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**Original paper**

# Purification performance evaluation of licorice aqueous solution using modified nanofiltration membranes

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**ABSTRACT**

The filtration performance of coupling modified polyethersulfone (PES) membrane by coupling diazonium reaction and 25 wt.% aniline modified polyethersulfone (APES /PES) blended membrane by radically diazonium reaction for treating of licorice aqueous solution was verified systematically and compared to bare NF PES membrane. The effect of operational pressure and cross-flow velocity on permeation flux and rejection were evaluated. All experiments were employed in a lab scale cross-flow filtration equipment with effective area of 40 $cm^2$. The applied operational pressure and cross-flow velocity were diverse from 6 to 12 bar and 0.5 to 2.5 cm/s respectively. The obtained results of rejection for licorice aqueous solution were between 84.4% to 99.2%. The durability and antifouling performance of membranes were assessed through long-term filtration of licorice aqueous solution.

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## 1. Introduction

Nowadays, membrane separations, as a green separation technology has been quickly developed in various separation process (Li et al. 2014; Hou et al. 2015, Zhang et al. 2016). Among different types of membrane, nanofiltration membranes with having incomparable properties such as narrow pore size distribution for achievement of high selectivity, high surface charges, highly porous and thin structure for assurance of favourable permeability attracted attention (Campbell et al. 2014; Shao et al. 2013; Shao et al. 2014; Shi et al. 2006; Szekely et al. 2014). Owing to existence of aforesaid characteristics, nanofiltration membranes plays a vital role in the separation processes. In addition to, NF membranes possessed special benefits such as high flux, low energy consumption, high rejection of divalent salts and cost-effective in compared to other membranes process (Hilal et al. 2004; Luo et al. 2013; Van der Bruggen et al. 2008). Hence, NF contained an outstanding exploit in desalination (Huang et al. 2011), dye rejection (Chidambaram et al. 2015), food industry and water purification (Luo et al. 2010).

However, polymeric membranes had some impediment involving low-grade thermal and chemical resistance, physical aging and fouling phenomenon (Xu et al. 2006). Therefore, to develop better nanofiltration membranes with superior antifouling capability, further studies have to focus on the surface modification methods such as coating (Zhang et al. 2015), vacuum-assisted assembly (Han et al. 2013), co-deposition (Lv et al. 2015), interfacial polymerization (Akbari et al. 2016; Fan et al. 2014; Zhang et al. 2013) and incorporation of nanoparticles (Dong et al. 2016; Vatanpour et al. 2012; Zinadini et al. 2014; Rajabi et al. 2015).

Licorice as one of the popular conventional herbal medicine, that was grown wild has been utilized in many countries especially China and Iran. Liquiritin (LQ) and glycyrrhizic acid (GA) are the main bioactive ingredients of liquorice. Pharmacological studies indicated that, GA possessed anti-oxidant, anti-inflammatory and anti-viral activity (Kondratenko et al. 2005; Obolentseve et al. 1999; Michael et al. 1995; Tolstikov et al. 1998). In addition to, it is worth noting that, GA has some clinical applications in the therapy of ulcer, kidney, liver, bronchitis, sore throat and spleen. Due to aforementioned preferences, GA extraction from the licorice aqueous solution is very important and is investigated by scientists studying over worldwide. The diverse separation procedures e.g. crystallization, high performance liquid chromatography, foam separation, adsorption and solvent extraction have been applied for GA recovery. However, most numerous of these procedures had some drawbacks such as expensive, low recovery and long-time consumption.

The leading goal of radically and coupling modification was flux increment and fouling mitigation of the nanofiltration PES membranes using diazonium chemistry. The purpose of this paper was systematically evaluation of the purification efficiency of bare and modified NF PES membranes using two different procedures of diazonium- induced grafting. Licorice aqueous solution was selected as a model foulant. The influence of effective key factors such as operational pressure and cross-flow velocity on the purification performance of licorice aqueous solution with calculation of permeate flux and rejection under various conditions were analysed. Long-term purification performance of coupling modified PES membrane and 25 wt.% APES/PES embedded membrane was investigated with calculation of flux reduction and compared to original NF PES membrane.

## 2. Materials and methods

### 2.1. Materials

Polyethersulfone (PES Ultrason E6020P) was bought from, BASF Company, Germany. The solvent of N, N-dimethylacetamide (DMAc) and the Polyvinylpyrrolidone (PVP) as pore former were obtained from, Merck. The atmospheric oxidized dark brown aniline and 4, 4-diaminodiphenyl sulfone were applied for diazonium-induced grafting processes. Hydrochloric acid 37%, iron powder and Sodium nitrite 97% were applied as received. Ultrapure water was utilized during experiments. Licorice powder was acquired from Parzhak Co., Iran.

### 2.2. Preparation of bare nanofiltration PES membranes

The flat sheets of original NF PES membranes were fabricated by phase inversion method. 20 wt. % PES and 1wt.% PVP were dispersed in certain amount of DMAc for preparation of casting solution. The resulted casting solution was kept in continuous stirring for 24 h for

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attainment of homogenous solution. Then, the dope solution was casted on a clean glass plates with a 150µm gap using self-made casting knife and promptly immersed in a coagulation bath of distilled water. After soak of obtained membrane in fresh water for 24h, the resulted membranes dried at room temperature (Zinadini et al. 2014).

### 2.3. Preparation of coupling-modified NF PES membranes

Initially a specified quantity of 4, 4- diaminodiphenyl sulfone (10 mmol) was dispersed in deionized water (40ml) by an addition of 100 ml HCl 0.5M. Subsequently, 10 mmol Sodium nitrite was dissolved in 15 ml deionized water. After acquisition of temperature of 5 ºC, the sodium nitrite solution was added gradually at diaminodiphenyl sulfone solution. Afterwards, the fabricated membrane was dipped in the resulted solution with temperature of 5 ºC for 240min. lastly, the coupling-modified PES membrane washed several times with ultrapure water and ethanol and dried at 70 ºC.

### 2.4. Preparation of 25 wt.% APES/PES embedded membrane

Initially aniline modified PES (APES) were synthesized by diazonium chemistry. For this purpose, specified quantity of air oxidized dark brown aniline (10 mmol) was dissolved to 37 ml of distilled water through an addition of 70 ml HCl 0.5M. Thereafter, sodium nitrite (16.6 mmol) was added to distilled water (10 ml). The sodium nitrite solution was added gradually at the solution of aniline at temperature of 5 ºC and 7g PES was dissolved to resulted solution and iron powder (700 mg) was sprinkled at obtained solution. Lastly, APES washed with distilled water and ethanol for several times and dried at 70 ºC. The 25 wt.% APES/PES blend membrane were prepared by phase inversion method (section 2.3).

### 2.5. Membrane performance

The permeate flux and rejection percentage of membranes were done in cross-flow filtration cell with effective membrane area of 40 $cm^2$. The permeate flux can be calculated from,

$$J = \frac{M}{A \cdot \Delta t} \tag{1}$$

where J, M, A and Δt are permeation flux, the mass of permeate, membrane effective area and time interval respectively.

The licorice solution was selected as foulant model. Liquiritin, isoliquiritin and glycyrrhizin are main ingredients of the licorice aqueous solution.

The licorice solution rejection was determined by the following expression (Zinadini et al. 2014):

$$R(\%)=(1-\frac{c_p}{c_f})\times 100 \tag{2}$$

where $c_p$ is the licorice solution concentration in permeate and $c_f$ is the licorice solution concentration in feed.

## 3. Results and discussion

### 3.1. Transmembrane pressure effect

Fig.1 exhibits the impacts of operational pressure (initial flux levels) on permeate flux on original-PES, coupling-PES and APES/PES modified membranes. For original NF PES membrane by enhancing the operational pressure from 6 to 12 bar, permeation flux was raised from 15 to 38.7 kg/$m^2$. h. For coupling modified NF PES membrane as the operational pressure was increased from 6 to 12 bar, permeation flux was improved from 44.6 to 75.1 kg/$m^2$. h. Increment of transmembrane pressure from 6 to 12 bar for 25 wt.% APES/PES blend membrane incur augmentation of permeation flux from 32 to 56.4 kg/$m^2$. h. As can be seen clearly, the modified membranes had higher initial flux levels than original NF PES membrane. It can be attributed to attendance of numerous number of hydrophilic groups induced by diazonium chemistry in modified membranes. The enhancement of permeation flux through the additional driving force (operational pressure increment) is forecasted. Although, increment of transmembrane pressure can raise the flux permeation. However, the higher initial flux permeation at greater operational pressure was consistent with more fouling and flux diminution. In fact, a high operational pressure supplies desirable conditions for fouling. Concentration polarization and fouling emerge to be essential factors in flux diminution (Belkhouche et al. 2009; Sohrabi et al. 2010). The observed results are accordant with the results of previous fouling studies by other researcher (Hong et al.1997; Tang et al. 2007; Wang et al. 2011).

The impact of transmembrane pressure on rejection of original, coupling and APES/PES modified membranes was tabulated in Fig. 2. The rejection of original and modified membranes under applied operational pressures is various between 84.4% and 99.2%. The results revealed that, the rejection was improved by increment of applied operational pressure and tends to be steady. It could be justified by fouling. Gradually enhancement of rejection can be related to the sediment of organic molecules on the membrane surface, that incur secondary barrier formation which precludes transit of other molecules via the membrane.

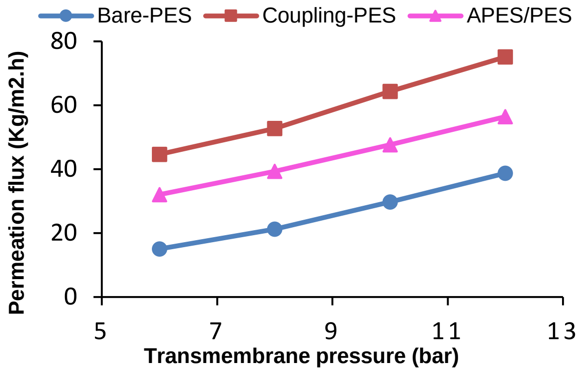


**Fig.1.** Impact of transmembrane pressure on permeation flux of membranes (v=1.5 cm/s, PH = 5.3).

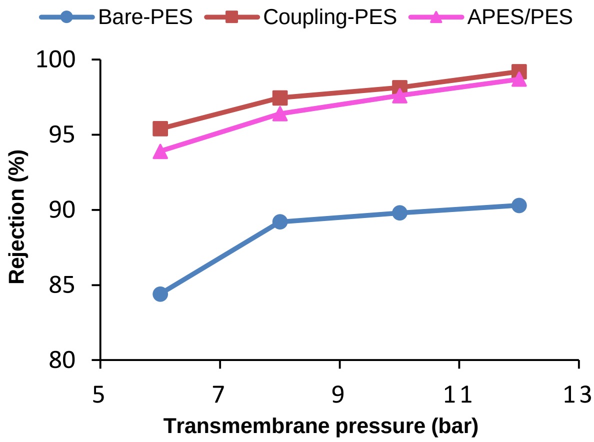


**Fig. 2.** Impact of transmembrane pressure on rejection of membranes (v=1.5 cm/s, PH = 5.3).

### 3.2. Efficacy of cross-flow velocity

Fig. 3, represents the impacts of cross-flow velocity on the permeation flux of original, coupling and APES/PES modified membranes. As observed the permeation flux was elevated with increment of the cross-flow velocity. For example, with increasing cross-flow velocity from 0.5 to 2.5 cm/s the permeation flux was enhanced from 8.3 to 18.42 kg/$m^2$.h, from 29.91 to 47.95 kg/$m^2$.h and from 19.65 to 34.87 kg/$m^2$.h for original, coupling and APES/PES modified membranes respectively. It is worth noting that, the cross-flow velocity possesses a major efficacy on concentration polarization. Factually, high cross-flow velocity incurs turbulence [46] and reduces the concentration polarization, that ultimately, leads to improvement of permeate flux.

The rejection of original, coupling and APES/PES modified membranes under applied cross-flow velocity is diverse between 83.8 % and 95.98 % (Fig.4). As can be seen the increment of cross-flow velocity leads to improvement of membranes rejection, that might be



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associated with subtraction of concentration polarization. In fact, lower concentration polarization in the proximity of the surface of membranes causes lower transit via the membrane or id est higher rejection. Similar observation has been reported by Xu and co-workers (Xu et al .2005).

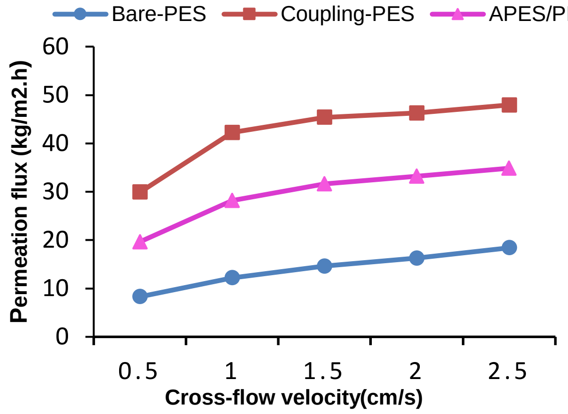


**Fig3.** Impacts of cross-flow velocity on permeation flux of membranes (p=6 bar, PH = 5.3).

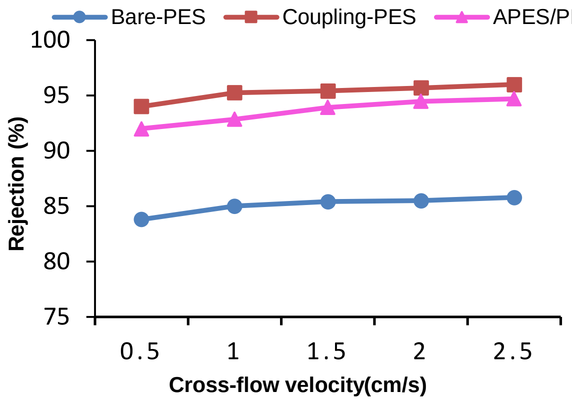


**Fig4.** Impacts of cross-flow velocity on rejection of membranes (p=6 bar, PH = 5.3).

### 3.3. Operation time efficacy

In order to membranes efficiency verification (selectivity and productivity) the licorice aqueous solution was forced to permeate through the original, coupling and APES/PES modified membranes for 4h. The results of flux profile against time are indicated in Fig5. During long-term filtration of the licorice aqueous solution, almost constant permeate flux was seen for coupling modified membrane and 25 wt.% APES/PES blend membrane. For coupling modified membrane initiate and terminal permeation flux of licorice aqueous solution was 45 and 41.8 kg/m$^2$.h respectively. After 4h filtration, the coupling modified membrane shown a lower flux reduction (7.12%) than the original membrane (31.43%).

In addition to, 25 wt.% APES/PES blend membrane exhibited 10.65% overall flux loss during long-term filtration. It could be justified by diazonium treatment, that causes improvement of membranes hydrophilicity. Membrane hydrophilicity increment incurring the prominent mitigation of licorice adsorbed amount on the membrane surface and consequently, considerable diminution of flux reduction tends of modified membranes through diazonium procedures.

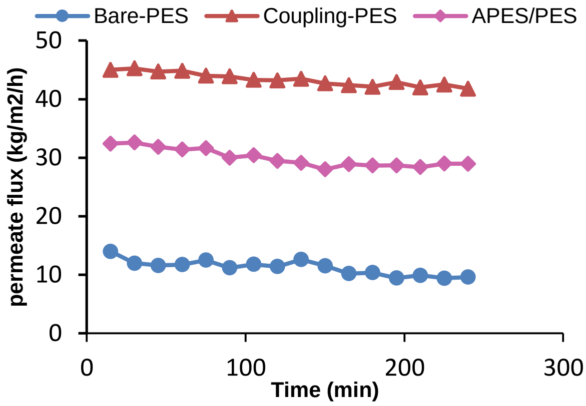


**Fig. 5.** The long term performance of the membranes at optimum condition (p=6 bar, v=1.5 cm/s, PH = 5.3).

### 3.4. Conclusions

The purification of licorice aqueous solution via original-PES, coupling modified-PES and 25 wt.% APES/PES blend membranes was performed. The results recommended that, the purification of licorice aqueous solution could be impressively carried out with utilization of both coupling modified PES and APES/PES blend membranes in comparison of original-PES membrane. The permeation flux was enhanced by enhancement of operational pressure. Membrane compression and fouling outwardly incurred a mitigation in permeate flux. For all of membranes, the rejection was increased with enhancing the operational pressure and cross-flow velocity.

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