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Pesticides removal from water using modified piperazine-based nanofiltration (NF) membranes

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ABSTRACT

This study attempted to explore the removal of two pesticides (atrazine and diazinon) from water by synthesized thin-film composite (TFC) polyamide nanofiltration (NF) membrane. Poly (piperazineamide) NF membranes were prepared by interfacial polymerization technique. In this work, the effects of addition of triethylamine (TEA) as an accelerator in aqueous phase were examined on the performance and morphology of TFC membranes. The morphological studies represented that a rough and dense film was fabricated on the PSf support membrane. The NF membranes performance was evaluated with 0.03 g/l atrazine and diazinon dissolved in distilled water as feed solution, separately. The modified membranes with TEA exhibited higher rejection and water flux compared to the other membranes. Moreover, in all experiments, diazinon was better rejected than atrazine. It was observed that the water permeability and diazinon rejection increased from 22 $l/m^2/h$ and 95.2% for the unmodified membrane to about 41.56 $l/m^2/h$ and 98.8% for the 2% (w/v) TEA modified membrane. This indicated a significant improvement in the performance of poly (piperazineamide) TFC NF membranes for pesticides removal.

Keywords: Nanofiltration membrane; Interfacial polymerization; Triethylamine; Pesticide removal

1. Introduction

In recent decades, water demand in most countries in the world has been increased significantly due to the developing industrial life and the increasing growth of various industries [1]. On the other hand, Iran is an active country in agriculture practice, palm, paddy, fruit, vegetables, and many other products for local consumption and some for export goals. The extensive amount of pesticides used in industry and agriculture is as major emerging contaminants in water sources [2].

Diazinon and atrazine are among the most commonly used pesticides in the world. Diazinon (*O*,*O*-Diethyl *O*-[4-methyl-6-(propan-2-yl) pyrimidin-2-yl] phosphorothioate) is an all-purpose indoor and outdoor commercial pest control product. Diazinon is an insecticide that belongs to a group of chemical known as organophosphates. It has the potential to dissolve in water, lasts for weeks or months depending on the soil environment, moves through soils and contaminates ground water. Meanwhile, the other pollutant

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studied is atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), which is a widely used herbicide (weed-killer). It is one of the most common chemical contaminant of ground and surface water. It is less expensive and persists longer in the soil than other herbicides, with its ability to remain in the environment for long periods of time [3].

Although pesticides are manufactured to be toxic and kill pest and unwanted organisms, they can damage non-target organisms and as a result cause serious environmental problem [5]. Thus, considering the limited water resources there is a necessity to attain and develop a methodology for pesticides removal from water supplies to decrease risk to both human and environment [6].

Removal of pesticides for the production of drinking water was traditionally conducted by activated carbon filtration. Although this process was effective, it was known as an expensive procedure which required frequent regeneration [2].

In recent years, NF membranes have been studied as potentially suitable means of pesticide removal, which have been offered appropriate alternative to the traditional methods for water treatment [7,8].

The membrane process is a successful separation technology due to the fast and energy efficient process without any phase change [9]. NF as a liquid separation membrane technology is an emerging desirable technique over the past few years because of its important advantages, such as low-operation pressure, high-permeate flux, and high retention of multivalent ions salts [10–13]. Nowadays, NF is mainly utilized in drinking water purification process steps, such as water softening [14,15] and removal of micropollutant [16]. Different industrial processes and researching projects have been investigated and demonstrated that NF membrane can be a suitable technique for specific components and organics removal, such as pesticides [17,18], heavy metal [19,20], dying [21,22], pharmacy [23], and food [24,25].

One of the most effective NF membrane preparation techniques is interfacial polymerization (IP) [26]. The composite membrane which is prepared by IP technique is comprised a selective thin-film layer on the top of a support membrane (usually UF membrane). The skin layer resulted by this technique will determine the performance and efficiency of the membrane containing solute rejection and water flux by the monomers applied in IP [27–30]. Even small changes in the monomers concentration or structure have strongly effect on the performance of the membrane [30,31].

The main aim of this study was to modify the TFC NF membrane in order to enhance the performance, especially the rejection value for pesticides removal from aqueous solution by addition of TEA into amine solution.

2. Experimental

2.1. Materials

The polysulfone (PSf, Udel P3500, Solvay Polymers) and dimethylformamide (DMF, 99.8%, Merck) were employed as the base polymer and solvent for preparation of UF support membranes, respectively. Piperazine (PIP, Merck) and triethylamine (TEA, Merck) were used as the monomer and additive in aqueous phase, respectively. Trimesoyl chloride (TMC, sigma-aldrich) and *n*-hexane (>0.95%, Merck) were employed as the monomer and solvent in organic phase. Distilled water was used for both aqueous phase and feed solution.

2.2. Preparation of PSf support membrane

For preparation NF membrane, a flat-sheet substrate was first fabricated via phase inversion induced by immersion precipitation [32]. A casting solution containing dissolved PSf (18% (w/v)) in dimethylformamide (DMF) was prepared by stirring for 8 h at room temperature. The stirring was performed at 200 rpm. After formation of a homogeneous solution, it was hold at room temperature for around 12 h to remove the air bubbles. Afterwards, the solution was spread using a homemade casting knife with a 100 μm knife thickness over commercial non-woven polyester which was attached to a clean glass. After casting, the support was immediately immersed into the coagulation bath for at least 24 h at room temperature.

2.3. Fabrication of thin-film composite membrane

Thin-film composite PA membranes were prepared by IP technique. Firstly, the UF support layer was glued to a clean glass plate via laboratory tape with a length/wide of 13/6 cm. The glued support layer was placed into the aqueous solution containing different concentration of PIP with or without TEA (Table 1) and allowed to soak for 2 min. The amine saturated support membrane was kept at vertical position at room temperature for at least 5 min in order to remove excess solution and any tiny bubbles. Afterwards, the membranes were immersed in organic solution including TMC and n-hexane for IP. After 30 s reaction time, the above-mentioned membranes were took out from organic phase and held in a hot air dryer of 80℃ for 5 min in order to further polymerization.

Table 1
Summary of the composite nanofiltration membranes' recipes

Code	PIP (w/v %)	TMC (w/v %)	TEA (w/v %)
NF_1	0.5	0.1	–
NF_2	1	0.1	–
NF_3	1.5	0.1	–
NF_4	2	0.1	–
NF_5	2	0.1	0.5
NF_6	2	0.1	1
NF_7	2	0.1	1.5
NF_8	2	0.1	2

2.4. Membrane characterization

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was employed to analyze the functional groups on the membrane surface and investigate if the interfacial polymerization was performed effectively. Totally 50 scans were measured during IR study for each sample. The resolution of apparatus was 4 cm^{-1}. The spectra of the sample were measured between 1,000 and 3,400 cm^{-1}.

The surface and cross section of membranes were examined using zeissEvo 50 scanning electron microscope (SEM, Carlzeispte Ltd). The membrane samples were frozen in liquid nitrogen and fractured. After drying in air, the broken samples were coated with gold for generating electric conductivity and were viewed at 25 kV.

Quantitative surface roughness analysis of the TFC NF membrane was performed using Atomic force microscope (AFM, Easyscan2 Flex). Small squares of the membrane (approximately 1 cm^2) were cut and glued on a glass substrate. The membrane surface was analyzed in a scan of 5 μm × 5 μm.

The contact angles were measured with a contact angle measuring apparatus (OCA 15 plus, Dataphysicy). Deionized water was used as the probe liquid in all measurements. For evaluation the membrane hydrophilicity, the contact angles between water and membrane surface were measured using CCD camera and angle measuring software. In order to minimize the experimental error, the contact angles were measured at five random sites of each sample.

2.5. Filtration and separation performance of the TFC NF membranes

Two pesticides, atrazine and diazinon, were selected as test compounds because they were appeared as the most important pollutant in surface water. Table 2 represents general relevant data of two mentioned pesticides. The performance of NF membranes was characterized with feed solution containing atrazine or diazinon at concentration of 0.03 g/l dissolved in distilled water. All experiments were carried out at room temperature in a batch type, dead-end, NF cell with a diameter of 5.1 cm and effective membrane filtration area of 20.417 cm^2. The top of the cell included a gas inlet. Nitrogen gas was applied to pressurize the cell to an operating pressure of 5×10^5 Pa (5 bar). Magnetic stirring heater (ARE Heating Magnetic stirrer) was used to exert a constant agitation during all of the experiments in order to reduce concentration polarization of the membranes. The concentration of the pesticides was measured by spectrophotometer (JENWAY 6305 UV/vis spectrophotometer) at the following wavelengths: $\lambda_{\text{atrazine}} = 222$ nm; $\lambda_{\text{diazinon}} = 247$ nm.

The permeation flow of membranes was calculated as follows:

$$j = \frac{V}{A\Delta t} \quad (1)$$

where V (l) is the permeation total volume during the experiment, A (m^2) is the membrane effective area, and Δt (h) is the sampling time. The rejection value was obtained by following equation:

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p and C_f represent permeate and feed concentration, respectively. All the data reported for the flux and rejection are the average of two measurements.

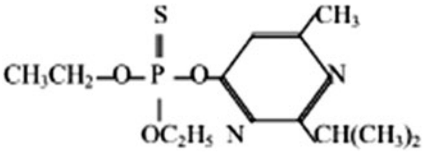
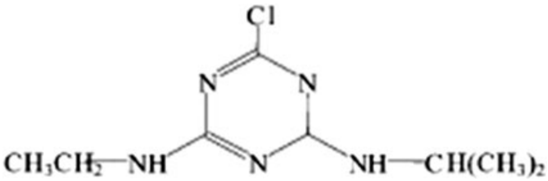
3. Result and discussion

3.1. FTIR-ATR spectroscopy of membranes

The mechanism of polymerization reaction between PIP and TMC is shown in Fig. 1. In interfacial polymerization process, an aryl halide (TMC) and an amine (PIP) were employed as reactants and triethylamine was used as acid acceptor. According to Fig. 1(a), the reaction between aryl halides and amines involves assailing an electron donor (amine) to an electrophilic carbonyl group (C=O) resulting in poly (piperazineamide) [33]. Moreover, as shown in Fig. 1(b), the partial hydrolysis of acyl chloride unit of TMC is expected to generate the carboxylic acid functional group (–COOH).

ATR-FTIR provides a convenient way to characterize the various bonds on the surface of PA TFC NF

Table 2
Properties of diazinon and atrazine [4]

Pesticide	Diazinon	Atrazine
Chemical structure		
Molecular size (nm)	0.834	0.674
Solubility in water	40 mg/L at 25	30 mg/L at 25
log K_{OW}	3.81	2.68

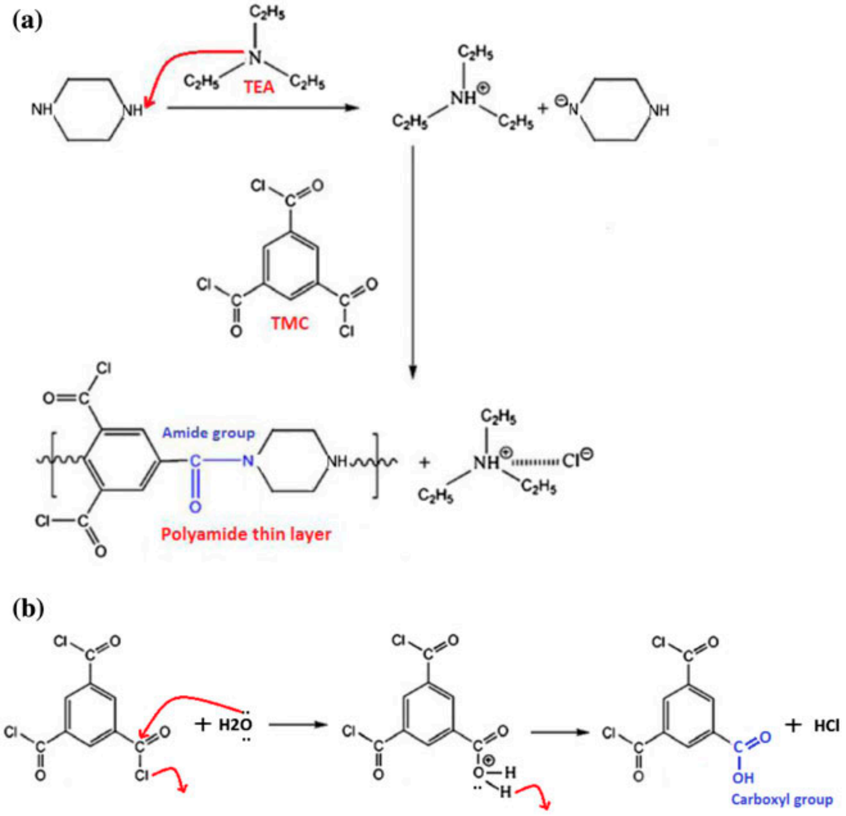


Fig. 1. The mechanism of (a) polymerization reaction between piperazine (PIP) and trimesoyl chloride (TMC) in the presence of triethylamine (TEA) and (b) partial hydrolysis of TMC.

membrane. According to ATR-FTIR spectra (Fig. 2), IP occurred since a strong band at ~1,677 cm^{-1} was appeared that is characteristic of the C=O peaks of amide functional group [34]. The peaks at ~1,594 cm^{-1} are assigned to C–N stretching in poly (piperazineamide). In addition, the weak peak characteristic of –COOH groups of the obtained skin layer is observed at ~3,399 cm^{-1} [32].

3.2. Morphological studies

The morphologies of the membranes were characterized by SEM and AFM. Fig. 3 shows the cross section and surface SEM micrographs of PSf supporting membrane and both unmodified and modified polypiperazine-amide TFC NF membrane. Fig. 3(a) and (b) illustrates the surface and cross-section SEM images of

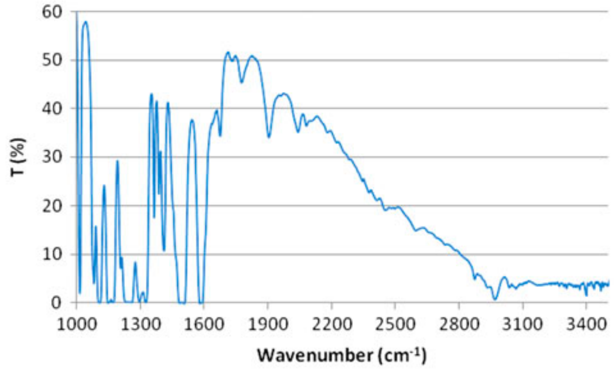


Fig. 2. FTIR-ATR spectra of polypiperazine-amine thin-film composite nanofiltration membrane.

the PSf support layer. Fig. 3(b) represents the spongy homogenous structure of the PSf support. The polymerization reaction between PIP and TMC leads to the formation of PA skin layer, as shown in Fig. 3(c) and (d) (without TEA). The surface SEM image of the TFC NF membrane (Fig. 3(c)) demonstrated the formation of a rough and uniform film on the surface of the PSf support membrane. Fig. 3(d) indicated that the active layer could be clearly distinguished on the top of the spongy support membrane. This top layer plays a key role in the separation process and rejection capability. Fig. 3(e) and (f) illustrates the surface and cross-section images of modified PA TFC membrane with TEA. As shown in Fig. 3(e), addition of TEA to the aqueous solution led to form a PA thin layer with more density. According to Fig. 3(f) a relatively dense and homogeneous skin layer was uniformly coated on the porous spongy substrate. Based on Fig. 3(e), it can be found that this structure approximately changed to the typical familiar dense "nodular" structure after adding TEA in aqueous phase, which can be evidence for potentiality in achieving denser structure and higher solute rejection.

Fig. 4 illustrates the surface AFM images of unmodified and modified PA TFC membranes, which cover an area of 5 × 5 μm. The dark and light regions show the depressions and the highest points, respectively. The surface roughness parameters of the membranes which are expressed in terms of the mean roughness (S_a), the root mean square of the Z data (S_q), the mean difference between the highest peaks and lowest valleys (S_z), and the mean pore sizes of the membrane surface were calculated by Nanosurf EasyScan software (Table 3). The values of average pore size were determined with the height profile of two-dimensional AFM images by Nanosurf EasyScan software. With considering the AFM images and surface roughness parameters, the significant changes in the structure of membrane surface were clearly observed. As shown in Fig. 4, the surface seems to be rough after polymerization of PIP and TMC onto the PSf membrane surface. Although the composite polyamide membrane is rough, the strong hydrophilic polar amide functional groups and carboxyl functional groups existing in skin layer are responsible for the high hydrophilicity of the composite polyamide membrane. As shown in Table 3, NF_1 (0.5% (w/v) of PIP) was indicated a membrane with the largest pore size. It is obvious that the roughness parameters of unmodified membranes enhanced by increasing of PIP concentration. On the other hand, by increasing of PIP concentration from 0.5% (w/v) to 2% (w/v), the surface mean pore size declined from 28.76 to 14.72 nm. Meanwhile, in the presence of TEA in aqueous phase, the property of skin layer was changed. A comparison of roughness parameters between NF_4 (2% (w/v) of PIP) and NF_8 (2% (w/v) of PIP and 2% (w/v) TEA) indicated that the surface of NF_8 was rougher than that of NF_4 due to the existence of TEA in the aqueous phase, which caused to form a dense thin layer on the PSf substrate. As can be seen in Fig. 4 and Table 3, the roughness of the membrane was obviously increased. Moreover, in the existence of 2% (w/v) TEA, the surface mean pore size was slightly reduced (11.5 nm compared to 14.72 nm for unmodified membrane).

3.3. Hydrophilicity studies

Water contact angle of the membrane surface are presented in Table 4. The water contact angle of the membranes was measured to determine their hydrophilic properties. The declining trend in the water contact angle obviously shows the enhancement of hydrophilicity of the membrane surface [33]. The contact angle data indicated that the addition of TEA led to decrease contact angle values. This indicated that the membrane hydrophilicity enhanced in the presence of TEA in aqueous phase. This is due to the positive effect of TEA on the polymerization reaction between PIP and TMC. TEA is known as a cross-linking catalyst in the formation of PA skin layer. As a result, a PA NF membrane with more hydrophilic amide functional groups ($-CONH_2$) and carboxyl functional groups ($-COOH$) was formed.

3.4. The effect of PIP and TEA concentration on the NF membrane performance

Figs. 5 and 6 show the relationship between the rejection and water flux of the membrane and PIP concentration, respectively. The water flux decreased

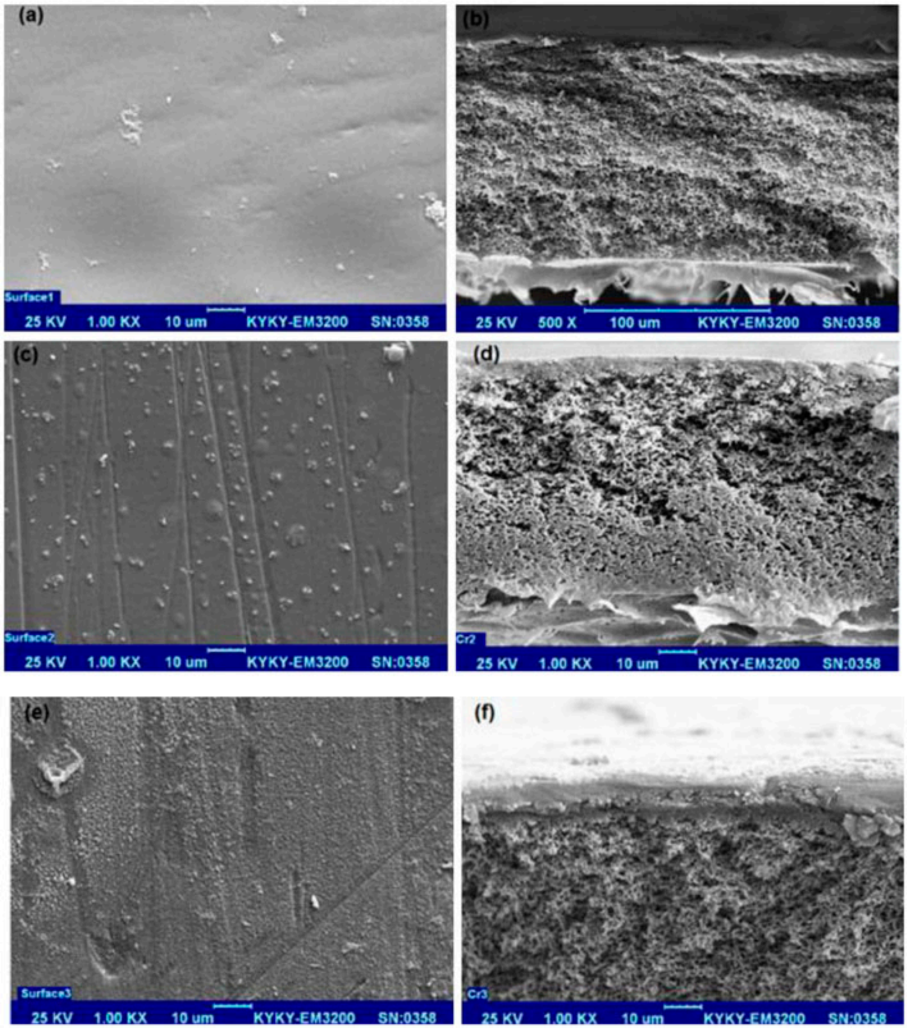


Fig. 3. SEM images of (a) surface of PSf support membrane, (b) cross section of PSf support membrane, (c) surface of unmodified PA TFC NF membrane, (d) cross section of unmodified PA TFC NF membrane, (e) surface of modified PA TFCNF membrane in the presence of 2 (w/v) TEA and (f) cross section of modified PA TFC NF membrane in the presence of TEA.

continuously as the amount of PIP increased, while the rejection of both of the pesticides increased. The rejection of artazine and diazinon increased to 51.74 and 46.46%, whereas PIP concentration increases from 0.5% (w/v) to 2% (w/v), respectively.

The changes in both of rejection and water flux of the membranes in association with the monomer (PIP) concentration may be explained in terms of the thickness and morphology of the membranes. Polymerization is expected to precede fast at higher monomer concentration and results in the formation of "thick and compact" polyamide skin layers. Thus, the pesticide rejection increased, whereas the water flux decreased [34]. Similarly, the rejection of the pesticides (atrazine and diazinon) increased as the TEA concentration in the aqueous phase increased (Fig. 7). Moreover, the water flux of the membranes also enhanced as the TEA concentration increased (Fig. 8). It can be found that the increase in water flux value might be obtained due to the formation of more hydrophilic amide functional groups (–$CONH_2$) and carboxyl functional groups (–COOH) on the membrane surface. In addition, the rising of rejection value can be explained by morphology and hydrophilic properties of the membranes. By adding TEA to aqueous solution, a thin-film layer with higher density and hydrophilicity could be formed, which leads to an increasing of the rejection value.

The SEM images of modified membrane compared with that of unmodified membrane indicated the formation of an ultra-thin layer with higher density. This can be explained by the existence of TEA in the aqueous phase. TEA is known as a week alkali, which is employed as a cross-linking catalyst in the formation of polyamide thin layer. As can be seen in Fig. 2(a), reaction mechanism illustrates that the nitrogen of TEA has a pair of free electrons that could be made available to the amine groups of PIP. This chemical bond accelerates the polycondensation reaction of polyamide thin-film production at the interface. Moreover, the polymerization reaction of PIP and TMC causes to produce hydrogen chloride (HCl). The presence of TEA as an acid acceptor in the aqueous PIP solution accelerates the PIP–TMC reaction and neutralizes the hydrogen chloride produced during polymerization reaction. The reduction of hydrogen chloride content from the reaction media improves the reaction equilibrium conversion. Therefore, the ultra-thin layer with higher density and molecular weight would be formed on the membrane surface [1].

The presented data show that the rejection value of the both pesticides are satisfactorily high, regularly following the order of their molecular size. The rejection value for the smaller molecule, atrazine, is lower than that for the larger one, diazinon. The prevailing mechanism of uncharged organic molecules rejection by NF membranes is size exclusion, but it is not sufficient. Membrane material and pore size distribution (PSD) also influence uncharged organic molecules rejection. According to Tables 1 and 3, it is obvious that all the pesticide molecules are smaller than membrane mean pore sizes shown in the membrane PSD.

Several reports [4,35,36] suggested that although molecular sieving effect must not be neglected, some

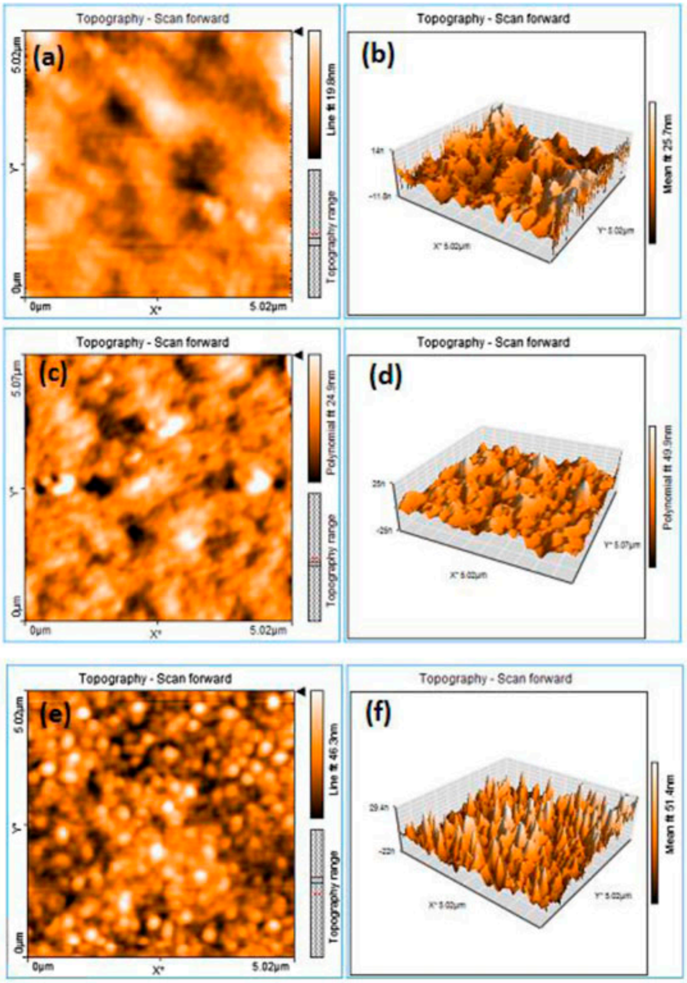


Fig. 4. Two- and three-dimensional AFM images of surface morphologies of (a) and (b) polypiperazine-amide NF_1 membrane, (c) and (d) polypiperazine-amide NF_2 membrane, (e) and (f) polypiperazine-amide NF_3 membrane, (g) and (h) polypiperazine-amide NF_4 membrane, (i) and (j) polypiperazine-amide NF_8 membrane.

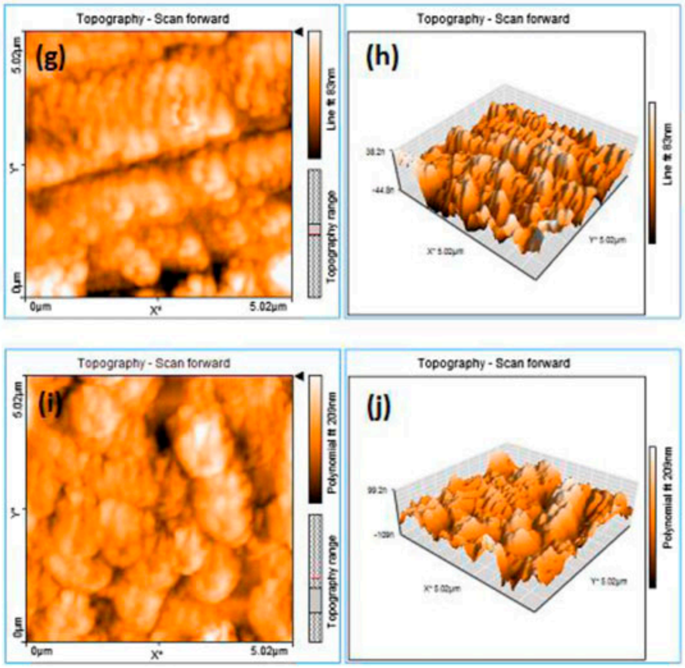


Fig. 4. (*Continued*).

Table 3
The roughness parameters of the membrane surface

Membrane	S_a (nm)	S_q (nm)	S_z (nm)	Mean pore size of surface (nm)
NF_1	2.72	3.49	48.87	28.76
NF_2	4.23	6.1	57.27	24.32
NF_3	6.53	6.31	62.83	20.34
NF_4	10.54	13.92	140.55	14.72
NF_8	24.7	31.50	225.79	11.5

specific physicochemical phenomena should also be considered. It was shown [37] that a positive correlation exists between the rejection of pesticide and its adsorption onto the membrane polymer. Although, adsorption may occur through hydrogen bonding between the pesticide molecules and the hydrophilic functional groups of the membrane material, it has been claimed that hydrophobic interactions between

Table 4
Water contact angle of the membrane surface

Membrane	Contact angle (°)
NF_5	50.85
NF_6	50.65
NF_7	48.25
NF_8	44.75

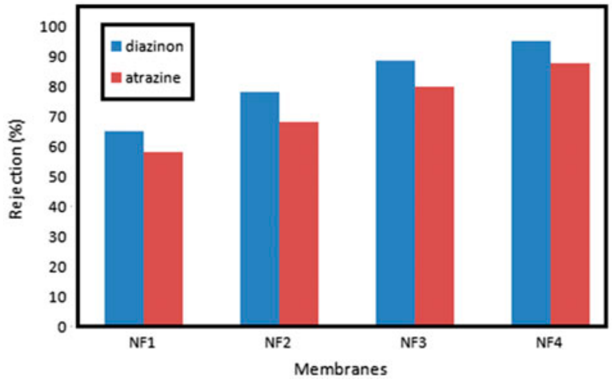


Fig. 5. Rejection of unmodified PA TFC NF membranes during filtration of 0.03 g/L pesticides solution.

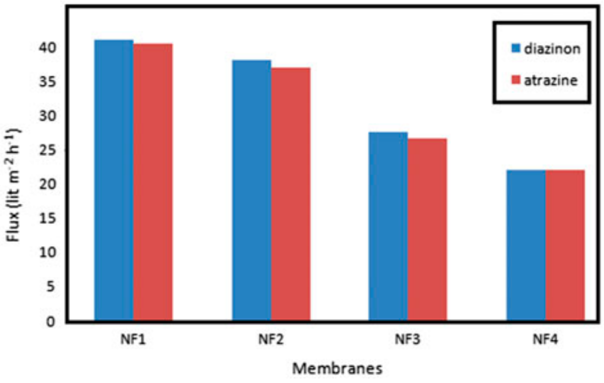


Fig. 6. Flux of unmodified PA TFC NF membranes during filtration of 0.03 g/L pesticides solution.

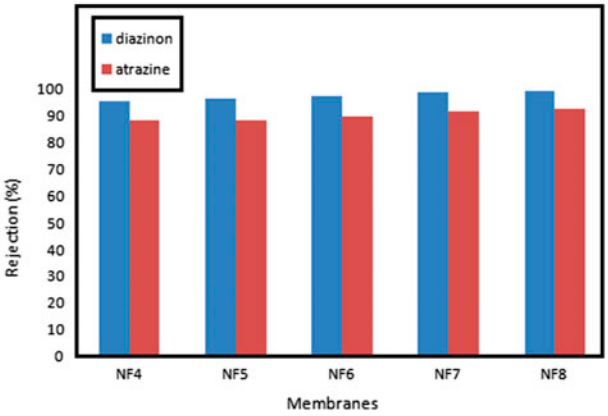


Fig. 7. Rejection of modified PA TFC NF membranes during filtration of 0.03 g/L pesticides solution.

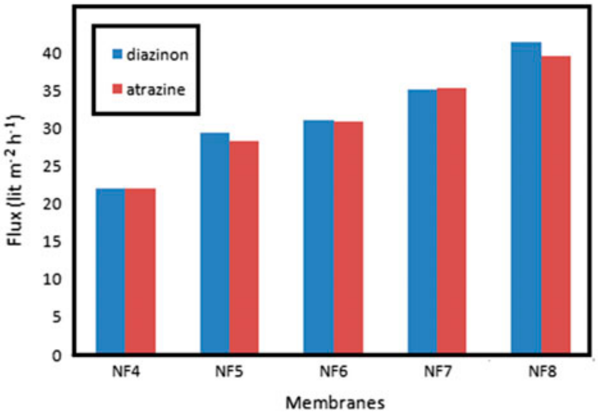


Fig. 8. Flux of modified PA TFC NF membranes during filtration of 0.03 g/L pesticides solution.

hydrocarbon (non-polar) segments of pesticide molecule and membrane are most efficient for pesticide adsorption on the membrane surfaces, which is considered to be the first step of the rejection mechanism [38]. The pesticide molecule hydrophobicity and its rejection by a membrane could be evaluated from the log K_{OW} (octanol-water partition coefficient) value of the pesticide [39]. log K_{OW} values of trace organic molecules differ between −3 and 7, with log $K_{OW} > 2$ distinguishing hydrophobic compounds [40]. As shown in Table 1, both of atrazine and diazinon are hydrophobic in nature. Moreover, according to contact angle data, the obtained PA NF membranes were hydrophilic. Pure water layer is simply formed on hydrophilic membrane, which avoids the adsorption of the hydrophobic pesticides on the membrane surface and leads to a rising of the rejection value [41]. Consequently, the higher the value of log K_{OW}, the better the rejection would be [2]. Therefore, the higher rejection of diazinon might be obtained due to its higher hydrophobicity.

4. Conclusion

Thin-film polyamide nanofiltration membranes were fabricated by interfacial polymerization of PIP and TMC on the PSf UF membrane. The performance of PIP-based NF membranes to retain atrazine and diazinon was investigated. In this study, the prepared TFC NF membranes were modified by addition of TEA to the aqueous phase. The effect of adding TEA on morphology and performance of PA NF membranes were examined. ATR-FTIR analysis proved the formation of the PA barrier layer on the PSf substrate. AFM, SEM, and contact angle measurements indicated that the modification of the thin-film layer with TEA led to increase the roughness, density and hydrophilicity of the PA/PSf composite membranes. It was found that the presence of TEA in aqueous phase increased the permeate flux and atrazine and diazinon rejections. The higher rejection of diazinon compared to atrazine was determined by the size and hydrophobicity (log K_{OW}) of the pesticides. The membrane prepared with high concentration of PIP (2% (w/v)) and modified with TEA (2% (w/v)) was found to be the most appropriate PA TFC NF membrane for the removal of pesticides.

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