The pure water flux increased from 1 to 18.8L/m²h, water contact angle decreased from 76° to 58°, an increase in BSA flux and decrease in membrane fouling was observed [22]. Yilmaz *et al.* described the impregnation of zeolite nanoparticles to PSf membrane and the modified membrane exhibited good heavy metal adsorption [23]. Leixi *et al.* prepared the PSf membrane embedded with Linda type zeolite nanoparticle which manifested

resistance to hydraulic shear detachment, enhanced hydrophilicity with water contact angle reduced from 66° to 40° and anti-biofouling ability [24]. Fu *et al.* incorporated the zeolites 4A into PSf membrane and confirmed the enrichment of pure water flux, rejection, thermal and mechanical stability [25]. From the above results, it can be ascertained that adding the hydrophilic additive would improve the PSf membrane filtration properties.

However, the use of zeolite ZSM-5 (see Figure 1) has not yet been reported as the hydrophilic additive to polymeric materials. In the present study, well-dispersed zeolite ZSM-5 has been used as a hydrophilic additive to modify PSf membrane. The PSf-ZZSM-5 mixed matrix membranes were prepared by diffusion induced phase separation method with different amounts of additive dosage ranging from 1.0 to 4.0 wt. %. Pore-forming agent polyvinylpyrrolidone (PVP) was used and the effect of the hydrophilic additive on the membrane surface structure and performance were scrutinized in detail. Dynamic water contact angle measurement was used to depict the membrane surface hydrophilicity. The surface charge of the membrane has been studied by using Electrokinetic analyzer. The performance of the modified membranes was studied in terms of water uptake capacity, water flux, and membrane hydraulic resistance. Additionally, antifouling and heavy metal ion rejection behavior were reconnoitered in detail.

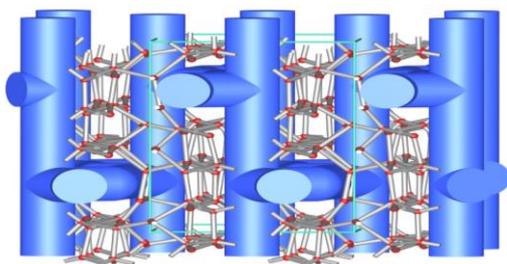


Figure 1 Topology of ZZSM-5

2.0 METHODS

2.1 Materials

PSf (Mw \sim 35,000), Polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich Co., India. ZZSM-5 was a gift sample from King Fahd University for Petroleum & Minerals, Saudi Arabia. N-methyl-2-pyrrolidone (NMP) was purchased from Merck India, Ltd. Bovine serum albumin (BSA) (Mw \sim 69 kDa) was purchased from CDH Chemicals, India. Polyethyleneimine (PEI) (Mw \sim 60,000) was purchased from Acros Organics, USA. Cadmium nitrate tetrahydrate and lead nitrate were purchased from Sigma-Aldrich Co., India.

2.2 Preparation of Membranes

PSf-ZZSM-5 mixed matrix membranes were prepared by phase inversion method [8]. The calculated amount of ZZSM-5 (0 wt. % to 4 wt. % of PSf dosage) was dispersed in a suitable volume of NMP and sonicated for 15 min at room temperature. The anticipated quantity of PSf (overall 20 wt. % of the polymer concentration of the final casting solution) was added to the above dispersed solution along with 2 wt. % of the invariable pore forming agent PVP and the solution was stirred for 24 h at 50°C to obtain a homogeneous casting solution. The obtained solution was kept for an hour without stirring at the similar temperature to discard imprisoned air. The casting solution was spread on a clean glass plate and cast using a doctor's blade. Then it was immersed into a water bath and allowed to stand in a coagulation bath for 24 h to confirm comprehensive phase inversion. A summary of the compositions of the membranes is given in Table 1.

Table 1 Casting solution composition

Membrane code	PSf(g)	NMP (g)	ZZSM-5 (g)	PVP (%)
PZM-0	18	80	0	2
PZM-1	18	79.8	0.18	2
PZM-2	18	79.6	0.36	2
PZM-3	18	79.4	0.54	2
PZM-4	18	79.2	0.72	2

^aW_{ZZSM-5} is the mass ratio of ZZSM-5 to PSf

2.3 Electrokinetic Analysis

Zeta-potential of the membranes surface was determined by a streaming current electro kinetic analyzer (SurPass, Anton Paae GmbH, Graz, Austria). The flow channel gap was set at 100 μ m, and a 1 mM KCl solution at 20 °C was used as the background electrolyte. Streaming current was determined in a pH range of 2–10, adjusted using HCl and NaOH. Membrane zeta potential (ζ) was calculated using the Helmholtz-Smoluchowski equ (1)

$$\zeta = \frac{dI}{dp} \frac{\mu}{\epsilon \epsilon_0} \frac{L}{A} \quad (1)$$

where dI/dp is the slope of the streaming current versus pressure, μ is the solution dynamic viscosity, ϵ is the dielectric constant of the solution, ϵ_0 is the vacuum permittivity, L is the streaming channel length and A is the cross-section of the streaming channel. Figure 2 is the schematic representation of the adjustable gap cell.

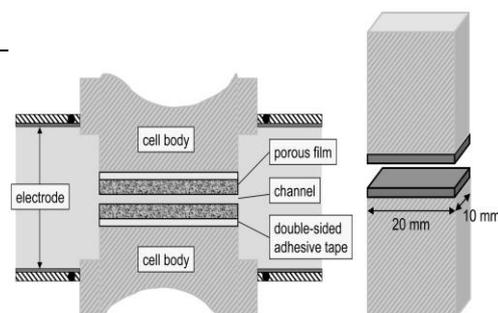


Figure 2 Vision along the streaming channel inside the adjustable-gap cell (top) and schematic representation of membrane mounting inside the adjustable-gap cell; right: cross section of samples holders [27]

2.4 Water Uptake and Contact Angle Measurement

The water uptake capacity of the membrane is a significant factor to govern its hydrophilicity. The dry membranes were cut into 2 cm² sized pieces and weighed. These membrane samples were soaked in distilled water for 24 h and weighed after smearing with blotting paper followed by the wet membranes were dried under vacuum at 70 °C for 24 h. The dry weights were determined and the percentage water content in the membrane was calculated using eqn (2)

$$\% \text{uptake} = \left(\frac{W_w - W_d}{W_w} \right) \times 100 \quad (2)$$

where W_w and W_d are the weight of wet and dry membrane samples respectively.

The change in the hydrophilicity of the prepared membranes after adding

the ZZSM-5 was confirmed by measuring the water contact angle (WCA). The surface hydrophilicity was measured by an FTA-200 Dynamic contact angle analyzer using the sessile droplet method. In order to minimize the experimental errors, the WCA measurement of each sample was measured three times and the average value was reported.

2.5 Pure Water Flux Study

The pure water flux (PWF) of the membranes were determined using dead end filtration unit at room temperature. Membrane area of 5 cm² was dipped in Deionized water for 24h before commencing the filtration. The setup was aided with a nitrogen cylinder as the pressure source. Each membrane was compacted at 5 bar pressure for 30 min before beginning the experiment. After compacting, deionized water was passed through the membrane for 80 min at 4 bar pressure to acquire PWF J_w (L/ m² h). The flux was calculated using the formula (3) and Figure 3 is the schematic illustration of the lab scale filtration arrangement.

$$J_w = \frac{Q}{\Delta t A} \quad (3)$$

where, J_w is PWF and 'Q' is the amount of water collected for Δt (h) time duration using a membrane of area 'A' (m²).

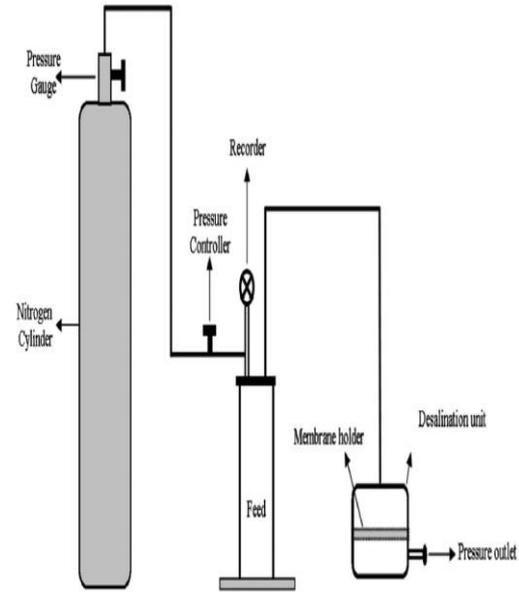


Figure 3 Schematic illustration of the lab scale filtration arrangement

2.6 Antifouling Properties

The membrane fouling behavior was examined using the reported literature [28]. In brief, the pure water flux of the membrane J_{w1} (L/(m² h)) was tested at 4 bar transmembrane pressure (TMP). Then, 0.8 g/L bovine serum albumin (BSA) aqueous solution was fed into the ultrafiltration system followed by the filtration of BSA for 80 minutes. The flux for BSA solution measured based on the quantity of water permeating the membranes is J_p (L/m²/h). The membrane was flushed with pure water for 10 minutes and then pure water flux of the membrane J_{w2} (L/(m² h)) was calculated. The flux recovery ratio (FRR) was calculated using Eq. (4) to assess the membrane antifouling property.

$$FRR (\%) = \frac{J_{w2}}{J_{w1}} \times 100 \quad (4)$$

The membrane fouling was further assessed by calculating the reversible R_{rev} and irreversible R_{irr} fouling ratio by following equation (5) and (6)

$$R_{\text{rev}} (\%) = \frac{J_{w2} - J_p}{J_{w1}} \times 100 \quad (5)$$

$$R_{\text{irr}} (\%) = \frac{J_{w1} - J_{w2}}{J_{w1}} \times 100 \quad (6)$$

2.7 Heavy Metal Rejection Study

The experiment was executed as per the literature procedure [8]. In brief, an aqueous solution of lead nitrate and cadmium nitrate was prepared in the presence of 1 wt. % of polyethyleneimine with an initial concentration of 1000 ppm. The pH of the subsequent solution was adjusted to 6 ± 0.5 using 0.1 M HCl or 0.1 M NaOH solution. The attained solution was stirred for 5 days at room temperature to persuade complex formation. The heavy metal ions rejected by the membranes were determined by calculating the metal ion concentration in the feed and permeate using an AAS (atomic absorption spectrometer). The percentage of metal ions rejected by the membranes were calculated using the eqn (7)

$$\% R = \left(1 - \frac{c_p}{c_f}\right) \times 100 \quad (7)$$

where C_p and C_f are the concentrations of heavy metal ions in the permeate and feed respectively.

3.0 RESULTS AND DISCUSSION

3.1 Electrokinetic Analysis

Zeta potential measurements for the pure PSf and modified membrane is shown in Figure 4. The modified membrane has hydroxyl and sulfone group which will be protonated at low pH leading to positive zeta potential value. Moreover at high pH the groups will be deprotonated causing negative zeta potential value. The modified membrane manifested higher zeta potential value (-43 mV) than the pure PSf membrane (-34 mV) due to the presence of ZSM-5 on the membrane surfaces. Evidently, the addition of ZSM-5 has capacity for improving the separation efficacy of pure PSf membrane since hydrophilicity and anti-fouling proficiency increase as the membrane surfaces become more hydrophilic, energetic and charged [29]. Figure 4 represents the zeta potential values.

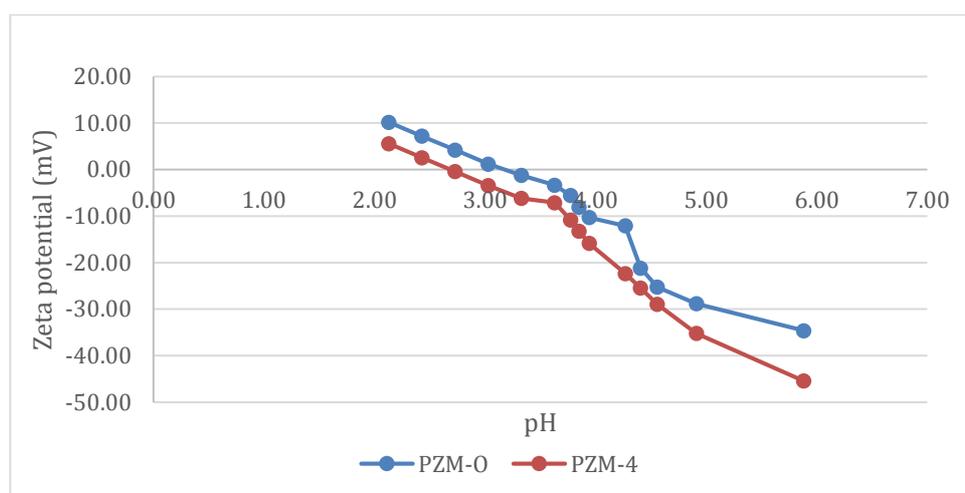


Figure 4 Zeta potential value of PZM-O and PZM-4

3.2 Water Uptake Capacity and Contact Angle

The hydrophilic nature of the membrane can be ascertained by measuring their water uptake capacity and contact angle. The water uptake capacity of the membrane depends on number of hydrophilic sites and the existence of macrovoids in the membrane [7]. The water uptake capacity of all the membranes is presented in Figure 5. The PZM-0 membrane has shown the water uptake capacity of 58.5% and it has been increased as ZSM-5 content increased.

The increase in water uptake capacity designates the increased hydrophilic sites and the increased macro voids in the membranes.

In general contact angle is the measure of surface hydrophilicity of the membrane, smaller the contact angle greater the hydrophilicity and vice versa. Moreover PZM-4 membrane has shown the contact angle of 72.7°. Since the contact of pristine PZM-0 membrane was 79.9°, the addition of ZSM-5 could have increased the hydrophilicity (Figure 5) of the membrane. The values are tabulated in Table 2.

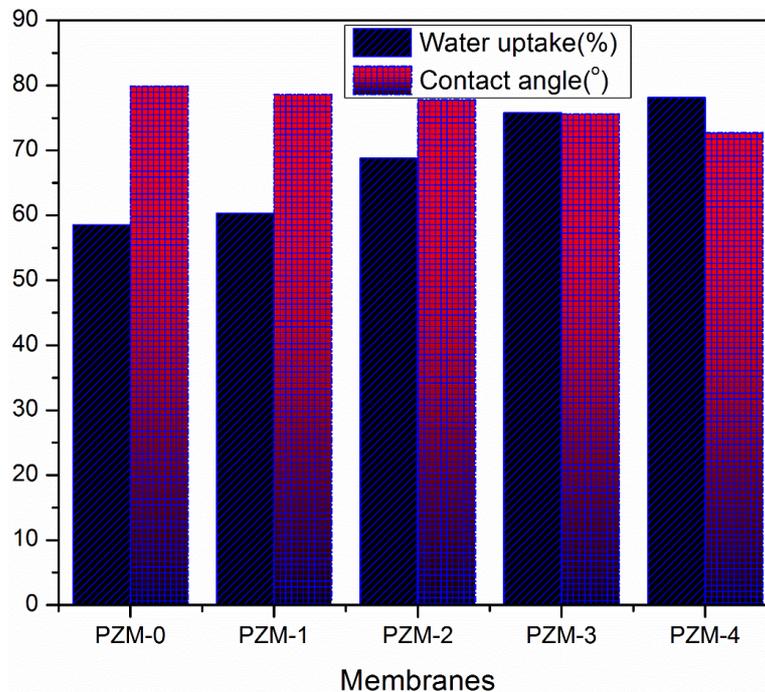


Figure 5 Water uptake capacity and contact angle of the membrane

Table 2 Properties of the prepared membranes

Membrane code	Contact angle (°)	Pure water flux (L/m ² h)
PZM-0	79.9	55.9119
PZM-1	78.6	101.5119
PZM-2	77.8	239.1382
PZM-3	75.6	291.9382
PZM-4	72.7	348.88

3.3 Pure Water Flux

Filtration experiment has been done to demonstrate the pure water flux (PWF) of the modified membrane. The PWF values are tabulated in Table 3. Here, the hydrophilicity is one of the prime factor which decides the permeation of water through the membrane. Figure 6 represents the PWF of the membrane. The PZM-0 membrane bared minimum flux of 81.13 L/m² h whereas the PZM-4 membrane uncovered maximum flux

of 393.02 L/m² h. The augmentation of flux can be attributed to the addition of hydrophilic additive ZZSM-5, as a result hydrophilicity of the membrane upsurges and the contact angle of the modified membrane diminutions than the pristine membrane. In addition, the zeolite ZSM-5 is microphorous aluminosilicates, which could be the supplementary reason for the increment of hydrophilicity. As a result ZZSM-5 would be good hydrophilic stuff.

Table 3 Filtration and antifouling performance of the membrane

Membrane code	Permeate flux (L/m ² h)			FRR and fouling performance (%)			
	J _{w1}	J _p	J _{w2}	FRR	R _t	R _r	R _{ir}
PZM-0	55.9119	3.45	15.3415	27.4387	93.82	21.26	72.56
PZM-1	101.5119	20.55	44.98045	44.31052	79.75	24.06	55.68
PZM-2	239.1382	46.53	151.7367	63.45148	80.54	43.99	36.
PZM-3	291.9382	50.23	195.5446	66.9815	82.79	49.77	33.01
PZM-4	348.8834	54.13	251.1118	71.97585	84.48	56.46	28.02

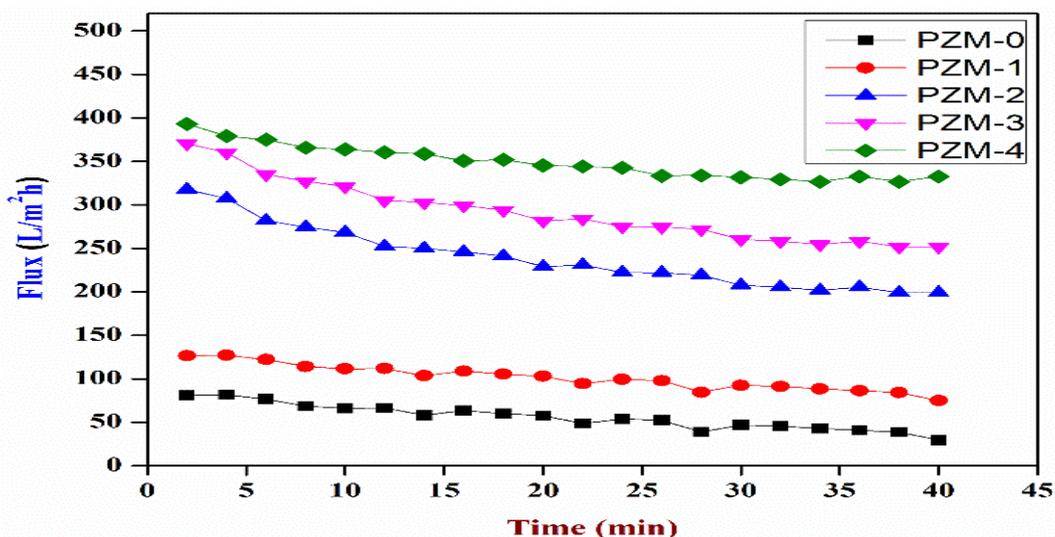


Figure 6 Time dependent pure water flux of the membrane

3.4 Antifouling Performance of the Membrane

It has been well documented that, all pressure driven processes are bound to

foul. It may lead to the decline of membrane performance. Fouling is caused by the deposition or adsorption of particles, proteins, colloids, salts, macromolecules, etc., on the

membrane surface or inside the pores [30]. As a result, the flux in the course of BSA rejection falloffs considerably compared to the pure water flux [28]. In addition, surface hydrophilicity plays a major role in fouling. Figure 7 shows the flux of the modified and unmodified membranes at 4 bar pressure at 28 °C in altered environments i.e. before BSA filtration, during BSA filtration and after BSA filtration. There was a decline in flux during BSA rejection on account of the adsorption or deposition of protein molecules on the membrane surface, which affects the hydrophilicity of the membrane as well. The prepared membranes are hydrophilic in nature so they have exhibited lower attraction on the way to protein binding. In order to examine the antifouling property, calculation of flux recovery ratio is the spot-on method [31]. The total fouling performance and flux recovery ratio (FRR) are tabulated in Table 4. The pristine membrane PZM-0 unveiled FRR of 27.43% and fouling ratio (R_f) of 93.82% in consequence of the

hydrophobic nature. The membrane PZM-4 exhibited FRR of 71.97% owing to the increased hydrophilicity by adding ZZSM-5. So the foulant could be removed by simple hydraulic cleaning. Therefore the membrane is having ample reversible nature. In addition, based on the FRR and total fouling performance it can be ascertained that the prepared membrane is having better antifouling properties and the obtained results are quite comparable with hydrophilic additives such as graphene oxide, silica and TiO_2 nanoparticles [32, 33, 34, 35].

3.5 Heavy Metal Ion Rejection Study

Heavy metal ions are toxic to human health and lead to the environmental pollution [15]. Since heavy metals are non-biodegradable one has to take prime action to control the heavy metal pollution. In the present study, rejection study of PSf and modified PSf have been demonstrated for Pb^{2+} and Cd^{2+} ions and presented in Figure 8.

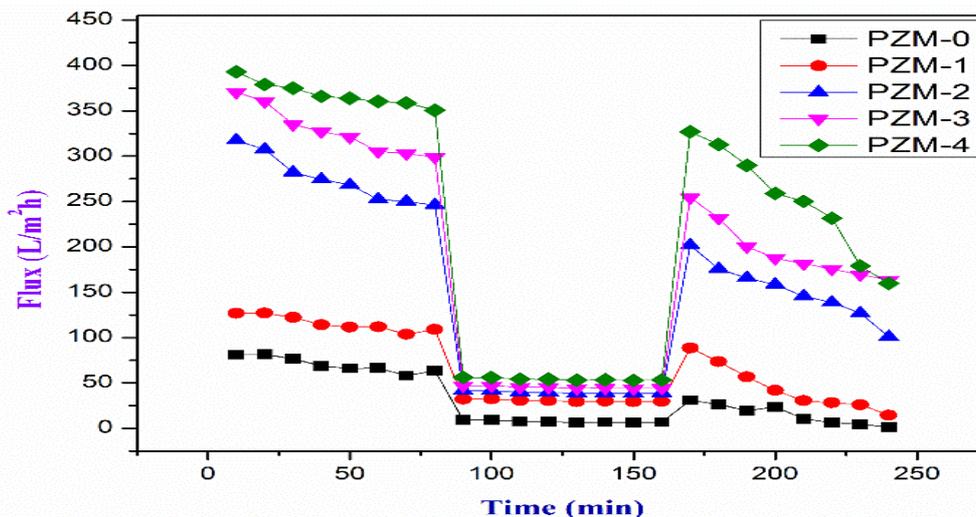


Figure 7 Flux against time for membranes at 4 bar pressure under three conditions: water flux for 80 min, 0.8 g L^{-1} BSA solution flux for 80 min, and water flux for 80 min after detailed washing with distilled water

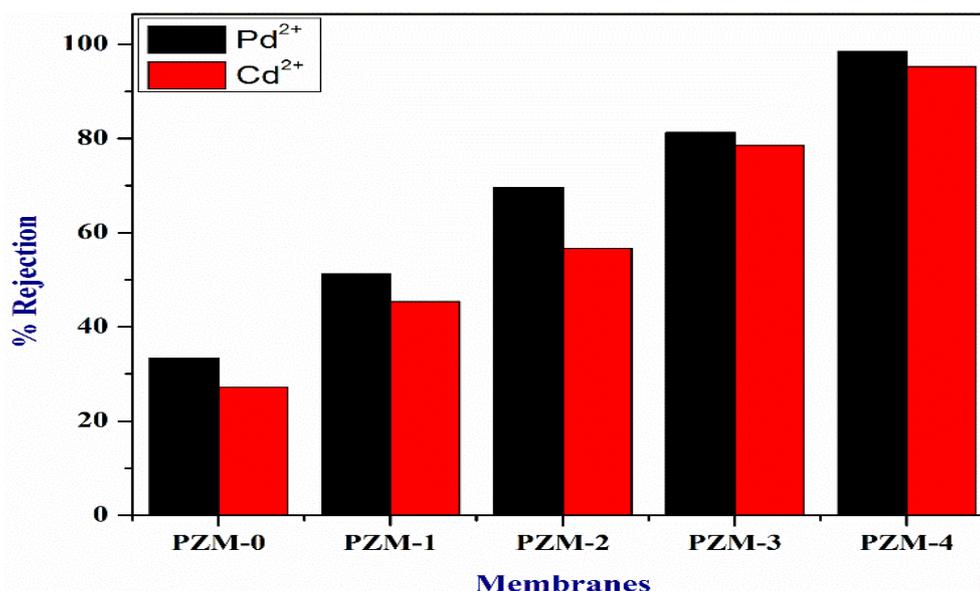


Figure 8 The heavy metal ions rejection of modified membranes

The membrane PZM-4 publicized the rejection of Pb²⁺ and Cd²⁺ ions were 98.56 and 95.32% respectively.

Moreover the PZM-0 exhibited rejection of Pb²⁺ and Cd²⁺ ions were 33.4 and 27.2% respectively. It is evident from the results that as the concentration of ZZSM-5 increases the rejection ability also increases. This is because, the PSf membrane is hydrophobic in nature, so the interaction between the heavy metal ions and the membrane is considerably less. By adding ZZSM-5 as hydrophilic additive, it increases the hydrophilicity of the modified membrane. The complexation capacity of the metal ions with polyethyleneimine (PEI) depends on the size of metal ion i.e. bigger Pb²⁺ ions complexes more effectively than the Cd²⁺ ions. As a result the bigger Pb²⁺ ions are rejected greater than the smaller Cd²⁺ ions [20]. The order of heavy metal rejection is Pb²⁺ > Cd²⁺ ions. It can also be comprehended that while complexing with PEI the size of metal ion increases since it forms metal complex [8].

4.0 CONCLUSION

The mixed matrix membranes were prepared by phase inversion method with different amount of ZSM-5 (0 to 4 wt. %). The results have been revealed that the modified membranes exhibited improved pure water flux, hydrophilicity and water uptake capacity. In addition the membrane PZM-4 has shown FRR of 71.9% and reversible fouling of reversible fouling ratio of 56.4%. Correspondingly, the modified membrane has ability to adsorb heavy metal ions such as Pb²⁺ and Cd²⁺ ions. Overall, the ZSM-5 is the effective hydrophilic additive for improving the performance of the membrane.

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