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Original Research

Synthesis of polyamide thin film composite nanofiltration membrane for Arsenic removal

Tran Le Hai[*], Nguyen Thi Nguyen, Mai Thanh Phong

ABSTRACT

Arsen (As) is one of the most detrimental substances in drinking water owing to its carcinogenic impact on human health. Among many techniques for removing Arsenic, membrane filtration process has emerged as an efficient technology for removing As from water. In this study, nanofiltration (NF) thin-film composite membrane based on polyamide is synthesized via interfacial polymerization between piperazine (PIP) in water and trimesoyl chloride (TMC) in hexane onto polyacrylonitrile (PAN) supporting substrate. The influence of PIP and TMC concentrations in the two insoluble solvents on the separation performance (flux and rejection) of the obtained membrane is studied. The physicochemical properties of the derived membranes are characterized by ATR-FTIR and pure water contact angle measurements. The separation performance of the membrane is evaluated for filtering pure water and 150 ppb arsenate (Na_2AsHSO_4) aqueous solution. The results indicate that the PIP and TMC concentrations affect the physicochemical properties and thus the separation performance of the polyamide membrane. The hydrophilicity of the membrane surface increases as rising the TMC concentration. Nevertheless, the increment of PIP concentration results in the decline of hydrophilic property of the membrane. The increase in TMC and PIP concentrations lead to increasing the As(V) rejection, while the TMC concentration is dominant to an increment of the thickness of the synthesized membrane. Thus, the permeability of the membrane decreases more significantly with an increase in TMC concentration. The PIP concentration of 2 wt.% and TMC concentration of 0.15 wt.% is found to produce the NF membrane for reducing As(V) in drinking water with high flux of 64 $Lm^{-2}\ h^{-1}$ and good rejection of 95%.

Key words: Arsenic, separation, nanofiltration, membrane

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INTRODUCTION

Arsenic contamination in water resources has been considered as a serious problem in the modern world since a variety of arsenic-containing compounds are widely known as potent carcinogens[1]. The removal of arsenic compounds by suitable methods, therefore, is crucial in water treatment. Different methods for removing arsenic from water have been studied such as, co-precipitation[2], adsorption[3], membrane filtration (*i.e.*, reverse osmosis – RO[4] and nanofiltration – NF[1]). Major drawbacks of co-precipitation and adsorption methods were reported including an addition of chemical reagents, high operating cost and production of the medium of sludge. Hence, membrane-based (RO and NF) techniques was introduced as a novel and effective approach for arsenic removal[5]. More particularly, NF has been extensively exploited due to its lower operating pressure and higher flux compared to RO[6].

There are several researches on removing arsenic by NF have been reported until now. For instance, Saitu *et al.* used thin-film composite polyamide membrane (192-NF300) from Osmonics Inc to remove arsenic with rejection of 95%[7]. Fiogi *et al.* used two commercial polyamide NF membranes (NF30 and NF90) to reject arsenate with the rejection of above 91% in which the rejection of NF30 was lower than that one of NF90[6]. According to our investigation, modern NF membranes have a thin film composite (TFC) structure that consists of the ultra-thin polyamide film over a microporous substrate. The higher permeability and selectivity of the TFC membranes are the key advantages compared to asymmetric membranes[8,9]. The separation performance of TFC NF membranes including permeability and selectivity are directly correlated with the structure and physicochemical properties of the ultra-thin polyamide (PA) film[10]. The selective polyamide active layer is synthesized by an interfacial polymerization (IP) process at the interface of two insoluble solvents. In the IP technique, processing parameters such as the monomer concentrations, types of monomers and reaction time could affect the physicochemical properties and separation performance of the membrane[11,12]. Therefore, many studies have focused on improving the properties of

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the top active layer. Previous studies reported that PIP and TMC can be used as reactants to produce PA-based NF membrane with high permeability and salt rejection[5–8].

In this work, the effect of the monomer concentration on the physicochemical properties and performance of the thin PA layer was investigated by removing pentavalent As from water. Particularly, synthetic PA layers were fabricated in this study from trimesoyl chloride (TMC) and piperazine (PIP) reagents on polyacrylonitrile (PAN)-support membranes through IP reaction.

MATERIAL AND METHODS

Material

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

Methods

PA thin film was hand-cast on the PAN substrate through interfacial polymerization[12]. PA based TFC membrane was formed by immersing the PAN 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 1 min, which resulted in the formation of an ultra-thin polyamide film over the PAN support. The derived membrane was vertically held for 2 min before it was immersed in a 200 ppm NaClO for 2 min and then dipped in 1,000 ppm $Na_2S_2O_5$ solution for 30 s. The membrane was finally dipped in DI water for 2 min. Before the obtained membrane can be used for the experiments, it was immersed in a DI water container with the water replaced regularly.

The derived membranes were characterized by using ATR-FTIR (IFS28, Bruker) and pure water sessile drop contact angles (DSA10, Kruss). The permeability of synthesized membrane was evaluated for pure water, 150 ppb arsenate (Na_2AsHSO_4) aqueous solution using a custom fabricated bench-scale cross-flow membrane process simulator (Figure 1). The experiments comprised steps of compaction, equilibration and cleaning under a fixed temperature of 25 °C. First, DI water was filtered through the membranes at 200 psi for at least 6 h. After achieving the stable flux, the permeability of membrane was determined by measuring the water flux under applied pressure of 150 psi. Next, the arsenate solution with a fixed concentration of 150 ppb was filtered through the membrane at 150 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 ICP analysis (ICP-AES, Horriba). The data of flux and arsenate rejection reported in this paper were based on the average of three experimental runs. Water flux can be determined from permeate water flow rate as follow:

$$J(Lm^{-2}h^{-1}) = \frac{Q_p}{A_m \times t} \tag{1}$$

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 arsenic rejection as shown below:

$$R_s(\%) = 1 - \frac{C_{Permeate}}{C_{Feed}} = 100\% \tag{2}$$

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

RESULTS - DISCUSSION

Influence of the TMC concentration

For an evaluation of the effect of the TMC concentration on the physicochemical properties and As separation performance of the NF membrane, the PIP concentration was fixed at 2.0 wt.% while the TMC concentration was varied from 0.05 wt.% to 2.0 wt.%.

The FTIR spectra of prepared membranes were depicted in Figure 2**a**. The characteristic peaks at wave number of 1448 cm^{-1} and 1625 cm^{-1} are assigned to the amide II band (C - N - H) and amide I band (N - C=O) of the PA thin film, respectively[13,14]. Additionally, the peak at a wave number of 1729 cm^{-1} belonged to the carboxylic groups, which is the result of the hydrolysis of unreacted acyl chloride[10–12]. The intensity of these peaks was found to increase with the increase of the TMC concentration. Therefore, the ratio of the peak intensity at 1729 cm^{-1} and 1625 cm^{-1} could be used to roughly estimate the degree of cross-linking in the PA membrane (**Figure** 2b). The results demonstrated that the cross-linking degree enhanced as increasing TMC concentration in the range from 0.05 wt.% to 0.15 wt.%. With the TMC concentration higher than 0.15 wt.%, the ratio of $I_{(COOH)}/I_{(CONH)}$ exhibited an opposite trend. It indicated that the IP

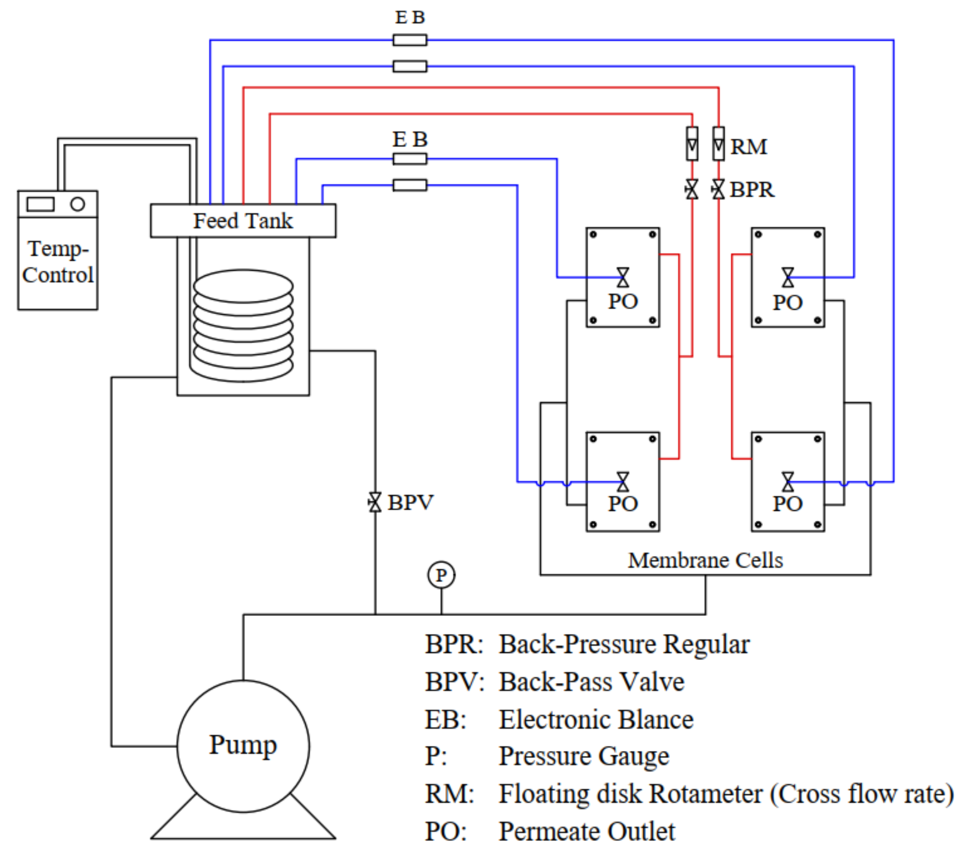
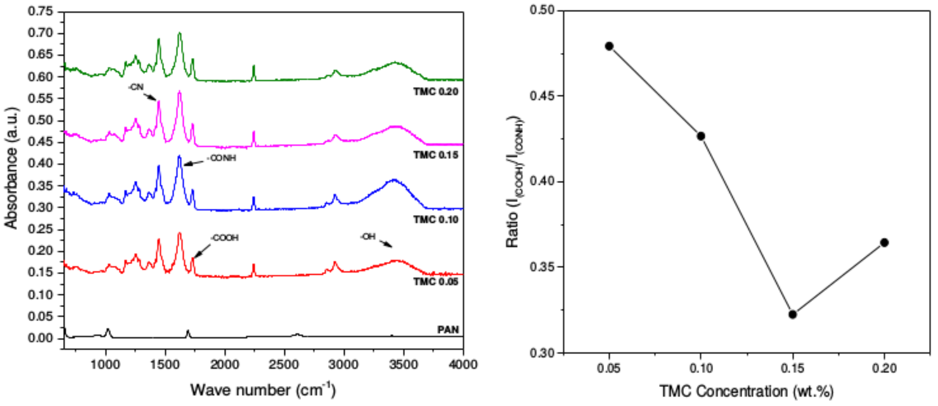


Figure 1: **Schematic illustration of the crossflow membrane process simulator.**



(a) (b)

Figure 2: **FTIR spectra of the PA membranes prepared with different TMC concentrations (a) and the ratio of the intensity of COOH and CONH groups (b).**

reaction was improved with the increase in TMC concentration from 0.05 wt.% to 0.15 wt.%.

The water contact angle representing the hydrophilicity of the TFC membrane surface was shown in Figure 3. As can be seen in Figure 3, the hydrophilicity of the prepared membrane increased with increasing TMC concentration. It can be explained by the increase in the number of carboxylic acid groups on the membrane surface through the kinetics of PA film formation[12]. The structure and morphology of PA membrane were controlled by the diffusion of PIP and TMC monomers into the interface between water and hexane solvents. The initial dense film was formed quickly and thereby limited the amount of the PIP monomers diffusing through the film to react with TMC in the organic phase. Thus, more acyl chloride functional groups were hydrolyzed with water to produce produced carboxylic acid groups on the surface of the PA membrane. As a result, the PA membrane was not fully cross-linked and the carboxylic acid functionality was associated with a more linear structure[10].

The flux and As(V) rejection of the PA membrane prepared by different TMC concentrations were described in Figure 4. The pure water flux of PAN which was employed as a support substrate nanofiltration membrane was 200 Lm^{-2} h^{-1}. The pronounced decrease in water permeability indicates that a dense film was formed on the top surface of the support. It was observed that the flux decreased sharply with increasing TMC concentration. However, the rejection of the membrane enhanced significantly with the TMC concentration in a range of 0.05 - 0.15 wt.%. The observed rejection changed slightly with a further increase in the TMC concentration. The results indicate that the increase in TMC concentration led to a thicker, denser and more hydrophilic PA membrane. This trend is in agreement with the previous reports on synthesizing PA membranes for desalination and softening water applications[13].

The interfacial polymerization occurred at the organic side of the interface of water and organic solvents which can be controlled by the diffusion of MPD and TMC[12–14]. Therefore, an increase in either MPD or TMC concentrations might enhance the driving force for diffusion of monomers to the reaction region to form rapidly a dense thin-film and thereby limited the growth of thickness of the membrane. However, increasing TMC concentration may induce a deficiency in the available MPD at the organic side of the interface. It would lead to an increase of a linear structural fraction with carboxylic acid functional groups, associated with a more hydrophilic surface in the organic site. From the results, it can be seen that the TMC concentration of 0.15 wt.% is suitable to form a PA membrane for arsenic removal with a good separation performance.

Influence of the PIP concentration

For studying the effect of the PIP concentration on the physicochemical properties and As(V) separation performance of the NF membrane, the TMC concentration was fixed at 0.15 wt.% while the PIP concentration was varied from 0.5 wt.% to 3.0 wt.%.

Figure 5 illustrated the FTIR spectra and the ratio of the intensity of COOH and CONH groups of the resulting membrane prepared by different PIP concentrations. It was found that the ratio of $I_{(COOH)}$ /$I_{(CONH)}$ sharply decreased with the increase in PIP concentration. Moreover, the water contact angle (**Figure 6**) was observed to increase with elevating the PIP concentration. It suggests that the cross-linking degree of the membrane was improved noticeably with an increase in the given PIP concentrations. Figure 7 described the water permeation flux and the arsenic rejection of the PA membrane. As can be seen in Figure 7, the permeation flux slightly reduced, while the As(V) rejection of the membrane improved remarkably with the PIP concentration varied from 0.5 wt.% to 2.0 wt.% and then leveled off with a further increase in the PIP concentration. By increasing PIP concentration, the diffusion of PIP to the reaction side of the interface was accelerated. Consequently, the reaction rate is faster and a dense PA film with high extent of cross-linking was formed. The dense film also plays as a role of a barrier, which prevents and blocks the diffusion of PIP to the organic side of the interface for reacting with TMC[12–14]. Therefore, the obtained membrane became thinner, denser, and more hydrophobic. It can be seen from the results that the PA membrane produced with the TMC concentration of 0.15 wt.% and the PIP concentration of 2.0 wt.% exhibited a good separation performance with permeation flux of 64 Lm^{-2} h^{-1} and As(V) rejection of 95%, respectively.

The performance stability of the prepared PA based NF membrane for arsenic removal is a vital factor for practical applications. Accordingly, a long-term separation test was carried out under 150 psi at 25 °C with 150 ppb arsenic aqueous solution. The permeation flux and arsenic rejection of the prepared membrane during 40 h of filtration are presented in Figure 8. It can be seen that the flux of this membrane slightly declined along the time while the rejection was almost stable. It indicates that the PA membrane prepared by interfacial polymerization exhibited a good performance stability.

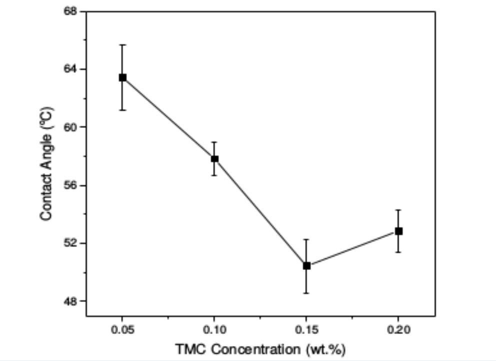


Figure 3: **Water contact angle of the membranes formed with different TMC concentrations.**

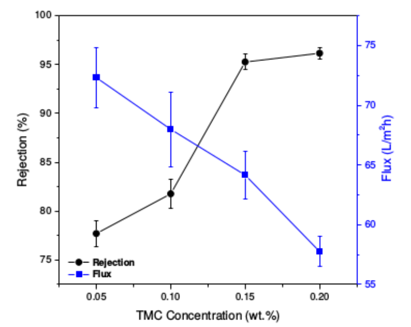
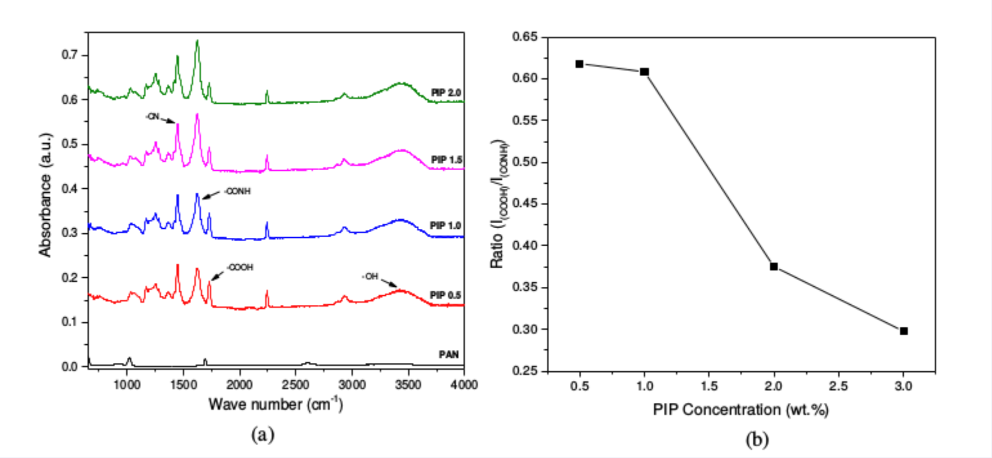


Figure 4: **As(V) separation performance of the membranes formed with different TMC concentrations.**



(a)

(b)

Figure 5: **FTIR spectra of the PA membranes prepared with different PIP concentrations (a) and the ratio of the intensity of COOH and CONH groups (b).**

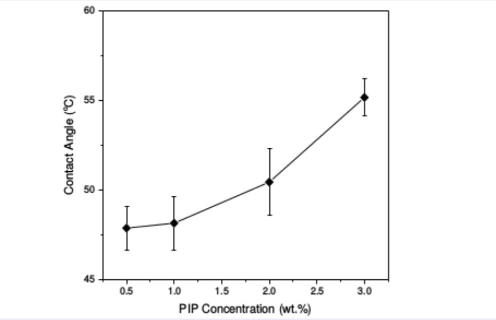


Figure 6: **Water contact angle of the membranes formed with different PIP concentrations.**

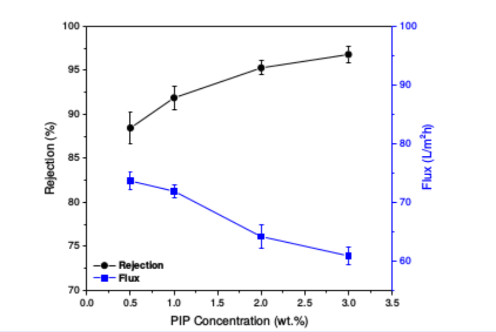


Figure 7: **As(V) separation performance of the membranes formed with different PIP concentrations.**

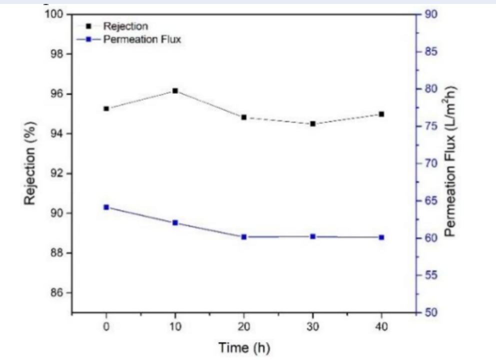


Figure 8: **Performance stability of the prepared membrane.**

CONCLUSION

The polyamide-based nanofiltration thin film composite membrane for the removal of Arsen was successfully synthesized via interfacial polycondensation between PIP in water and TMC in n-hexane solvents. Both the TMC and PIP concentrations were found to affect the physicochemical properties and separation performance of the PA membrane. The increase in TMC concentration resulted in the improvement of the hydrophilicity and crosslinking degree of the resulting membrane. Meanwhile the increment of PIP concentration was observed to form a denser, thinner and more hydrophobic membrane. The PA membrane produced with the TMC concentration of 0.15 wt.% and the PIP concentration of 2.0 wt.% exhibited a good separation performance with water permeation flux of 64 Lm^{-2} h^{-1} and arsenic rejection of 95%, respectively.

ABBREVIATION

As: arsen
MFD: multi-flash distillation
RO: reverse osmosis
NF: nanofiltration
TFC: thin film composite
IP: interfacial polymerization
PIP: piperazine
TMC: trimesoyl chloride
PAN: polyacrylonitrile
PA: polyamide
ATR-FTIR: attenuated total reflectance – Fourier transform infra-red
DI: deionized
ICP: Inductively Coupled Plasma
ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHORS' CONTRIBUTIONS

Tran Le Hai and Nguyen Thi Nguyen designed and performed the experiments. Tran Le Hai and Mai Thanh Phong contributed to the final manuscript. Tran Le Hai supervised the project.

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Bài Nghiên cứu

Tổng hợp màng lọc nano polyamid dạng màng mỏng compozit để khử Arsen

Trần Lê Hải*, **Nguyễn Thị Nguyên, Mai Thanh Phong**

TÓM TẮT
Arsen (As) là một trong những tác chất có hại nhất trong nước uống vì có khả năng gây ung thư cho con người. Trong rất nhiều các kỹ thuật dùng để loại bỏ As, quá trình lọc màng nổi lên như một kỹ thuật hiệu quả để loại bỏ As trong nước. Trong nghiên cứu này, màng lọc nano dạng màng mỏng compozit trên cơ sở vật liệu polyamid được tạo ra để loại bỏ As(V). Lớp chọn lọc polyamid được tổng hợp bằng phản ứng trùng hợp tại bề mặt phân pha giữa piperazine (PIP) trong nước và trimesoyl chloride (TMC) trong hexane trên lớp đế xốp polyacrylonitril (PAN). Ảnh hưởng của nồng độ PIP và TMC trong hai dung môi không hòa tan vào nhau lên hoạt động phân tách của màng (thông lượng và hiệu suất lọc) đã được nghiên cứu. Các tính chất hóa lý của màng được xác định bằng phương pháp phổ ATR-FTIR và đo góc tiếp xúc với nước cất. Hoạt động phân tách của màng được đánh giá bằng quá trình lọc nước cất và dung dịch 150 ppb arsenat (Na_2AsHSO_4). Kết quả cho thấy nồng độ PIP và TMC đều có ảnh hưởng lên tính chất hóa lý và hoạt động phân tách của màng polyamid. Tính ưa nước của bề mặt màng tăng khi tăng nồng độ TMC. Tuy nhiên sự gia tăng nồng độ PIP lại làm giảm tính ưa nước của màng. Tăng nồng độ PIP và TMC đều làm tăng hiệu suất lọc As(V), trong đó nồng độ TMC ảnh hưởng lớn đến sự gia tăng chiều dày của màng tạo thành. Do đó, độ thẩm thấu của màng giảm đáng kể khi tăng nồng độ TMC. Nồng độ PIP 2 %kl và nồng độ TMC 0,15 %kl là thích hợp để tạo ra màng NF để khử As(V) trong nước uống với thông lượng cao 64 $Lm^{-2}h^{-1}$ và hiệu suất lọc tốt 95%.

Từ khoá: Arsenic, phân riêng, lọc nano, màng lọc

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