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REMOVAL OF HEAVY METAL IONS IN WATER USING MODIFIED POLYAMIDE THIN FILM COMPOSITE MEMBRANES

Thu Hong Anh Ngo
Department of Chemical Technology, VNU University of Science, 334 Nguyen Trai, Thanh Xuan District, Hanoi, Vietnam

Dung Thi Tran
Department of Chemical Technology, VNU University of Science, 334 Nguyen Trai, Thanh Xuan District, Hanoi, Vietnam
tranthidung@hus.edu.vn

Abstract

Heavy metals in the wastewater can pollute the water resources because they are durable, have a high toxicity in the environment and body tissues. Thus, the treatment of wastewaters containing heavy metal ions has attracted much attention, because they can economically provide water for industrial production, decrease the wastewater discharge amount, and minimize the effluent pollutant concentration. In some methods for treatment of heavy metal ions, membrane separation is considered as a great promise technique, because of their high efficiency, easy operation, and space saving. The commercial thin film composite polyamide (TFC-PA) membranes are used for the wastewater treatments, due to a high permeate flux, as well as a great rejection for relatively wide operation of temperature and pH range. However, *TFC-PA membranes are sensitive to fouling. The improvement of the fouling resistance of TFC-PA membrane can be achieved through the surface modification techniques. In this work, the surface of TFC-PA membrane has been successfully modified by the UV-photo-induced grafting of poly(ethylene glycol) (PEG) and acrylic acid (AA). The separation performance of the modified membranes has been investigated, through the possibility for removal of heavy metals such as Ni (II), Cu (II), Fe (III) and Cr (III) in water, and in electroplating wastewater. The experimental results indicated that the separation performance of the PEG-grafted and AA-grafted membranes is significantly improved, with an increased membrane flux at a great retention. The antifouling property of the modified membrane is also improved, with a higher maintained flux ratio, and a lower irreversible fouling factor in comparison with those of the unmodified one.*

Keywords

Polyamide Thin Film Composite Membrane, Surface Modification, UV-photo-induced Grafting, Poly(ethylene glycol), Acrylic Acid, Heavy Metal Ions, Separation Performance, Antifouling, Electroplating Wastewater

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1. Introduction

Recently, polyamide thin film composite (TFC-PA) membranes are most popularly used for wastewater treatment, because they exhibit high flux and inorganic, organic rejections, a wide range of temperature and pH operating, and high stability to biological attacks (Bruggen, Mänttäri & Nyström, 2008), (Ding, Yin & Deng, 2014), (Kang & Cao, 2012). This is the reason that the use of TFC-PA membrane has increased in the desalination and treatment of wastewater (Al-Rashdi, Johnson & Hilal, 2013).

The industrial wastewaters such as metal plating facilities, pesticide industries and coal-fired power plants contain heavy metal ions (Maher, Sadeghi & Moheb, 2014), (Haneef & Akintug, 2016). Heavy metal pollution has become more serious environmental today (Fu & Wang, 2011). There are many papers related elimination of heavy metal using Nanofiltration (NF) and reverse osmosis (RO) membranes. Hani Abu Qdais *et al.* (Qdais & Moussa, 2004) used both RO and NF technologies for the treatment of copper ions in wastewater. The results showed that the RO and NF membranes were capable of reducing the ion concentration to 99.4 % and

97.0 % removal, respectively. Saber Mehdipour *et al.* (Mehdipour, Vatanpour & Kariminia, 2015) used polyamide nanofiltration membrane for the removal of lead ions. The maximum lead rejection (using lead nitrate solution) was 97.5 and 96.5 % at 30 bar and 40 bar, respectively. B.A.M. Al-Rashdi *et al.* (Al-Rashdi, Johnson & Hilal, 2013) used NF270 to remove about 99.0 %, 89.0 %, and 74.0 % of cadmium, manganese and lead, respectively with 1000 mg/L concentration at pH = 1.5 and 4 bar pressure.

Using nanofiltration to remove heavy metal ions, the fouling phenomenon, which often occurred during filtration and led to the reducing of membrane separation capacity, is still a major concern (Qdais & Moussa, 2004), (Mehdipour, Vatanpour & Kariminia, 2015). The reducing of water flux is due to the adsorption of soluble metal hydroxide species on the membrane surface, the formation of a cake layer of metal hydroxide precipitate, concentration polarization, and osmotic pressure (Fu & Wang, 2011), (Qdais & Moussa, 2004), (Mehdipour, Vatanpour & Kariminia, 2015).

Photo-induced grafting polymerization is one of the useful methods to modify the membrane surface for antifouling and improvement of separation property. This method has several advantages such as mild reaction conditions, low temperature, high selectivity and easily incorporated into the end stages of a manufacturing process (Hilal et al., 2003)

In this work, the possibility for removal of heavy metal ions in water using modified composite membranes was investigated. The commercial thin film polyamide composite membranes surface was modified by UV-photo-induced graft polymerization technique, using poly (ethylene glycol) (PEG) and acrylic acid (AA) for grafting. PEG has been chosen because it is a neutral, hydrophilic polymer with flexible long chains, large exclusion volume, unique coordination with surrounding water molecules in an aqueous medium (C.Sagle et al., 2009), (Li & Wang, 2010), (Wagner et al., 2011), (Ostuni et al., 2001), (Kang et al., 2007), (Gullinkala & Escobar, 2010), and AA is a negative, hydrophilic polymer. The changes in membrane surface characteristics due to modification were performed through FTIR-ATR spectra, membrane morphology and the surface wettability. The filtration performance of membranes was determined through the separation property and the fouling resistance for removal of heavy metals such as Cu (II), Ni (II), Fe (III) and Cr (III) in water.

2. Experimental

2.1. Materials and methods

Thin film composite membranes (TFC-PA) purchased from Dow Chemical Company were cut and soaked in 25 % (v) aqueous isopropanol (Sigma – Aldrich) solutions for 60 min, then washed carefully and placed in pure water until using for graft experiments. Poly(ethylene glycol) (99.0 %, M_w 600, Wako) and acrylic acid (AA) (purity 99.0 %, Xilong Chemicals, China) were used for grafting without further purification. Other substances such as $CuSO_4.5H_2O$ (98.5 %, China), $NiSO_4.6H_2O$ (98.5 %, China), $Fe_2(SO_4)_3$ (99.0 %, China) and $CrCl_3.6H_2O$ (99.0 %, China) were used to prepare the feed solutions for separation experiments.

The photochemical grafting of PEG and AA onto the TFC-PA membrane surface was carried out under the UV irradiation, using an immersion method performing at ambient conditions. The process involves the absorption of UV light to abstract hydrogen atoms from substrate, forming the surface radical sites required for grafting (Ngo, Tran & Dinh, 2016), (Ngo & Tran, 2017). The membranes were immersed in the PEG and AA solutions under the UV irradiation. After grafting, the membranes were washed carefully with de-ionized water, and then kept wet until they were used for the filtration experiments. The surface characteristics of the grafted membranes have been determined through the ATR-FTIR, SEM and AFM images.

Membrane separation performance was evaluated through filtration experiments for removal of heavy metals such as Cu (II), Ni (II), Fe (III) and Cr (III) in water, using membrane test cell (Osmonics, USA). The separation property has been examined through membrane retention (R, %) and flux (J, $L/m^2.h$) at a certain pressure driving force. The flux ratio (J/J_o) was used to compare the changes in flux values during filtration between the grafted membranes (J) and ungrafted one (J_o); the concentrations of heavy meatl ions in the retentate and filtrate were determined through an atomic absorption spectrometry (AAS) (AA6800, Shimazu). The fouling resistance property of membranes was estimated through the maintained flux values (FM, %) during filtration. The higher flux maintaining value, the better fouling resistance property could be obtained. The irreversible fouling factors were calculated by the formula: $FR_w = [(J_{wo} –$

J_w).100/J_{wo}] (%), where J_{wo} is the pure water flux of membrane before using for filtration heavy metal solution and J_w is that of membrane after using for filtration these solutions.

3. Results and discussion

3.1. Separation property

Figures 1 and 2 showed the comparison in the retention and normalized flux (J/J_o) between the base and modified membranes, grafted with PEG and AA at the different grafting conditions, for removal of 0.5 g/L Ni (II).

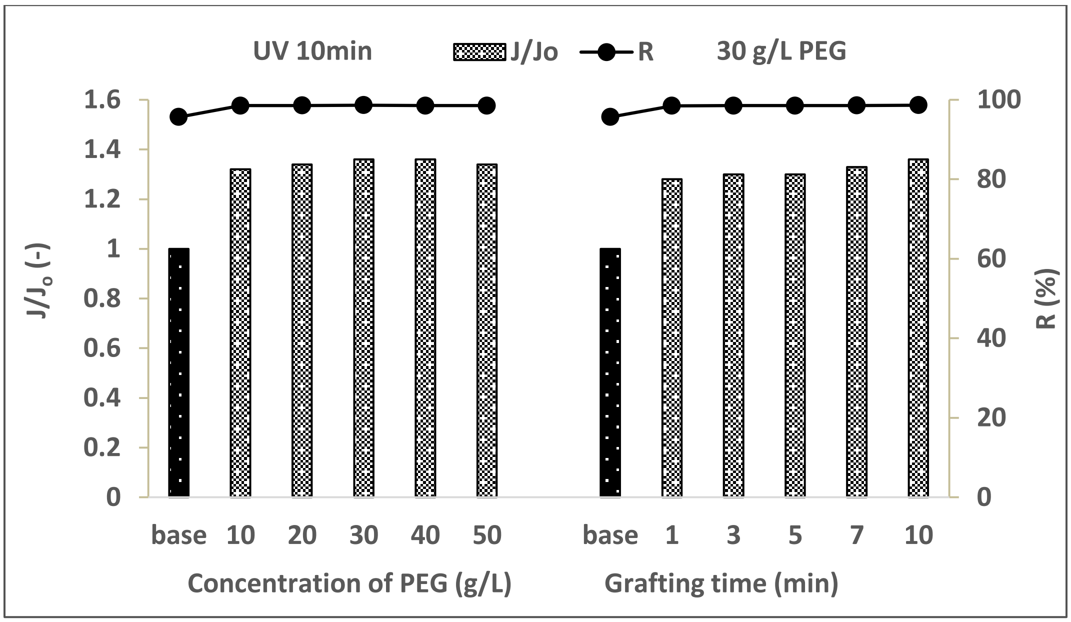


Figure 1: *Separation performance of the base and PEG-modified membranes*

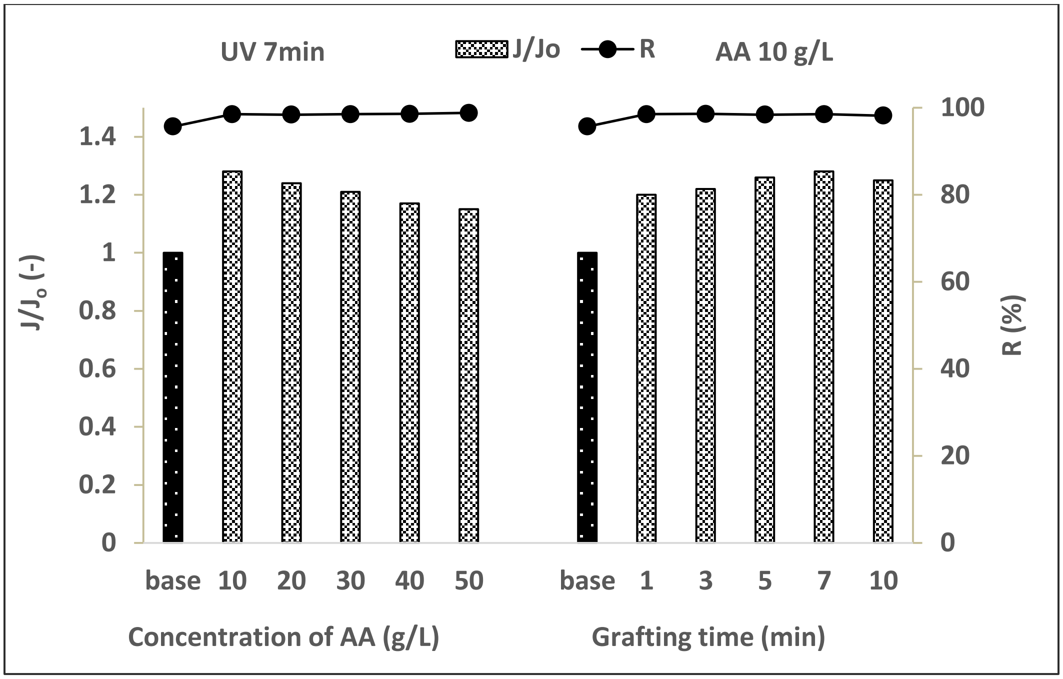


Figure 2: *Separation performance of the base and AA-modified membranes*

The results demonstrated that all the modified membranes had a very good retention; meanwhile the flux was highly improved as compared to that of the base. Under the relevant grafting conditions, the normalized flux of the PEG-grafted and AA-grafted membranes could be 1.3 times and 1.2 times or higher than the base, respectively; meanwhile, the retention was almost stable at high value (98.0 %). The flux enhancement is due to the formation of the hydrophilic PEG-grafted and AA-grafted layers, while the improvement of the retention is due to the more compact of the membrane surfaces after grafting.

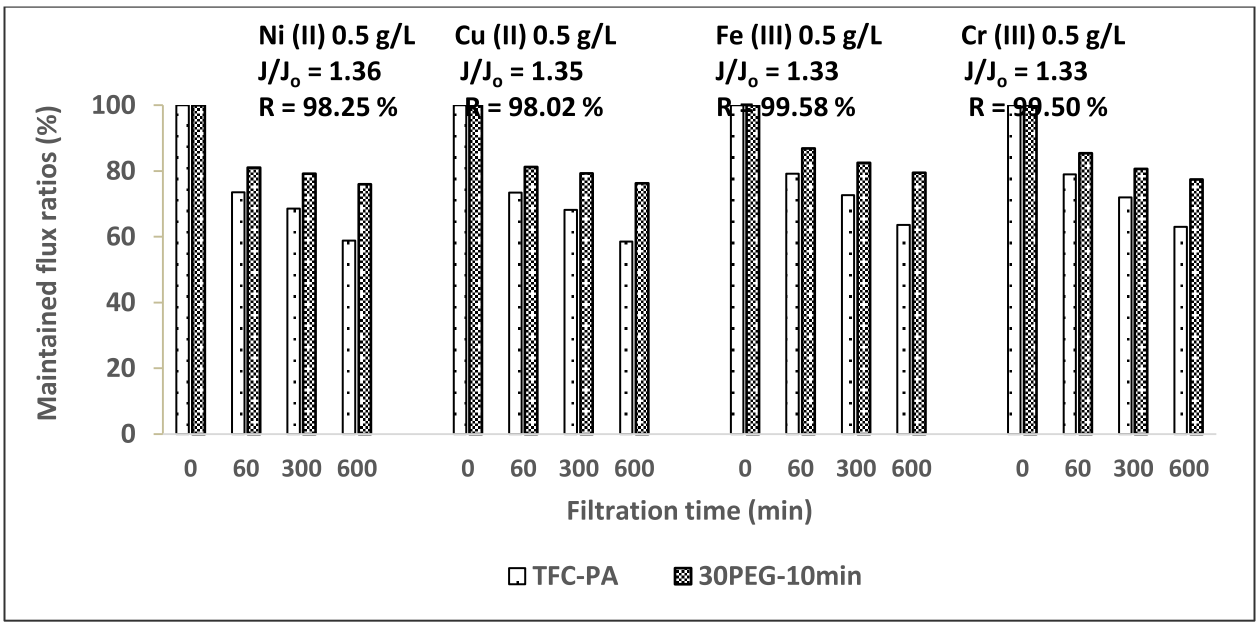
3.2. Antifouling property

The grafted layer could have a highly impact on the membrane fouling resistance. The antifouling property could be improved if membrane surface becomes more hydrophilic, lower roughness and/or has the same charge with the foulants. In this work, the changes of membrane antifouling property have been evaluated through the maintained flux ratios and the irreversible fouling factors. The grafted 30PEG-10min and 10AA-7min membranes have been chosen for filtration experiments.

Figure 3 showed a comparison in the maintained flux ratios between the base and the modified membranes for separation of various metal ions in a feed solution. The results illustrated that the flux decline of PEG-grafted and AA-grafted membranes is less than the base.

Kochkodan et al. (Kochkodan, Johnson & Hilal, 2014) suggested that the electrostatic charge of membranes is especially an important consideration in reducing the membrane fouling. In this work, the maintained flux ratios of PEG-grafted membranes were higher than that of AA-grafted membranes and the base because PEG is a neutral polymer, thus it can decrease the fouling caused by the metal ions on the membrane surface.

Figure 4 showed a comparison in the irreversible fouling factors FR_w between membranes for filtration of the different heavy metal ion feed solutions. The results indicated the lower irreversible fouling factors of PEG-grafted and AA-grafted membranes compared to the base. In addition, the PEG-grafted membrane had a lower irreversible fouling factors than the AA-grafted one.



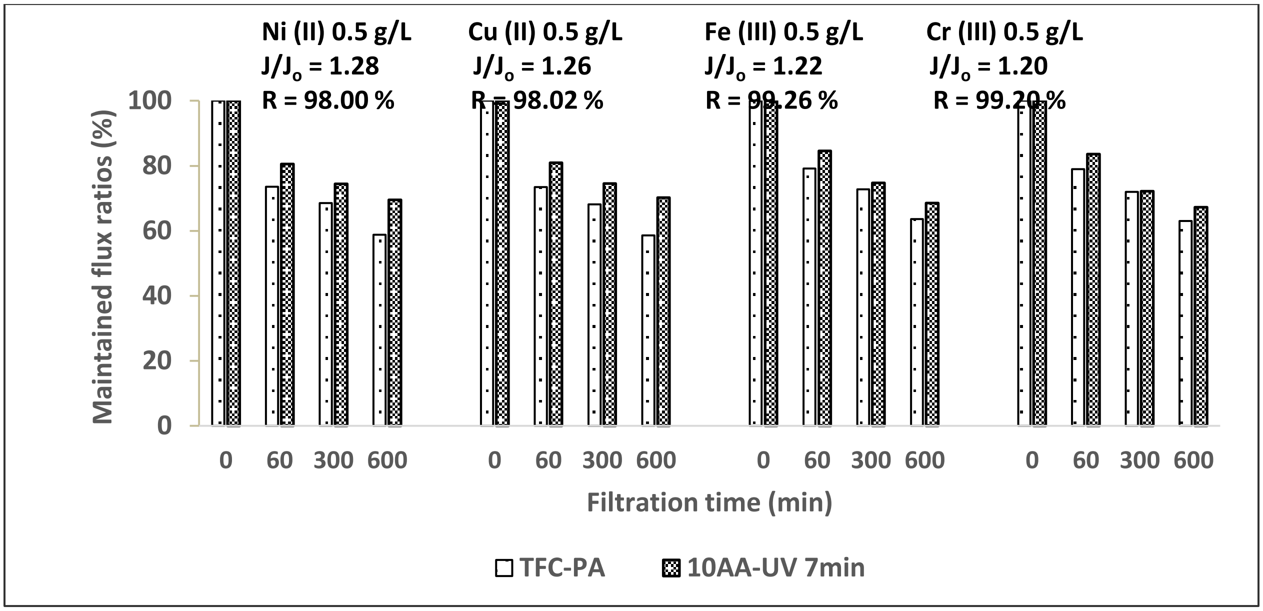


Figure 3: *Maintained flux ratios of the base and grafted membranes*

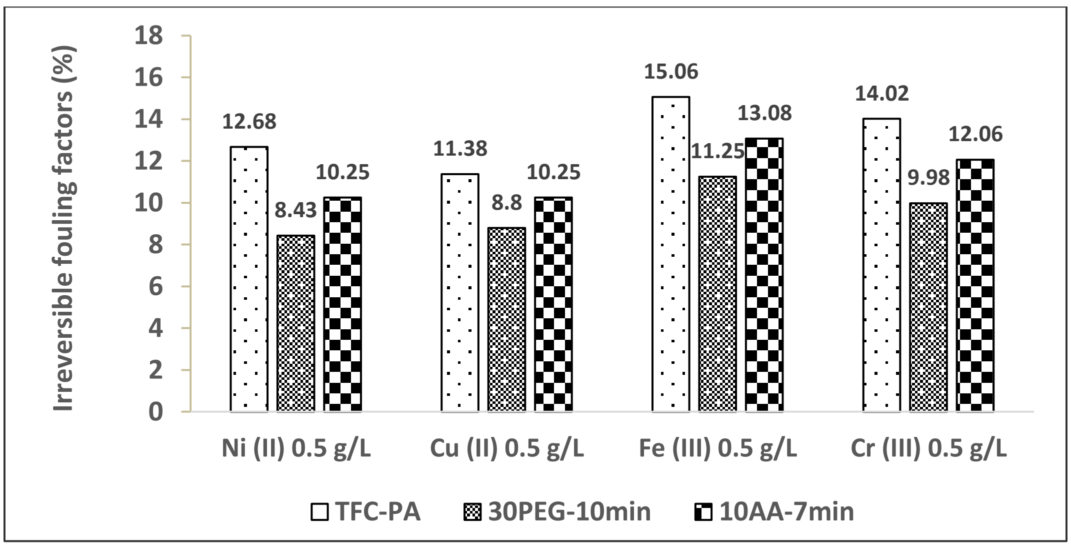


Figure 4: *Irreversible fouling factors of the base and grafted membranes*

3.3. Removal of residual chromium in electroplating wastewater

The chromium electroplating industry discharges a large volume of wastewater, which usually contains hazardous Cr (VI) at pH below of 3. There are many methods that are currently being used for treatment of electroplating wastewater. Recently, membrane technology is a potential method that could be used for treatment of an electroplating effluent.

In this experiment, the possibility for removal of residual chromium in untreated electroplating wastewater of the base TFC-PA membrane and the AA and PEG grafted membranes had been investigated and compared. The characteristics of untreated chromium electroplating wastewater sample were given in the Table 1.

Table 1: *Chromium electroplating wastewater sample*

Factors	Value	Factors	Value
pH	2.50	TSS (mg/L)	35
TOC (mg/L)	25.44	Cr (VI) (mg/L)	5060

To remove residual chromium, the electroplating wastewater sample was filtered through the TFC-PA membrane and the grafted ones. The filtrate had been re-filtered in several times and the experimental results were shown in the Table 2.

Table 2: *Removal of residual chromium in electroplating wastewater*

Filteration times	Concentration of Cr (VI) (mg/L) in filtrate		
	Base TFC-PA	***AA-grafted***	***PEG-grafted***
1	250.126	80.572	65.931
2	11.256	1.128	0.725
3	0.473	0.016	0.007
4	0.020		

The experimental results indicated that the grafted membranes have a better separation performance than the base membrane. The concentration of Cr (VI) was reduced to 0.02 mg/L by re-filtering of 4 times for the base, and it was 0.016 or 0.007 mg/L after re-filtering of 3 times through the AA-grafted or PEG-grafted membranes, respectively.

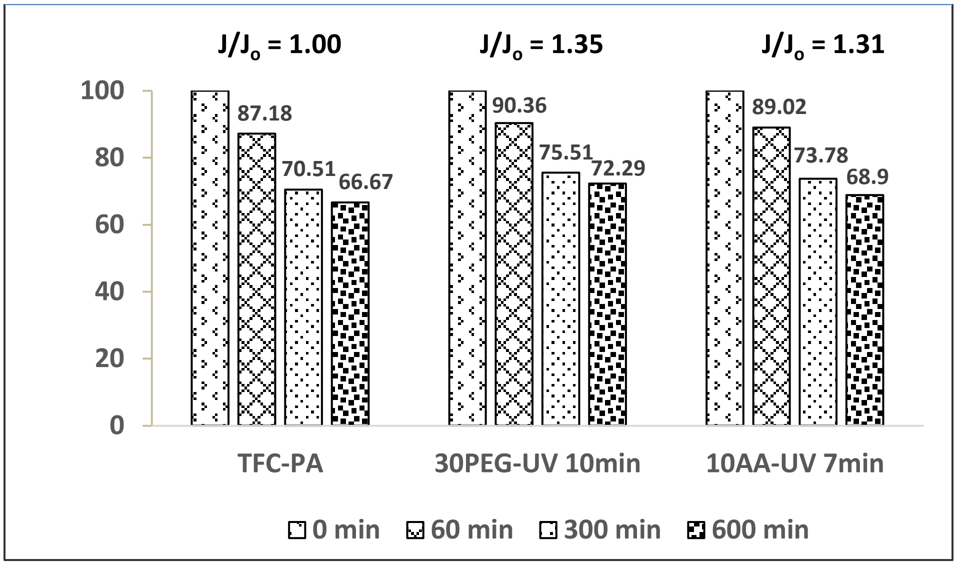


Figure 5: *Maintained flux ratios of the base and modified membranes*

The comparison in the flux and maintained flux ratios between the base and grafted membranes is given in the Figure 5. As shown in the figure, the maintained flux ratios of the grafted membranes was higher than the base, while fluxes were also significantly improved with approximately 1.35 and 1.31 of the normalized flux ratios for the PEG-grafted and AA-grafted membranes, respectively.

4. Conclusion

The surface of thin film composite polyamide membrane has been successfully modified by the UV-photo-induced grafting of poly (ethylene glycol) and acrylic acid. The separation performance of the modified membranes was highly improved with the increased membrane flux at the stable high retention for removal of heavy metal ions in the feed solutions. The antifouling property of the membrane was also improved because of the higher maintained flux ratios during filtration and the lower irreversible fouling factors as compared to that of the unmodified one. The modified membranes showed the good possibility for removal of residual chromium in electroplating wastewater. The concentration of residual chromium can be reduced to below 0.02 mg/L after re-filtering of 3 times through the PEG-grafted and AA-grafted membranes; while the fluxes of the grafted membranes were higher than of 30 to 35 % compared to the ungrafted membrane.

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