

Effect of PVP concentration on prepared PEI membranes for potential use on water treatment: effect of additive on membranes prepared for water treatment

Öykü Mutlu Salmanli, Sevgi Güneş Durak, Güler Türkoğlu Demirkol and Neşe Tüfekci

ABSTRACT

In this work, a series of polyetherimide (PEI) flat sheet membranes were produced with different concentrations of polyvinylpyrrolidone (PVP) addition via the phase inversion method. The effects of additions on membrane morphology and performance were investigated. Synthesized membrane had the properties of ultrafiltration membrane. Although PEI is not widely used for water treatment, in this study, the ferrous iron removal rate was investigated and good results were obtained. Through the membrane production experiments, the PEI content was 22 wt%. PVP was added as a pore-forming agent with concentrations of 2, 4 and 8 wt%. N-methyl-2-pyrrolidone (NMP) was used as solvent. Distilled water was used for the coagulation bath. After production, all membranes were characterized by using contact angle, permeability, porosity, and scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT/IR) analyses. With the increasing doses of PVP addition, the permeability of the PEI membranes produced in this study increased, while porosity results were changeable. The permeability was 23 L/m² h bar for the membrane with 2 wt% PVP content, while the permeability for the membrane with 8 wt% PVP content was 32 L/m² h bar. Contact angles increased with PVP addition to PEI membranes. With the increasing PVP concentration, the finger-like pores and the pores located in the sub-layer expanded.

Key words | ferrous iron, membrane preparation, PEI, PVP, ultrafiltration, water treatment

INTRODUCTION

Water is one of the most fundamental and most important needs of human beings. But, with increasing industrial and technological facilities and with increasing population, water resources are being polluted and getting scarce. To overcome these problems and protect water sources, a lot of technologies have been developed in recent centuries. Membrane processes are one of the emerging technologies. Polymeric membranes are widely used for water and wastewater treatment.

There are various techniques for membrane production. The selection of the appropriate method depends on the material and the final membrane application. Sintering,

stretching, track-etching, phase inversion and electro-spinning are some of the techniques widely used for membrane production for water and wastewater treatment applications (Mutlu-Salmanli 2018).

Phase inversion is one of these techniques. It based on the solvent–non-solvent exchange process that occurs between the coagulation bath and film. While casting the membrane, all experimental conditions, like the dope solution and coagulation bath composition, temperature, speed and evaporation time etc. affect membrane performance (Zhao *et al.* 2011). A lot of polymers like polyethersulfone (PES), cellulose acetate (CA),

Öykü Mutlu Salmanli (corresponding author)
Istanbul Technical University,
Faculty of Civil Engineering, Environmental
Engineering Department,
34469 Maslak, Istanbul,
Turkey
E-mail: mutluoyku@itu.edu.tr

Sevgi Güneş Durak
Nevşehir Hacı Bektaş Veli University,
Faculty of Engineering and Architecture,
Environmental Engineering Department,
50300 Nevşehir,
Turkey

Güler Türkoğlu Demirkol
Neşe Tüfekci
Istanbul University-Cerrahpaşa,
Faculty of Engineering, Environmental Engineering
Department,
34320 Avcılar, Istanbul,
Turkey

polyacrylonitrile (PAN), polypropylene (PP) and polyetherimide (PEI) can be used for polymeric membrane production via the phase inversion method. In this study, PEI was selected as the main polymer for production of membranes. PEI has quite a few advantages. Good tensile strength, high mechanical and chemical stability and also high heat distortion and temperature and commercial availability are some of these advantages (Namvar-Mahboub & Pakizeh 2013; Naim *et al.* 2014; Shamsabadi *et al.* 2015).

Additives such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), carbon nanotube (CNT), metal nanoparticles and chitosan are used to enhance membrane properties for different objectives. Sulfonated poly(ether ether ketone) (SPEEK) was used as modifier by Bowen *et al.* (2005) for PEI membranes. They reported that the addition of SPEEK enhanced the flux and NaCl rejection of membranes compared with the pristine membrane. Thuyavan *et al.* (2015) used TiO₂ nanoparticles with SPEEK as an additive for PEI membranes to modify them for desalination applications (Thuyavan *et al.* 2015). Polydimethylsiloxane (PDMS) was used for preparation of PEI membranes by Shamsabadi *et al.* (2014) for separation of hydrogen from H₂/CH₄ mixed gas. Naim *et al.* (2014) used PEG as an additive to PVDF/PEI hollow fiber membranes for CO₂ stripping. Garcia-Ivars *et al.* (2014) used both PEG and Al₂O₃ nanoparticles for preparing PES, PEI and PS membranes for enhancing the hydrophilicity of the membranes. Namvar-Mahboub & Pakizeh (2013) prepared PEI support layers for nano-thin-film composite (TFC) membranes by using modified SiO₂ for obtaining the stable support.

Among these additives, PVP is a good water-soluble polymer that is widely used as a pore-forming agent for membrane preparation because of its features like solubility, environmental stability, easy processability, increase in membrane porosity and ability of interconnecting the pores. Beside those it is also non-toxic (Cranford *et al.* 1999; Torrestiana-Sanchez *et al.* 1999; Mallakpour & Naghdi 2016). PVP suppresses the formation of macro-voids in the membranes, enhances the permeate flux as well as porosity and pore numbers of membranes prepared via the phase inversion technique (Cranford *et al.* 1999; Han & Nam 2002; Zhao *et al.* 2011). Han & Nam (2002) reported that 5 wt% PVP addition to polysulfone (PSf) membranes enhanced the permeate flux but with the

increasing doses of PVP, the flux decreased. Gebru & Das (2017) investigated the effect of PVP and PEG additives on cellulose acetate membrane morphology and found the PVP-added membranes have finger-like structure and greater macro-voids. Saljoughi & Mohammadi (2009) found that addition of 0 to 3 wt% PVP to the dope solution increased the formation of macro-voids and pure water flux, while addition of 3 to 6 wt% PVP suppressed macro-voids and decreased flux.

In the present study, PEI was used to prepare flat sheet polymeric ultrafiltration membranes by using the phase inversion method. PEI was selected because of its good chemical, thermal and mechanical stability, good film-forming properties, and high glass-transition temperature as indicated in many studies (Naim & Ismail 2013; Namvar-Mahboub & Pakizeh 2013; Naim *et al.* 2014; Shamsabadi *et al.* 2015). PVP was selected as an additive and the effects of PVP concentration on membrane properties and performance were investigated. In addition, the removal efficiency of ferrous iron with the synthesized membrane was investigated.

MATERIALS AND METHODS

Materials

Polyetherimide (PEI) polymer was purchased from Sigma Aldrich. N-methyl-2-pyrrolidone (NMP) was used as a solvent for this study. It was supplied by Merck. Polyvinylpyrrolidone (PVP) with molecular weight of 10,000 was used as pore-forming agent and purchased from Sigma Aldrich. Milli-Q water was used for the coagulation bath at ambient temperature.

Membrane preparation

The PEI and PVP were dried in an oven for at least 4 hours before use. Polymer concentration was selected as 22 wt% and PVP concentrations were 2, 4 and 8 wt%. Firstly the appropriate amount of PVP was added to the NMP solvent and mixed until obtaining a homogeneous solution. Then the PEI polymer was added to this solution and mixed at the proper stirring rate at a temperature of 50 °C. An

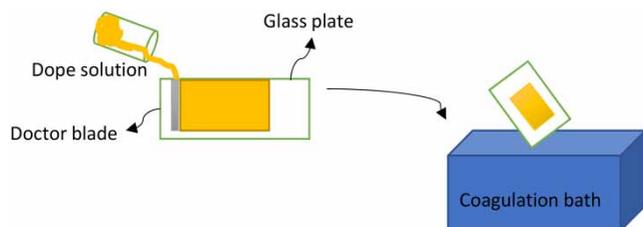


Figure 1 | Membrane preparation via phase inversion.

ultrasound bath was used to remove air bubbles from the dope solutions. After solution degassing, it was cast onto a glass plate with a doctor blade of 200 μm thickness. After 30 seconds interval for evaporation, the glass plate was immersed in the distilled water coagulation bath at room temperature (Figure 1). Membranes were kept in distilled water at $+4\text{ }^\circ\text{C}$ for at least 1 week for complete removal of residual solvent from the membranes. After this period the membranes were ready for analysis.

Membrane characterization

Membranes were characterized by using contact angle, pure water permeability, porosity, and scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT/IR) analyses.

Permeability tests were conducted as pure water permeability with dead end membrane cells that had 300 mL capacity and 14.6 cm^2 membrane area. The pure water permeability was determined according to the following equation:

$$R = \frac{J}{P} \quad (1)$$

where R is the permeability ($\text{L}/\text{m}^2\text{ h bar}$), J is the flux ($\text{L}/\text{m}^2\text{ h}$) and P is the pressure as bar.

For determining the permeability under three different pressures, the water fluxes for all membranes were recorded and permeability values were calculated from the slope of the line which gives pressure versus flux. This procedure was repeated at least three times for each membrane and the averaged values were reported.

Contact angle measurements of membranes were determined with a One Attension branded contact angle meter by using the sessile drop technique. Distilled water was used to determine contact angles of membranes. Water

was dropped onto the straight membrane surface via micro-syringe. At least three measurements were conducted for each membrane sample and the values were averaged.

The dry wet weight method was used for determining membrane porosity as explained in the literature (Ma et al. 2012; Garcia-Ivars et al. 2014; Hebbar et al. 2015).

Membranes were always kept in distilled water before being weighed. Superficial water was mopped with filter paper. Afterwards, the membrane was placed in an air-circulating oven at $60\text{ }^\circ\text{C}$ for 24 hours and then further dried in a vacuum oven before the dry weight was measured. The porosity of the membrane was calculated using the following equation:

$$P(\%) = \frac{(m_1 - m_2)}{\rho_w \times A \times \delta} \times 100 \quad (2)$$

where membrane wet and dry weights (g) are m_1 and m_2 , respectively, ρ_w is the density of pure water (g/cm^3), A is the area of the membrane in the wet state (cm^2) and δ is the thickness of the membrane in the wet state (cm). The membrane porosity of each sample was measured three times and the average value was reported.

For the morphological and structural analyses of membranes, SEM and FT/IR were used, respectively. The SEM images of membranes were carried out on the membrane cross-section by using an FEI Quanta Feg 250 SEM. A Perkin Elmer Spectrum 100 FT-IR was used for observing the structural changes of pristine and PVP-added membranes.

Treatment performance

After characterization, membranes were tested with surface water in a submerged membrane experimental setup. Ferrous iron removal efficiencies of the produced membranes were observed. Both feed water and permeate water of the membranes were analysed via inductively coupled plasma optical emission spectrometry (ICP-OES). Removal efficiencies were reported as removal rate.

The rejection (R) for each membrane in the surface water is given by:

$$R = 1 - \frac{\text{ferrous iron concentration in permeate}}{\text{ferrous iron concentration in feed}} \quad (3)$$

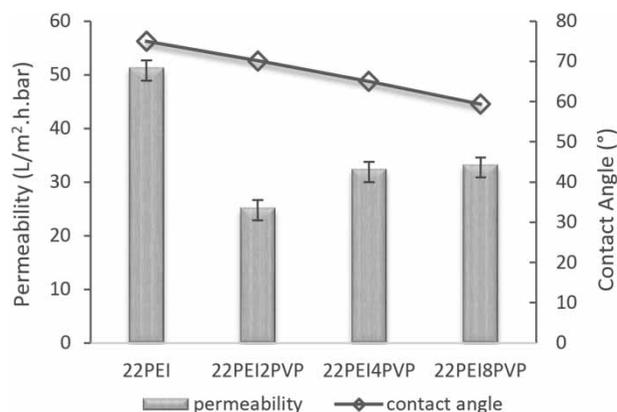


Figure 2 | Permeability and contact angle results.

RESULTS AND DISCUSSION

As seen in [Figure 2](#), the adding of PVP decreased the pure water permeability. However, the permeability of membranes increased with the increasing doses of PVP. This may be due to the fact that PVP is not very well dispersed in PEI. The permeability of the plain PEI membrane was the highest, but among the PVP-added ones the PEI 8PVP had the highest. The permeability of the PEI 2PVP membrane was about 23 L/m² h bar while it was 32 L/m² h bar for PEI 4PVP and 33 L/m² h for PEI 8PVP membranes.

The contact angles decreased with the adding and also with the increasing doses of PVP. This means that the membranes became more hydrophilic with the increasing doses of PVP. [Zhao et al. \(2011\)](#) reported that with the addition of PVP to the membrane casting solution, extra PVP would be washed away during the formation of the membrane. This PVP loss increased the hydrophilicity of the membrane ([Zhao et al. 2011](#)). As the concentration of the main polymer in the membrane solution decreases, a reduction in contact angle also occurred ([Ochoa et al. 2003](#)).

The porosity results for the membranes were close to each other, as shown in [Figure 3](#). But it is possible to say that it generally showed an increasing trend with increasing PVP concentration, which may be interpreted as an indication of increase in hydrophilicity as well as increase in number of pores of the membranes. As the molecular weight of PVP used in the study was lower than the molecular weight of the PEI polymer, as the percentage of PVP increased and the percentage of PEI decreased in the

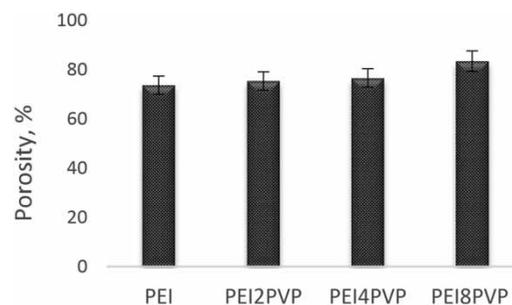


Figure 3 | Porosity results of membranes.

membrane solution, an increase in the porosity of the membrane occurred ([Güneş-Durak et al. 2018](#)).

As is clearly seen from the images in [Figure 4](#), the membranes have an asymmetric structure consisting of an intense upper layer as outer layer and air surface, and a porous sublayer. The outer layer acts as the separation layer. The sub-layer has finger-like gaps and the near-sub-surface layer has large gaps ([Ma et al. 2012](#)). For evaluating the effect of PVP, [Figure 4\(a\)–4\(d\)](#) is compared and is possible to say that the finger-like pores and pores located in the sub-layer expanded with increasing PVP concentration.

It is seen in [Figure 5](#) that there are many peaks at different wavelengths in the FT/IR spectrum of pure and PVP-added PEI membranes. Each wavelength represents organic bonds and groups on the membrane. When FT/IR spectra of the PEI membrane are taken into account, typical imide carbonyl asymmetric and symmetric stretches of characteristic imide groups are observed at 1,777 cm⁻¹ and 1,718 cm⁻¹, C-N stretching and bending at 1,355 cm⁻¹ and 742 cm⁻¹, and a C-O-C aromatic ether group at 1,235 cm⁻¹ wavelength ([Le-Clech et al. 2006](#)). C-H stretching due to CH₃ at 2,969 cm⁻¹ wavelength is observed.

Inorganic pollutants are a group of inorganic substances that accumulate on the membrane surface or pores. Iron is one of these pollutants. The formation of membrane contamination of these pollutants is due to pH change and oxidation ([Iorhemen et al. 2016](#)).

Ferrous iron removal efficiencies of membranes are given in [Figure 6](#). In this study, the membrane module was submerged in an aeration tank. In this process, Fe, which is in the form of Fe²⁺ in the aeration tank where the membrane is located, is oxidized and transformed into Fe(OH)₃ flocs. Fe(OH)₃ has a catalytic effect on the oxidation of ferrous

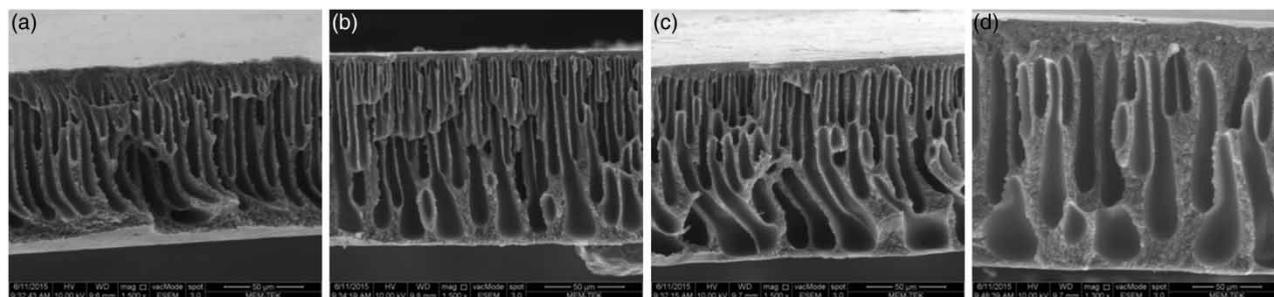


Figure 4 | SEM images of (a) plain PEI membrane, (b) 2 wt% PVP PEI membrane, (c) 4 wt% PVP PEI membrane, (d) 8 wt% PVP PEI membrane.

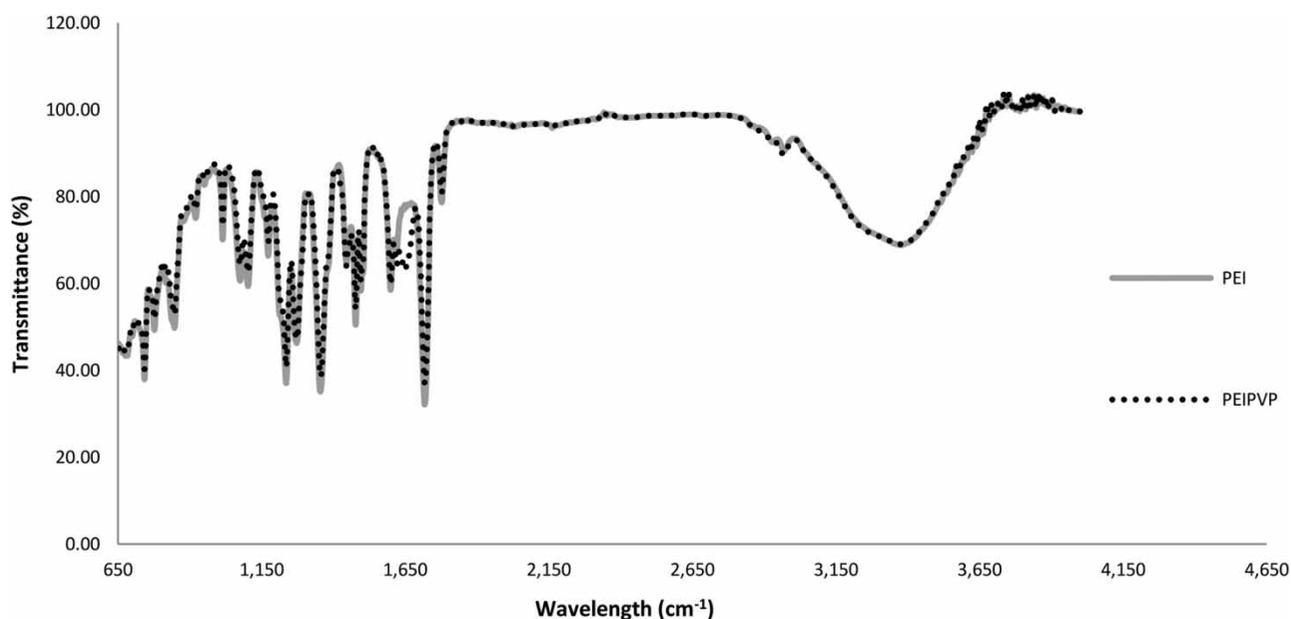


Figure 5 | FT/IR spectrum of PEI and PEI PVP membranes.

iron so that the oxidation is faster (Tüfekci & Sarkaya 1996). Significant iron removal efficiencies were obtained at a working pH of 8–8.5 as seen in Figure 6. $\text{Fe}(\text{OH})_3$ flocs increased

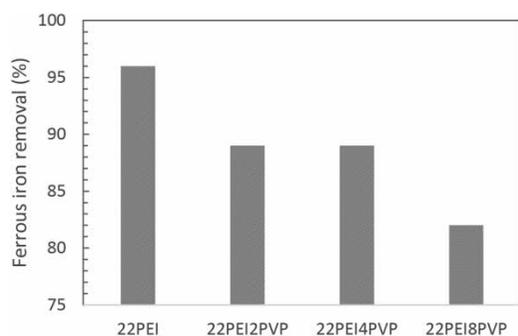


Figure 6 | Ferrous iron removal efficiencies (pH = 8.5, temperature = 25 °C, alkalinity = 2×10^{-2} eq/l and $p\text{O}_2 = 0.21$ atm.).

Fe^{2+} removal efficiencies by adsorption/surface oxidation. Also these flocs were bigger for passing through the membrane pores and so were adsorbed onto the membrane surface and formed a cake layer that acted as a second filter layer. As a result membrane removal efficiency increased, and also it can be said that iron oxide reduces the pressure in the membrane thereby reducing the fouling.

The highest removal was achieved via pristine PEI membrane while PVP addition decreased the efficiency similarly to the study of Jasiewicz & Pietrzak (2013). Their results also showed that the highest iron ion removal efficiency was achieved with the lowest content of PVP membrane (Jasiewicz & Pietrzak 2013). In this study, the lowest ferrous iron removal efficiency was 82% and the highest was 96%. All the results are also high and acceptable. The results

showed that the produced PEI membranes are effective for ferrous iron removal which means that they can be used for water treatment.

As PVP is used as a pore-forming polymer in phase inversion methods, pore size and number of pores increase in a membrane with increasing PVP content. Accordingly, ferrous iron could not be sufficiently retained by the membranes and there was a reduction in the removal efficiency.

CONCLUSION

The present work was aimed at investigating the effects of PVP concentration on PEI polymeric membrane performance, structure and formation. Flat sheet membranes were prepared successfully by using PEI polymer and PVP as a pore-forming agent and were characterized and compared. The results showed that PVP addition did not enhance the permeability of PEI polymeric flat sheet membranes. But with increasing doses of PVP the permeability of the membranes increased while the addition and the increasing doses decreased the contact angles and increased the porosity of the membranes. With the addition of PVP, nearly hydrophobic membranes became hydrophilic. All the membranes were found to have asymmetric structure as seen from SEM images. Membranes were also tested for water treatment and all membranes showed promising results in terms of ferrous iron removal. A submerged membrane process was used for iron removal. Very high removal efficiencies were obtained by the occurrence of adsorption, oxidation and filtration processes together in the submerged membrane process used for iron removal.

The results showed that these PVP-added and plain membranes have potential to be used in water treatment. PEI polymer is not preferred for water treatment by researchers generally, but the present work showed that this type of polymeric membrane can be used as an ultrafiltration membrane for water treatment applications.

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