A Comparison Study for The Performance of Polyethersulfone Ultrafiltration Mixed Matrix Membranes in The Removal of Heavy Metal Ions from Aqueous Solutions

Haider N. Alfalahy and Sama M. Al-Jubouri

Department of Chemical Engineering, College of Engineering, University of Baghdad, Aljadria, Baghdad. Postcode: 10071, Iraq.

Abstract

Polyethersulfone (PES) ultrafiltration membrane blending NaX zeolite crystals as a hydrophilic additive was examined for zinc (II) and lead ions Pb (II) removal from aqueous solutions. The effect of NaX zeolite content on the permeation flux and removal efficiency was studied. The results showed that adding zeolite to the polymer matrix enhanced the permeation flux. The permeation flux of all the zeolite/PES matrix membranes was higher than the pristine membrane. No significant improvement was observed in the removal of Zn (II) ions using all prepared membranes as the removal percentage did not raise above 29.2%. However, the removal percentage of Pb (II) ions was enhanced to 97% using a membrane containing 0.9%wt. zeolite. Also, it was found that this membrane has a higher ion exchange capacity than the other prepared membranes. Two isotherm models (Langmuir model, and Freundlich model) were employed in the analysis of the ion exchange equilibrium data. The experimental data best fitted the Langmuir model with R² of 0.889 than the Freundlich model.

Keywords: Mixed matrix membranes; NaX zeolite; lead ions; zinc ions; ultrafiltration; ion exchange capacity

Received on 22/03/2022, Accepted on 03/05/2022, published on 30/06/2022

https://doi.org/10.31699/IJCPE.2022.2.3

I- Introduction

Water is one of the most important natural resources on the earth. It has been found that one of the main reasons for water pollution are human and industrial activities such as metal plating, mining activities, fertilizer industries, etc. which create potential sources of toxic heavy metal ions in the aquatic environment [1], [2]. Zn (II) and Pb (II) are among the toxic heavy metals found in industrial wastewater [3]. Zn (II) can cause irritability, muscle stiffness, loss of appetite, and nausea, while Pb (II) causes anemia, permanent brain damage, kidney dysfunction, and different symptoms related to the nervous system. Therefore, it’s necessary to treat industrial wastewater from these toxic metals before discharging into ecosystems [4], [5].

Chemical precipitation and coagulation–floculation have been widely utilized to treat industrial wastewater. However, the main drawbacks associated with applying these techniques are sludge production, the unfeasibility of direct reusing heavy metals, and the consumption of excessive chemicals [6].

Other treatment methods such as adsorption and ion exchange are inexpensive and effective for treating the contaminated effluents containing only low concentrations of contaminants [7], [8], [9]. Using membrane techniques for environmental protection has several advantages, including eliminating the need for chemical materials, reducing energy consumption, continuous separation mode, separation at moderate environmental conditions, operating in hybrid processes (easily connected to other unit processes), and working as a modular system (possibility of rising the capacity) [10].

The main factors controlling the flow rate and the heavy metal removal efficiency across a membrane are the characteristics of the membrane, such as the porosity, pore size, pore size distribution, surface charge, membrane thickness, degree of membrane hydrophilicity, and presence of functional groups that assist the separation process and solution flow [11], [12].

Polyethersulfone (PES) has beneficial properties, including high chemical, mechanical, thermal, and hydraulic stability, good processing, acceptable heat aging resistance, and film-forming characteristics make it an excellent polymer for the synthesis of UF membrane [13].

However, one of the main drawbacks of the PES ultrafiltration membrane in water treatment is membrane fouling, which can reduce the water flux either permanently or temporarily [14]. Fouling occurs when pollutants deposite on the surface of a membrane or inside the pores of a membrane, resulting in decrease the efficiency of the membrane.
The PES ultrafiltration membrane is used in wastewater to eliminate prevalent and harmful water matters, such as colloids, pathogens, proteins, and viruses but it is less able to remove heavy metal ions [15], [16]. Zeolites have demonstrated their ability to improve membranes’ water flux, permeability, and antifouling properties, as reported in several studies [17]–[19].

This study identified the need to develop a PES ultrafiltration membrane through fabrication of MMM’s by adding zeolite fillers to the casting solution of a PES UF membrane. The resultant membrane holds the favorable properties of nanofiltration membranes in the removal of heavy metal ions such as providing higher separation efficiency and antifouling performance. Besides, they hold some preferable properties of ultrafiltration membranes such as consuming less energy due to operation at low pressure, and thus low operation cost.

The equations and models that were used to conduct this work consist of the equations that were used to collect the data including the permeate flux, ion exchange capacity, and the ions rejection; and the equations presenting the results of isotherms including the Langmuir and Freundlich isotherm models. The permeate flux (J) was calculated using Equation 1 [20]:

$$J = \frac{V}{A \times t}$$  \hspace{1cm} (1)

Where: \( J \) and \( V \) are the permeate flux (L/m².h) and the volume of permeate (L), respectively. \( A \) and \( t \) are the effective area of membrane (m²) and the run time (h).

The remaining concentration of heavy metal ions in permeate was determined by atomic absorption spectroscopy analysis. This analysis was conducted using atomic absorption spectrometer device (model: USA 5000). The metal ions rejection (\( %R \)) was calculated using Equation 2 [21]:

$$%R = \left(1 - \frac{C_e}{C_o}\right) \times 100$$  \hspace{1cm} (2)

The ion exchange capacity results were calculated using Equation 3 [22]:

$$q_e = (C_i - C_e) \times \frac{V}{W}$$  \hspace{1cm} (3)

Where: \( q_e \) (mg/g) is the amount of Pb (II) ion removed per a unit mass of ion-exchange membrane, \( V \) (l) is the solution volume, \( W \) (g) is the weight of membrane, \( C_i \) (mg/l) and \( C_e \) (mg/l) are the concentrations of Pb (II) ions at \( t = 0 \) and \( t = \text{equilibrium time (min)} \), respectively.

The Langmuir and Freundlich isotherm models were used to elucidate the ion-exchange behavior of the studied membranes. The correlation factor (R²) was used to assess the validity of the model with respect to the experimental data. The maximum value of R² indicates a better fit of the model to the experimental data [22]. The Langmuir isotherm model describes capturing of Pb (II) ions as by monolayer sites at a homogenous surface. This model is expressed using Equation 4 [22], [23]:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}}$$  \hspace{1cm} (4)

Where: \( q_e \) (mg/g) is the amount of Pb (II) ion removed per a unit mass of ion-exchanger membrane \( C_e \) (mg/l) is the equilibrium concentration of Pb (II) ions. \( q_{max} \) (mg/g) is the Langmuir constant and it is a maximum ion exchange capacity of Pb (II) ions, \( K_L \) (l/mg) is a Langmuir constant relating to the free energy of ion-exchange corresponds to the affinity among the Pb (II) ion and membrane surface [22].

The Freundlich isothermal model describes capturing of Pb (II) as an ionic exchange by multilayer sites at a heterogeneous surface. This model is expressed in a linearized form using Equation 5 [22], [24]:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

Where: \( K_F \) (mg/g) represents the Freundlich constant denoting the ion exchange capacity, and \( 1/n \) (unitless) represents the Freundlich constant denoting the intensity of the reaction and energy heterogeneity. A larger value of \( K_F \) indicates good ion exchange efficiency for the M3 membrane, whereas if the value of \( 1/n \) is less than 1, it represents a favorable ion exchange [22], [25].

2- Experimental

2.1 Experimental procedure of UF separation

The compositions of the used membranes in this study are mentioned in Table 1. The synthesis procedures of these membranes, characterization methods and their results were reported in [26].

<table>
<thead>
<tr>
<th>Membrane sample code</th>
<th>N. dimethyl formamide (%wt.)</th>
<th>PES (%wt.)</th>
<th>Zeolite (%wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>M1</td>
<td>79.7</td>
<td>20</td>
<td>0.3</td>
</tr>
<tr>
<td>M2</td>
<td>79.7</td>
<td>20</td>
<td>0.6</td>
</tr>
<tr>
<td>M3</td>
<td>79.1</td>
<td>20</td>
<td>0.9</td>
</tr>
<tr>
<td>M4</td>
<td>78.8</td>
<td>20</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The performance of the membranes was examined by a crossflow UF system in which the feed stream flow tangentially to the membrane surface. The effective area of each flat sheet membrane piece was 16.24 cm². All UF experiments were conducted at an operating pressure of 1.6 bar and feed flow rate of 0.75 L/min. The efficiency of the prepared membranes to obtain high flux was studied using using Zn (II) and Pb (II) ions solutions. The results of permeate flux were compared with the flux of a pristine membrane (PES) and matrix membranes (zeolite/PES). The efficiency of the prepared membranes to obtain the highest rejection percentage of heavy metal ions with good flux was studied using Zn (II) and Pb (II) ions solutions. Each membrane sample was pre-compacted for at least 45 min until the flux stabilized at 1.6 bar.
Then, the filtration experiments were conducted at steady pressure of 1.6 bar and a feed flow rate of 0.75 L/min. The readings of permeate flux were taken at intervals of 15, 30, 45, 60, 90, and 120 min.

The effect of changing NaX zeolite concentrations on the ion exchange capacity of zeolite embedded in the prepared MMM’s to remove Pb (II) ions was studied at the equilibrium time. The ion exchange isotherms were examined using M3 membrane for the experiments performed at different initial Pb (II) concentrations of 50, 100, 150, and 200 ppm.

3- Results and Discussion

3.1. Effect Of NaX Zeolite Content on the Permeation Flux

Fig. 1 and Fig. 2 show the results of permeate flux for a pristine PES membrane and MMM’s using 50 ppm of Zn (II) and Pb (II) solutions at different times. Figure 1 shows that permeate flux of Zn (II) solution significantly improved by zeolite/PES membranes. It can be seen that the permeate flux of pristine PES membrane was 6 L/m².h and increased to 180, 138, 44, and 61 L/m².h for M1, M2, M3, and M4, respectively. However, the water flux of M3 and M4 was less than M1 and M2. As early mentioned, this can be attributed to the reduction in porosity of the membrane with increasing NaX zeolite content. The same behavior of MMM’s was obtained when they were applied for Pb (II) ions in the UF (see Fig. 2).

Also, Fig. 1 and Fig. 2 show that the permeate flux slightly decreased with increasing the operation time for MMM’s. This decline in the permeate flux can be attributed to increase the aggregations of heavy metals on the membrane surface (cake-layer) leading to blocking the membrane pores.

This layer caused shrinkage in the pore size that leads to decreasing the permeate flux. The same behavior was obtained by Abdullah, (2021), [13].

Fig. 1. The effect of NaX zeolite loading on the permeate flux. (Experimental conditions: Zn (II) ions concentration 50 ppm, transmembrane pressure of 1.6 bar)

Fig. 2. The effect of NaX zeolite loading on permeate flux. (Experimental conditions: Pb (II) ions concentration 50 ppm, transmembrane pressure of 1.6 bar)

3.2. Effect of NaX zeolite content on the Zinc (II) and Lead (II) removal

Fig. 3 and Fig. 4 show the effect of the NaX zeolite loadings in the casting solution of PES-based membrane on the Zn (II) and Pb (II) ions rejection from solutions containing 50 ppm of Zn (II) and Pb (II) ions. Figure 3 shows obtaining of low rejection of Zn (II) ions. The rejection did not exceed 30% for all the prepared membranes. On the contrary, Figure 4 shows obtaining of higher rejection of Pb (II) ions. As it is known that the separation process is affected by the exchange with sodium ions at the active sites within the matrix membrane and by the sieving process which depends on the ionic radius relative to pore size.

The ionic radius of Pb (II) ion (119 pm) is larger than the ionic radius of Zn (II) ion (74 pm). This means that Zn (II) ion has larger hydration radius than Pb (II) ion, therefore, Zn (II) cations possessed more tendency than Pb (II) cations to adhere with water molecules and pass through the membrane pores together with water molecules in the permeate. Consequently, Pb (II) ions rejection was higher than Zn (II) ions rejection. Similar behavior was obtained by Hadi et. al, (2020) and Yurekli, (2016), [12], [29].

Fig. 4 shows that the highest rejection of Pb (II) ions was 97% by M3 membrane containing 0.9 %wt. zeolite and it was selected to conduct the next studies. This result can be attributed to the uniform distribution of NaX zeolite crystals which provides selective voids (active sites) for capturing Pb (II) ions.

However, increasing NaX zeolite above 0.9 %wt. reduced the rejection of Pb (II). This is due to agglomeration of zeolite crystals which resulted in non-homogenous distribution within the matrix membrane which in turn led to the generation of non-selective voids between nanoparticles and the polymer. Therefore, the water flux increased but the rejection of Pb (II) ions decreased. This behavior is in agreement with Sadiq et. al, (2020), [30].
According to the UF results obtained using the prepared MMMs’ above, the ion-exchange capacity of the zeolite incorporated in the prepared MMMs’ will be examined by conducting ion-exchange experiments for Pb (II) ions solutions.

Fig. 3. Effect of NaX zeolite content on Zn (II) ions rejection, (Experimental conditions: Zn (II) ions concentration of 50 ppm, transmembrane pressure of 1.6 bar)

3.3. Ion Exchange Capacity

The ion exchange capacity of MMM’s increased with increase the number of active sites within the matrix membrane. Figure 5 shows that the ion exchange capacity increased with increasing the content of NaX zeolite added to the casting solution.

The value of ion exchange capacity was 1380 mg/g for M1 and increased to 1937.1 mg/g for M2. While, the maximum value of ion exchange capacity (3637.5 mg/g) was obtained for M3. The ion exchange capacity increased due to increasing the concentration of NaX zeolite added to the casting solution forming membranes with more available active sites for capturing of Pb (II) ions [31].

However, the ion exchange capacity decreased when the concentration of NaX zeolite increased to 1.2 %wt. which is possibly due to agglomeration of crystals that reduced the active sites within a membrane. The same behavior was observed by Zhang et. al, (2018), [32].

Fig. 5. The ion exchange capacity of the membranes used for Pb (II) ions removal, (Experimental conditions: Pb (II) ions concentration of 50 ppm, pH of 6, feed temperature of 25 °C, transmembrane pressure of 1.6 bar)

3.4. Ion Exchange Isotherm

Fig. 6 (A) and (B) show the plots of the Langmuir isotherm model and Freundlich isotherm model. The correlation factor ($R^2$) of Langmuir and Freundlich isotherms are presented in Table 2. It can be seen that the removal of Pb (II) ions by M3 is best fitted with the Langmuir isotherm model ($R^2$ value of 0.8809) in comparison with Freundlich isotherm model with $R^2 = 0.4798$.

This result indicates occurring of homogeneous ion exchange (monolayer sites) on the zeolite crystals occupying the upper surface of the ion exchanger membrane. These results conflict with the results obtained by zeolite/carbon used for heavy metals removal [25].

Referring to this previous study, the Freundlich isotherm model successfully agreed with the experimental data of manganese (II) ion removal by the ion-exchange process and was more fitted than the Langmuir isotherm model.

The obtained results can be attributed to as difference in the surface properties of the ion exchanger material. In the current study, PES support was incorporated with zeolite, whereas in the abovementioned previous work, the support was not used in the removal process. Therefore, in the current study, PES has an effect in the removal process as a result of the electrostatic attraction force besides the zeolite which favors the monolayer sites uptake on the upper layer of the M3 membrane.

The Langmuir constant $K_L$ and the maximum ion exchange capacity $q_{max}$ were calculated from the slope (see Figure 6 .A) and presented in Table 2. The Langmuir monolayer ion exchange capacity ($q_{max}$) was 10000 mg/g, the Langmuir equilibrium constant, ($K_L$) was 0.0555 l/mg.

Regarding the magnitude of Freundlich constants, $K_f$ (ion exchange capacity) and 1/n (reaction intensity) were estimated from the slop (see Fig. 6.B and Table 2). $K_f$ and 1/n were 4451.961 mg/g and 0.0914 respectively.
Table 2. Isotherm parameters for the Pb (II) ions removal by M3 membrane

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>q_{max} (mg/g)</th>
<th>K_L</th>
<th>R^2</th>
<th>K_f (mg/g)</th>
<th>1/n</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>10000</td>
<td>0.0555</td>
<td>4451.961</td>
<td>0.0914</td>
<td>0.4798</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. A) Plots of the Langmuir model B) Plots of the Freundlich isotherm model. (M3, pH of 6, and TMP of 1.6 bar)

4- Conclusions

In conclusion, the permeation flux of all matrix membranes (i.e., M1, M2, M3, and M4) was higher than that of the pristine PES membrane (M0). The highest rejection of Pb (II) ions was 97% by adding 0.9 %wt. of NaX zeolite for M3 membrane. However, the results showed all prepared membranes gave the same efficiency for Zn (II) ions removal. The maximum value of ion exchange capacity was of 3637.5 mg/g for the modified-membrane with 0.9 %wt. of NaX zeolite. Langmuir isotherm model is the best-fitted model compared with Freundlich isotherm model for describing the data of Pb (II) ions removal by M3 membrane.

References


دراسة مقارنة لإداء أغشية المصفوفة المختلطة للترشيح الفائق من البولي إيثير سلفون

في إزالة أيونات المعادن الثقيلة من المحاليل المائية

حيدر نزار عبد الأمير و سما محمد عبد الله

جامعة بغداد, كلية الهندسة, قسم الهندسة الكيميائية

الخلاصة

تم فحص غشاء الترشيح الفائق PES الذي تم مزجه مع بلورات زيولايت NaX كمادة محبة للماء لإزالة أيونات الزنك (II) والرصاص (II) من المحاليل المائية. تمت دراسة تأثير محتوى الزيولايت على تدفق التفاضل النافذية وكفاءة الإزالة. أظهرت النتائج أن إضافة الزيولايت إلى مصفوفة البوليمر عزز تدفق التفاضل النافذية. كان تدفق التفاضل النافذية لجميع أغشية مصفوفة زيولايت– PES أعلى من الغشاء الخالي من زيولايت NaX. لم يلاحظ أي تحسن كبير في إزالة أيونات الزنك (II) باستخدام جميع الأغشية المعدة. حيث أن نسبة الإزالة لم ترتفع فوق 29.2%. مع ذلك، تم تحسين نسبة إزالة أيونات الرصاص (II) إلى 97% باستخدام غشاء يحتوي على 0.9% بالوزن من الزيولايت. كذلك، وجد أن هذا الغشاء لديه قدرة تبادل أيوني أعلى من الأغشية الأخرى المعدة. تم استخدام نموذجين إيزوبيرم (نموذج لانجمير ونموذج فروندليش) في تحليل بيانات توازن التبادل الأيوني. تلامذ البيانات التجريبية نموذج لانجمير بشكل أفضل مع R2 عند 0.889 من نموذج فروندليش.

الكلمات الدالة: أغشية مصفوفة مختلطة, زيولايت NaX, أيونات الرصاص, أيونات الزنك, الترشيح الفائق, سعة التبادل الأيوني.