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Effect of preparation conditions on arsenic rejection performance of polyamide-based thin film composite membranes

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Abstract:

Herein, a polyamide-based thin film composite (TFC) membrane was fabricated for the removal of arsenic (As) from water. The polyamide thin film was synthesized through interfacial polymerization (IP) onto a polysulfone porous substrate. A Box-Behnken design of response surface methodology was used to investigate the effect of preparation conditions, including piperazine (PIP) concentration, trimesoyl chloride (TMC) concentration, and reaction time on the As rejection and permeate flux of the synthesized membrane. The separation performance of the prepared membranes from 15 designed experiments was conducted with an arsenate (Na_2AsHSO_4) solution of 150 ppm at a pressure of 40 psi and a temperature of 25°C. The analysis of variance revealed the regression models to be adequate. From the regression analysis, the flux and As rejection were expressed by quadratic equations as a function of PIP concentration, TMC concentration, and reaction time. It was observed that the PIP concentration, TMC concentration, and reaction time had a significant effect on the flux and As rejection of the polyamide membrane. Moreover, a strong impact from the interaction of PIP and TMC was also observed on rejection of the resulting membrane. Using the desirability function approach to analyse the regression model, the optimal preparation conditions of the polyamide membrane were a PIP concentration of 2.5 wt.%, TMC concentration of 0.11 wt.%, and reaction time of 40 sec. The membrane exhibited a good As rejection of 95%.

Keywords: **arsenic, composite, membrane, polyamide, thin film.**

Classification numbers: **2.2, 2.3**

Introduction

Inorganic arsenic is a well-known carcinogen and one of the most harmful chemical contaminants found in drinking water around the world. Long-term ingestion of arsenic from water and food can cause cancer and skin lesions. According to the WHO, approximately 50 countries have As content in their drinking water at a value higher than 10 µg/l, which is the recommended safety limit set by the WHO [1]. Water pollution by As in Vietnam is a serious concern with the As content in groundwater ranging from 0.1 to higher than 0.5 mg/l, which exceeds the WHO standard by 10 to 50-fold. There are numerous methods employed to reduce As from water, such as co-precipitation [2], adsorption [3], and membrane filtration i.e. reverse osmosis RO [4] and nanofiltration (NF) [5]. Among these, the NF membrane process has emerged as an efficient approach for As removal from water due to its high permeate flux, good quality freshwater, and low operating cost [6].

The modern NF membranes have a TFC structure that consists of an ultra-thin polyamide film over a microporous substrate. The separation performance of TFC NF membranes, in terms of permeability and selectivity, are directly correlated with the structural and physicochemical properties of the ultra-thin polyamide film [7]. The selective polyamide active layer is synthesized by the IP process at the interface of two insoluble solvents. In this IP technique,

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many parameters, such as the monomer concentrations, types of monomers, and reaction time, could affect the physicochemical properties and separation performance of the membrane [8-14]. To the best of our knowledge, previous investigations were conducted using only one factor at a time, where only one variable was changed at each experimental trial. Consequently, no correlation between parameters were observed and thus could not indicate the optimum condition.

In this work, a polyamide thin film was synthesized through interfacial polymerization onto a polysulfone porous substrate. The Box-Behnken design of response surface methodology was used to investigate the effect of influential preparation conditions, including PIP concentration, TMC concentration, and reaction time, on the As rejection and permeate flux of the synthesized membrane. The result of this study is expected to contribute to a deeper understanding of the influence of preparation conditions on the As rejection of the membrane and to provide valuable data for preparing PA-based NF membranes for As removal from water.

Materials and methods

Materials

Polysulfone porous support substrates (PS20) were provided by Dow-Filmtec (USA). Piperazine and trimesoyl chloride with a purity of 99% were received from Sigma-Aldrich (USA). Deionized (DI) water and hexane (99%) were used as solvents for the synthesis of the polyamide membranes. Arsenate (Na_2AsHSO_4) was purchased from Guangzhou Zio Chemical (China).

Methods

The polyamide thin film was hand-cast on the PS20 substrate through IP [12]. The polyamide-based TFC membrane was formed by immersing the PS20 support membrane in a PIP aqueous solution for 2 min. Excess PIP solution was removed from the support membrane surface using an air knife (Exair Corporation) at about 4-6 psi. The PIP saturated support membrane was then immersed into the TMC-hexane solution for 20-70 s. The derived membrane was held vertically for 2 min before it was immersed in 200 ppm NaClO for 2 min and then dipped in 1,000 ppm $Na_2S_2O_5$ solution for 30 s. Finally, tthe membrane was dipped in DI water for 2 min. Before the obtained membrane could be used for the experiments, it was immersed in a DI water container with the water regularly replaced.

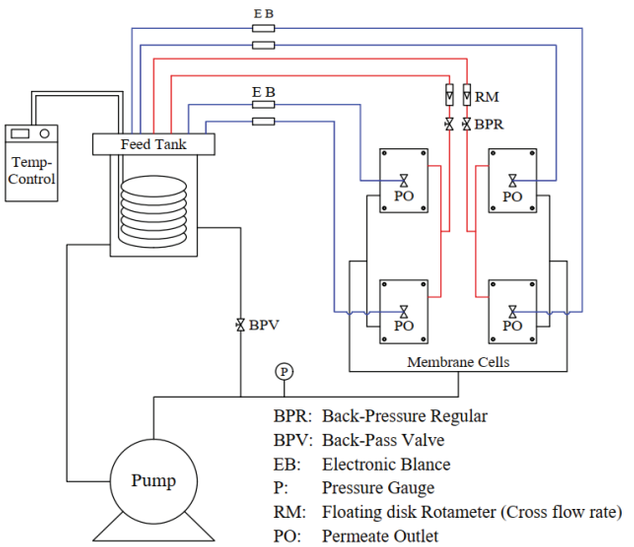

Fig. 1. Schematic illustration of the crossflow membrane process simulator.

The permeability of the synthesized membrane was evaluated for pure water and 150 ppb arsenate (Na_2AsHSO_4) aqueous solution using a custom fabricated bench-scale crossflow membrane process simulator (Fig. 1). The experiments were comprised of steps of compaction, equilibration, and cleaning under a fixed temperature of 25°C. First, DI water was filtered through the membranes at 45 psi for at least 6 h. After achieving a stable flux, the permeability of the membrane was determined by measuring the water flux under an applied pressure of 40 psi. Next, an arsenate solution with a fixed concentration of 150 ppb was filtered through the membrane at 40 psi. The flux was measured after the system performance was stable for at least 30 min. The concentration of As(V) in the feed and permeate solutions were determined via inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES, Horriba). The data of flux and arsenate rejection reported in this work were based on the average of three experimental runs that have an error lower than 5%. Water flux can be determined from permeate water flow rate as follows:

$$J(lm^{-2}h^{-1}) = \frac{Q_P}{A_m \times t} \quad (1)$$

where Q_P is the permeate water flow rate, A_m is the effective membrane area (0.0024 m^2), and t is the filtration time. The As(V) concentrations in the feed and permeate solutions were used to calculate the observed As rejection as shown below:

$$R_S(\%) = \left(1 - \frac{C_{permeate}}{C_{Feed}}\right) \times 100 \quad (2)$$

where $C_{Permeate}$ and C_{Feed} are the As concentration in feed and permeate sides, respectively.

Table 1. Actual and coded levels of independent variables.

Variables	Factor	Level		
	X_i	*Low (-1)*	*Middle (0)*	*High (+1)*
PIP concentration (wt.%)	X_1	1.0	2.5	4.0
TMC concentration (wt.%)	X_2	0.05	0.10	0.15
Reaction time (s)	X_3	20	45	70

Based on preliminary experiments, three preparation conditions including PIP concentration, TMC concentration, and reaction time were determined as the most essential parameters. Therefore, the PIP and TMC concentrations and reaction times were chosen as independent variables and designated as X_1, X_2, and X_3, respectively. Table 1 describes the actual values and coded levels of the preparation conditions, which were varied over three levels as high level (+1), middle level (0), and low level (-1), respectively.

Table 2. The Box-Behnken design and corresponding flux and As rejection.

Run number	PIP conc., X_1 (wt.%)	TMC conc., X_2 (wt.%)	Reaction time, X_3 (sec.)	Flux, Y_1 ($lm^{-2}h^{-1}$)	Rejection, Y_2 (%)
1	1.0	0.05	45	56.70	26.4
2	1.0	0.15	45	5.35	91.1
3	4.0	0.05	45	0.90	96.0
4	4.0	0.10	70	0.85	92.3
5	2.5	0.05	20	28.85	60.9
6	1.0	0.10	20	44.35	35.3
7	2.5	0.05	70	7.30	87.0
8	1.0	0.10	70	13.95	82.8
9	4.0	0.10	20	8.50	95.9
10	2.5	0.10	45	6.95	96.6
11	2.5	0.10	45	9.80	96.5
12	2.5	0.10	45	12.75	94.0
13	2.5	0.15	20	9.35	95.4
14	4.0	0.15	45	5.15	96.8
15	2.5	0.15	70	5.40	96.7

The Box-Behnken statistical design (BBD) was employed to establish a mathematical model representing the correlation between individual factors and the predicted responses (i.e. permeation flux and As rejection). According to the BBD, 15 experimental runs were required to investigate the three variables. The experimental plan is shown in Table 2. A second-order model is generally used for describing the mathematical relationship between the variables (x_i) and responses (y_i), as shown in Eq. 3:

$$Y = b_o + \sum_{i=1}^{n} b_i X_i + \sum_{i\neq 1}^{n} b_{ij} X_i X_j + \sum_{i=1}^{n} b_{ii} X_i^2 + \varepsilon \quad (3)$$

where, Y is the predicted responses of flux or As rejection; X_i and X_j are independent factors in coded levels; b_i, b_{ii}, and b_{ij} are the coefficients of the linear, quadratic, and interaction terms of the model, respectively; b_o, n, and ε are the constant coefficient, number of studied factors, and random error of the model, respectively.

The response surface methodology (RSM) and statistical analysis of variance (ANOVA) were performed via Design-Expert software 8.0. The significance of variables, fitness, and adequacy of the developed models were judged statistically using R^2, adjusted R^2, F-value, and p-value. The terms of the models were retained or removed based on the probability value with a limit of 95 % confidence. Finally, the response surfaces obtained from the regression models were generated to visualize the individual and interactive effects of the influential factors.

Table 3. ANOVA response surface model of permeation flux and As rejection.

	Permeation Flux					As rejection				
	DF	*Sum of square*	*Mean square*	*F-value*	*p-value*	*DF*	*Sum of square*	*Mean square*	*F-value*	*p-value*
Model	6	3,447.8	574.6	18.3	0.0003	9	7,392.1	821.3	42.20	0.0003
X_1	1	1,376.8	1,376.8	43.7	0.0002	1	2,638.7	2,638.7	135.6	< 0.0001
X_2	1	586.5	586.5	18.6	0.0026	1	1,505.0	1,505.0	77.3	0.0003
X_3	1	504.8	504.8	16.0	0.0039	1	635.9	635.9	32.7	0.0023
X_1X_2	1	772.8	772.8	24.6	0.0011	1	1,022.2	1,022.2	52.5	0.0008
X_1X_3	1	129.4	129.4	4.1	0.0772	1	652.3	652.3	33.5	0.0022
X_2X_3	1	77.4	77.4	2.5	0.1554	1	153.6	153.62	7.9	0.0376
X_1^2	-	-	-	-	-	1	653.1	653.1	33.6	0.0022
X_2^2	-	-	-	-	-	1	86.8	86.8	4.5	0.0884
X_3^2	-	-	-	-	-	1	126.3	126.3	6.5	0.0514
Residual	8	251.9	31.5	-	-	5	97.3	19.5	-	-
Lack of fit	6	235.5	39.2	4.7	0.1873	3	93.1	31.0	14.7	0.1643
Pure error	2	16.8	8.4	-	-	2	4.2	2.1	-	-
Model summary										
SD	5.61					4.41				
R^2(%)	93.19					98.70				
Adj. R^2 (%)	88.09					96.36				

Results and discussion

Model fitting and statistical analysis

The observed flux (Y_1) and As rejection (Y_2) recorded through the designed experiments in RSM are reported in Table 2. The F-value tests were conducted with ANOVA for calculating the significance of the mathematical models. The results showed that the two-factor interaction model was proposed for the flux response (y_1), as shown in Eq. 4. Meanwhile, the quadratic model expressed in Eq. 5 was obtained for predicting the As rejection response (y_2):

$$y_1 = +14.41 - 13.12x_1 - 8.56x_2 - 7.94x_3 + 13.90x_1x_2 + 5.69x_1x_3 + 4.40x_2x_3 \quad (4)$$

$$y_2 = +95.72 + 18.16x_1 + 13.72x_2 + 8.91x_3 - 15.99x_1x_2 - 12.77x_1x_3 - 6.20x_2x_3 - 13.30x_1^2 - 4.85x_2^2 - 5.85x_3^2 \quad (5)$$

where x_1, x_2, and x_3 are the code values of PIP, TMC concentrations, and reaction time, respectively. The effect of each variable of the developed model on the responses are specified with a negative or positive symbol before the term.

The adequacy of the obtained models and the significance of the model terms and their interactions was validated using ANOVA. As can be seen in Table 3, the F-value of the model for flux is 18.25 and the p-value is lower than 0.05, which implies that the regression model is significant. The R^2 value for the predicted flux model is 93.19 %, indicating that only 6.81% of the experimental variations cannot be explained by the model. Moreover, the adjusted R^2 of 88.09% is in reasonable agreement with the R^2 value. For the developed model for As rejection, the F-value is 42.2 and the p-value is lower than 0.05, which shows the high significance of the model. The R^2 value of 93.19 % indicates that more than 90 % of the variation in the data is explained by the model, whereas, the adjusted R^2 of 96.36 % shows a good agreement with the R^2 value. These results illustrate the statistical validity of the predicted models. Thus, the developed models can be used to navigate the separation performance of the prepared membrane within the range of studied variables.

According to ANOVA analysis, the p-value of PIP and TMC concentrations, reaction time, and interaction between PIP and TMC concentrations are less than 0.05, which indicates the significance of these factors on the permeation flux of the prepared membrane. On the contrary, the other factors are insignificant or less significant in the developed model. For the As rejection, according to the analysis, it was found that the PIP concentration, TMC concentration, reaction time, interactions effects of PIP-TMC concentration, PIP concentration-reaction time, and TMC concentration-reaction time are the most effective parameters. However, the rest of the factors show an insignificant influence due to a p-value higher than 0.05.

Based on the ANOVA results, the non-significant or less significant factors were eliminated from the models for flux and As rejection. Thereby, the final models in terms of actual factors are expressed in Eq. (6) and Eq. (7):

$$Y_1 = +146.9 - 34.1X_1 - 792.9X_2 - 1.0X_3 + 185.3X_1X_2 \quad (6)$$

$$Y_2 = -167.2 + 78.3X_1 + 1{,}418.2X_2 + 2.5X_3 - 213.1X_1X_2 - 0.3X_1X_3 - 5.0X_2X_3 - 5.9X_1^2 \quad (7)$$

Evaluation of model factors on permeation flux and As rejection

Equation (6) illustrates the influence of the preparation conditions on permeation flux of the prepared membrane. It can be seen that the reaction time affects the flux less significantly than the PIP and TMC concentrations. Particularly, the PIP concentration is the most significant parameter on the flux and the interaction effect between the PIP concentration and TMC concentration plays an important role in controlling the flux of the membrane.

Figure 2 shows the response surface and contour plots that demonstrate the interactive influence of PIP and TMC concentration on the flux at a constant reaction time of 45 s. The flux was observed to decrease considerably when increasing the PIP or TMC concentration, but the decrement of the flux by the increase of PIP concentration is more significant than that of TMC concentration. This reduction in flux can be related to the growth of the membrane thickness [13]. The polymerization occurs at the interface between the TMC/hexane and PIP/water phases towards the organic phase due to the low solubility of TMC in water [14]. Thereby, PIP, with a concentration in great excess over TMC, is commonly utilized to accelerate the diffusion of the diamine monomer into the organic phase. Park, et al. [15] reported that with high TMC concentration (>0.1 wt.%), the kinetics of IP is dominantly governed by the PIP concentration and the increase in PIP concentration induces the creation of a thicker polyamide membrane.

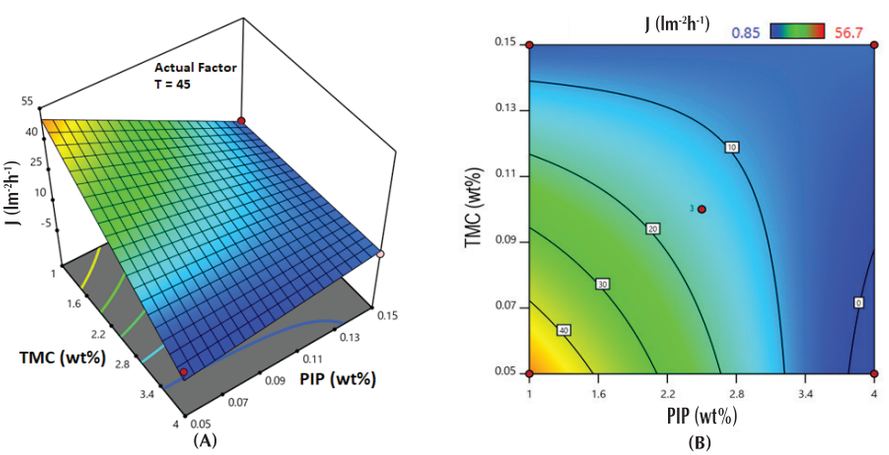

Fig. 2. (A) Response surface and (B) contour plots of PIP and TMC concentration effects on the permeation flux of the fabricated membrane.

The flux depends on not only the thickness but also on the hydrophilicity of the membrane. The higher hydrophilicity of the membrane surface, the stronger the affinity between the membrane and water molecules, and thus the flux of the membrane improves. The number of carboxylic groups related to the hydrophilicity of the membrane is generated by the hydrolysis of unreacted acyl halide groups in the TMC monomer [12]. Saha and Joshi found that an increasing TMC concentration can cause a rise in both the thickness and hydrophilicity of the membrane [14]. In this present work, the increase in thickness dominates the hydrophilicity of the membrane when increasing the TMC concentration. However, the decline in flux by increasing PIP concentration is more considerable than that caused by increasing TMC concentration.

Evaluation of model factors on As rejection

The response surface and contour plots showing the interaction impacts of PIP-TMC concentration, PIP concentration-reaction time, and TMC concentration-reaction time on the As rejection of the prepared membrane are illustrated in Fig. 3. It is apparent that the As rejection improves with an increase in PIP concentration, TMC concentration, and reaction time. Regarding Fig. 3(A, B), the As rejection strongly depends on the PIP concentration, while the TMC concentration shows a weaker factor.

It can be explained by the "self-limiting" mechanism of IP that the faster diffusion of the PIP monomers to the organic phase to bond with the TMC monomers forms an initial thin film with high crosslinking [16]. This dense thin film is regarded as a barrier that hinders the diffusion of PIP monomers to the reaction zone. As a result, the reaction is limited and then terminates. Over a variety of TMC concentrations from 0.05 to 0.15 wt.%, the As rejection increases sharply with an increase in m-phenylenediamine (MPD) concentration due to the formation of amide crosslinking in the prepared membrane. However, when the PIP concentration is much greater than the TMC concentration, the As rejection and permeant flux show a decreasing trend due to the expansion of the reaction zone that causes a thicker and looser structure membrane [14-16].

As shown in Fig. 3 (C, D, E, F), the increase in TMC concentration is demonstrated to extend the crosslinking

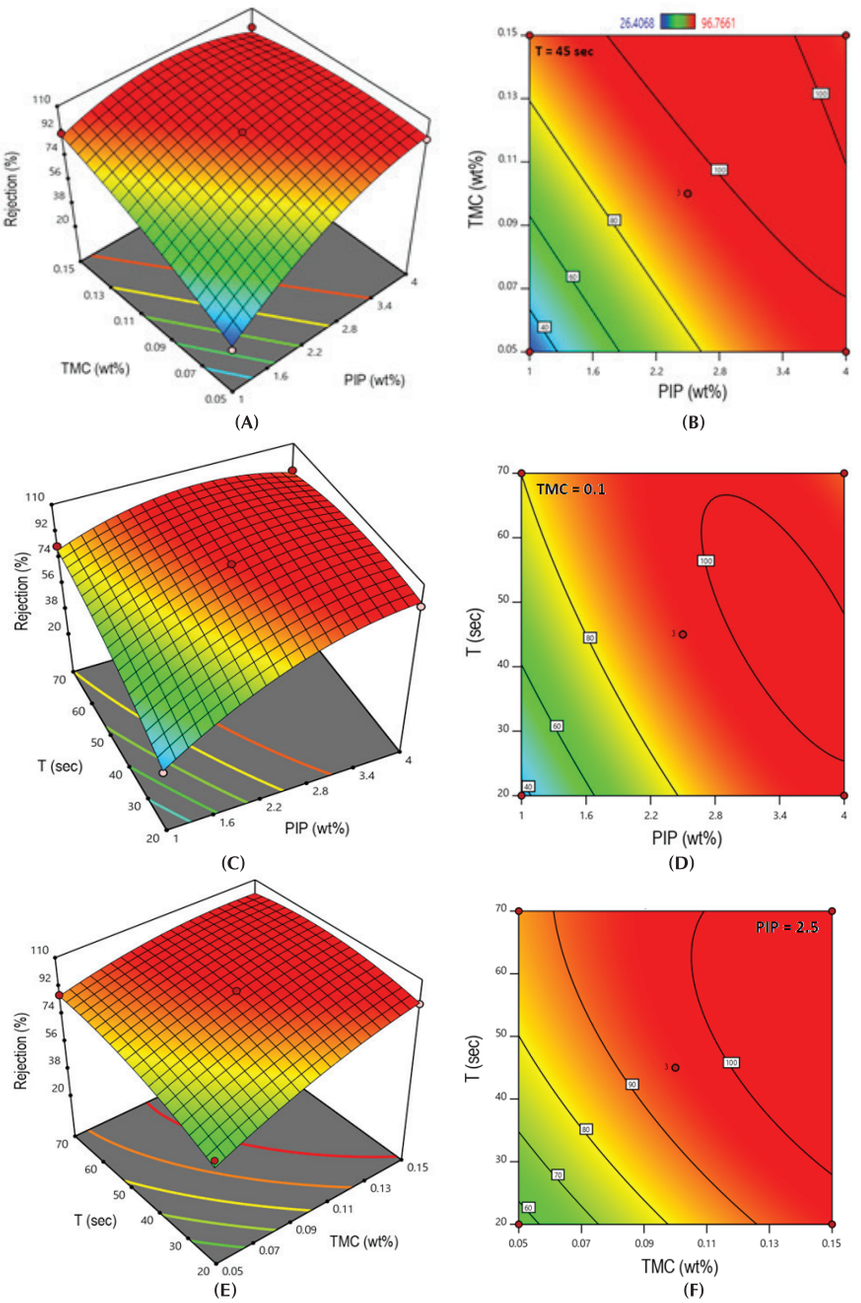

Fig. 3. Response surface (A) and contour plots (B) of the PIP - TMC concentration, (C,D) PIP concentration - reaction time, and (E,F) TMC concentration - reaction time effects on As rejection of the prepared membrane.

and thus enhance the As rejection of the resulting membrane. On the other hand, prolonging the reaction time can facilitate crosslinking to form a membrane with high As rejection. This result is in agreement with previous studies [11-16]. Saha and Joshi [14] suggested that increasing the TMC concentration could reduce the amine/acyl chloride ratio to form a thinner and denser membrane. Furthermore, Kadhom, et al. [16] observed that the polyamide membrane prepared via interfacial polymerization with short reaction time (within 15 s) exhibited a high flux and low ion rejection because the unreacted TMC monomers were hydrolysed to form linear amide moiety with carboxylic acid groups instead of a crosslinking structure.

Optimization

The results indicate a trade-off between the permeation flux and As rejection of the polyamide membrane. Thus, the increase of permeation flux is accompanied by the sacrifice of As rejection. Therefore, it could be suggested that the determination of the optimal ratio of PIP/TMC concentration and corresponding reaction time is required to achieve a membrane with high flux for As removal from water. Response surface optimization, combined with desirability function approach, was applied to maximize the permeation flux and As rejection. In order to obtain the optimum preparation conditions for a high-separation performance membrane, the desired goals in terms of flux and As rejection were defined as maxima. Fig. 4 illustrated the desirability, predicted flux, and As rejection as a function of preparation conditions. The results showed that the maximum permeation flux and As rejection of 13.9 $lm^{-2}h^{-1}$ and 96.7%, respectively, were achieved with a PIP concentration of 2.5 wt.%, TMC concentration of 0.11 wt.%, and reaction time of 40 s. An experiment with the optimized conditions was performed and the flux and As rejection of the prepared membrane were recorded to validate the optimization result as well as the regression models. The obtained flux and As rejection were 14.2±0.8 $lm^{-2}h^{-1}$ and 95.01±0.13% respectively, which demonstrates the validity of the statistical models to optimize the preparation conditions of the polyamide membrane for removing As from water.

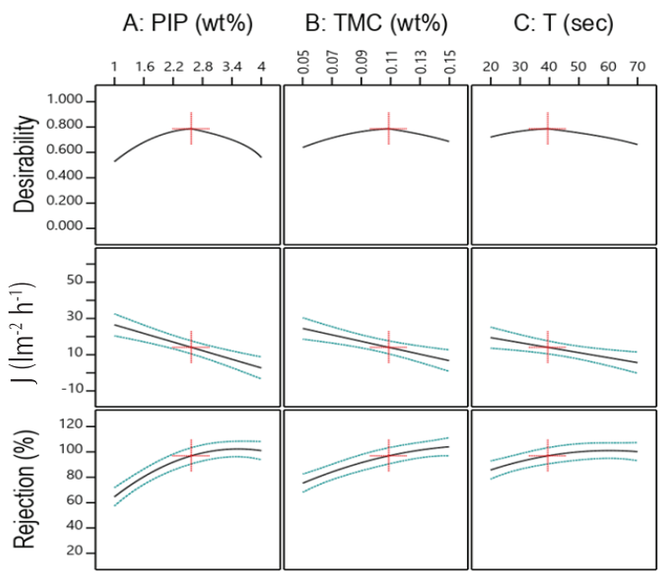

Fig. 4. The desirability, predicted flux, and As rejection as a function of preparation conditions.

Conclusions

A polyamide-based TFC membrane was fabricated for As removal from water. The polyamide membrane was synthesized through IP onto a polysulfone porous substrate. RSM, using Box-Behnken design, was applied to determine the effects of three important preparation conditions, including PIP concentration, TMC concentration, and reaction time, on the As rejection and permeate flux of the synthesized membrane. The study revealed that the PIP concentration was the most significant factor that influenced the flux and As rejection of the resulting membrane, while the reaction time was the least significant parameter. Furthermore, the small deviation between the predicted and actual results indicated the accuracy and validity of the regression models. According to the RSM, the optimal conditions to fabricate the polyamide membrane are PIP concentration of 2.5 wt.%, TMC concentration of 0.11 wt.%, and reaction time of 40 s.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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