Preparation of hydrophile nanofiltration membranes using κ-Carrageenan as additive and application to treatment of anionic colored wastewater

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ABSTRACT

The expansion of various industries, such as the textile industry in the world, has led to the production of dye wastewater, which has caused a lot of pollution and damage to the environment. Therefore, the use of efficient methods such as nanofiltration to treat these wastewaters is one of the most important issues related to the environment. In the present study, in order to prepare the nanofiltration membrane by interfacial polymerization method, piperazine, and toluene diisocyanate monomers in the aqueous and organic phases were used. κ-Carrageenan biopolymer was used in the process of membrane modification to increase the hydrophilicity of the membrane surface and enhance a negative surface charge on it and thus improve the performance of the final membrane in removing anionic pollutes. After preparing nanofiltration membranes, they were tested to remove the anionic dyes. The results showed that the presence of κ-Carrageenan increased the hydrophilicity of the membrane surface and ultimately increased the flux of the membrane, and at the same time not only did not reduce the rejection of the anionic dyes, but increased somewhat. Finally, scanning electron microscopy, atomic force microscopy, Fourier-transform infrared spectroscopy, contact angle, and zeta potential analyzes were used. The results obtained by measuring contact angle confirmed hydrophilicity increase of the membrane surface in the presence of κ-Carrageenan and approved negative surface charge by measuring zeta potential.

Keywords: Nanofiltration; Interfacial polymerization; κ-Carrageenan; Anionic dyes; Negative charge

1. Introduction

Simultaneously with the industrialization of countries and the urban development, dye wastewater from various industries, especially the printing industry and the textile industry, have caused alarming problems in the world [1]. It is estimated that 280,000 tons of wastewater enter the environment every year, including a variety of industrial dyes [2], which is one of the main sources of pollutants that contain complex elements that are very difficult and time consuming to deal with. When dye wastewater enters the environment, it contaminates natural water resources, endangers plants and animal species, and causes diseases such as cancer, asthma, and anemia in humans [3,4]. Therefore, it is important to eliminate dyes and other pollutes and create a suitable environment for access to healthy, quality, and cost-effective water to prevent environmental pollution [5].

For many years, due to lack of facilities and progress, simple methods were used to treat wastewaters. However, today various chemical, physical, and biological methods are used to remove dye from the wastewater, including physical methods such as precipitation, adsorption, reverse osmosis, and filtration [6,7].

Among the available methods, membrane processes play an important role in water purification technology due to advances in membrane fabrication techniques

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and low energy consumption [8]. One of these processes is nanofiltration membranes, which are among the new membrane technologies. In recent years, nanofiltration has been used in various stages of the water treatment process, such as reducing the hardness and amount of salt in water, decolorizing, and removing all kinds of chemical and microbial pollutes. In industrial processes, nanofiltration is also used to remove certain materials such as various dyes from water [9,10].

Nanofiltration is one of the effective methods for removing dye groups from wastewaters. Nanofiltration membranes are formed in several ways, of which interfacial polymerization is the most common. In this technique, a thin active layer is formed on the surface of the membrane through the reaction and copolymerization of two active monomers that dissolve in two immiscible liquids [11,12]. In this reaction, one phase usually contains a nucleophile reactant such as amines and the other contains an electrophile reactant such as isocyanates [13].

Numerous studies have been conducted today to use new monomers in the interfacial polymerization process to improve the functional properties of nanofiltration membranes, including flux, rejection, and fouling. These studies are categorized according to the monomers that affect the surface charge of the active layer, hydrophilicity, and structure [14]. An example of these new monomers is the κ-Carrageenan biopolymer, which is extracted from specific species of red seaweeds [15,16]. κ-Carrageenan, a family of the linear sulfated polysaccharides, is a natural, inexpensive, and environmentally friendly polymer that increases the flux by creating hydrophilic property in membrane and due to having negatively functional groups [17,18], it can enhance a surface charge on active layer surface and using the Donnan repulsion to improve the rejection of anionic dye of wastewater.

In the present study, piperazine monomer in the aqueous phase and toluene diisocyanate in the organic phase were used to interfacial polymerization process. κ-Carrageenan biopolymer was also used as an additive to increase the hydrophilicity of the membrane and enhance a negative charge on the membrane surface.

2. Experiments and methods

2.1. Materials

Polyacrylonitrile (PAN) is a fiber made from textile waste, *n*-hexane and dimethyl formamide (DMF) from Chem Lab (Belgium), piperazine, and polyethylene glycol (PEG) with a molecular weight of 2,000 from Merck (Germany), κ-Carrageenan from Bio. Basic (Canada), 2,4-toluene diisocyanate from Sigma Aldrich, (United States) acid orange 7, acid red 114, and acid blue 92 from Yazd Alvan.

2.2. Fabrication of polymeric substrate membrane

In this study, phase inversion process is used to prepare the porous substrate of membrane [19]. Initially, for polymer solution, PAN 18 w/w%, DMF solvent 78 w/w%, and PEG2000 4 w/w% as a pore former [20] are placed on a magnetic stirrer at 70°C for 48 h. After the dissolution

process is complete, the solution is placed in an ultrasonic bath for 30 min to obtain a completely homogeneous solution. The prepared solution is then casted using a casting knife with a thickness of 255 μm and immediately placed in a water bath at 25°C. After immersion of the cast solution, the solvent surrounding the polymer moves into the non-solvent (water) and causes rapid coagulation of the polymer, formation of the structure, pores, and morphology of the polymer film, and as a result, the ultrafiltration membrane is formed. The resulting membrane is cut to the appropriate size and kept in distilled water until used for the interfacial polymerization process.

2.3. Modification of membrane surface by interfacial polymerization method

In order to perform the interfacial polymerization reaction and to modify the substrate surface [14] prepared from the previous section, two immiscible liquids (aqueous and organic phases) are required. In this study, the aqueous phase containing piperazine monomer and the organic phase including toluene diisocyanate monomer have been used to form the polyurea active layer. Thus, the substrate membrane is first immersed in the aqueous phase with a concentration of monomer piperazine of 2 w/v%, and after 2 min, it is removed from the solution and dried on a filter paper. Then the organic phase, which is prepared by dissolving the 0.3 w/v% toluene diisocyanate monomer in *n*-hexane, is poured on the membrane for 1 min to polymerization reaction. In the next step, the membrane is placed in an oven at 70°C for 5 min and after removing the membrane from the oven, it is kept in distilled water until tested.

2.4. Use of κ-Carrageenan biopolymer in membrane surface modification

To investigate the effect of κ-Carrageenan on membrane performance, 0.06 w/v% κ-Carrageenan is dissolved in distilled water at a temperature of 70°C and added to the aqueous phase containing piperazine and it is used for the interfacial polymerization reaction in the mentioned method (section 3.2 – SEM analysis). In order to better compare the modified membranes via interfacial polymerization in the presence κ-Carrageenan (PAN/PIP/κ-Car) and without the presence of κ-Carrageenan (PAN/PIP), all reaction conditions, including immersion time in the aqueous phase, time of polymerization reaction, duration of stay in the oven, and oven temperature are kept constant.

2.5. Membrane performance test

In this study, in order to investigate the performance of nanofiltration membranes, a cross flow filtration system has been used, which a schematic is presented in Fig. 1.

Initially, the feed tank is filled with feed solutions containing a variety of anionic dyes (Table 1) with specific concentrations, and after placing the desired membrane inside the cell, by turning on the pump, the filtration starts under constant pressure. After sufficient time and the filtration process has reached a stable state, the amount

of output water is measured in units of time and according to the cross-sectional area of the membrane in contact with the feed solution, flux, and membrane permeability [21] calculated from Eq. (1):

$$L_p = \frac{J_w}{\Delta P}\left(L/m^2 \cdot h \cdot bar\right) \tag{1}$$

where the J_w is flux of water permeated through membrane and ΔP is the effective pressure on the membrane.

Also, in order to calculate the rejection rate of feed solutions containing anionic dyes, the absorption rates of feed and permeate solutions were measured using an absorption spectrophotometer (GBC Scientific Equipment Ltd., – Cintra 101 – UV-visible spectrometer, Australia). Finally, their rejection rate [19] was calculated using Eq. (2).

$$R\left(\%\right) = \left[1 - \frac{C_p}{C_a}\right] \times 100 \tag{2}$$

where C_p and C_a are the concentrations of permeate and feed solutions, respectively.

2.6. Determining the characteristics of nanofiltral membranes

Infrared spectroscopy (FT-IR IBB Bomem MB-100, Canada) was used to investigate the chemical structure of nanofiltral membranes, and scanning electron microscopy (SEM; VEGA\\TESCAN-LMU, Czech Republic) was used to observe their morphology. Also the atomic force microscopy (AFM; multi-model AFM) was used to investigate the roughness parameter of the membranes surface fabricated during this study. In addition, in order to study the hydrophilicity of the membranes surface, contact angle analysis (VEHO USB microscope 400×) was performed. Finally, by measuring the zeta potential (BROOKHAVEN OMNI/nanobook), United States for modified membranes, the effect of κ-Carrageenan biopolymer on the surface charge of the membranes was determined.

3. Discussion and results

3.1. FT-IR analysis

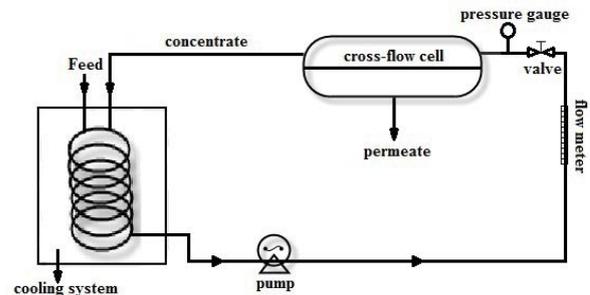In the present study, Fourier-transform infrared spectroscopy (FT-IR) spectroscopy has been used to investigate

Fig. 1. Schematic of cross-flow filtration system.

Table 1
Types of anionic dyes used in this study

Dyes	Chemical formula	Structural formula	M_w (g/mol)	λ_{max} (nm)
Acid orange 7	$C_{16}H_{11}N_2NaO_4S$		350.32	484
Acid red 114	$C_{37}H_{28}N_4Na_2O_{10}S_3$		830.8	511
Acid blue 92	$C_{26}H_{16}N_3Na_3O_{10}S_3$		695.58	569
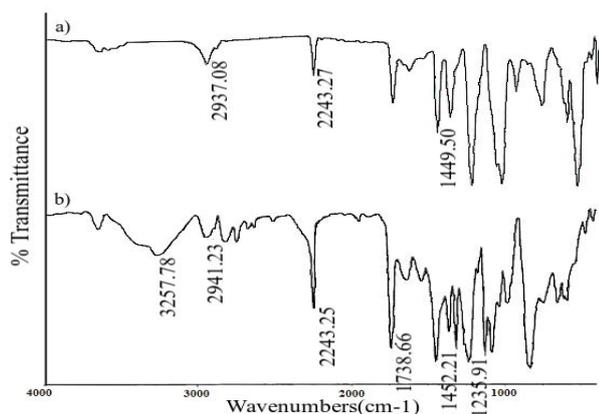
Fig. 2. FT-IR spectra obtained from (a) substrate membrane and (b) PAN/PIP membrane.

Fig. 3. FT-IR spectra obtained from (a) PAN/PIP/κ-Car (0.06 w/v%) membrane and (b) κ-Carrageenan powder.

and identify synthesized membrane compounds [22]. Fig. 2 the spectra of the substrate membrane and PAN/PIP membrane show that after examining the absorption peaks in the FT-IR spectra obtained from both membranes, the results are presented as follows:

According to Fig. 2a, a medium-intensity peak at 2,243 cm^{-1} indicates the presence of a nitrile group (C≡N) in the PAN polymer chain. Absorption in the 2,937 cm^{-1} region is also related to the stretching vibration of the C–H bond in the PAN, and the absorption peak in the 1,449 cm^{-1} region also indicates the bending vibration of CH$_2$ groups in the PAN chain. In Fig. 2b, in addition to the peaks related to the substrate membrane, the presence of peaks in the 3,257 cm^{-1} region indicates the stretching N–H bond. Also, the peak observed in 1,738 cm^{-1} shows C=O bond and in 1,235 cm^{-1} region it proves the presence of C–N [23]. Therefore, as expected, the spectra obtained from the sample membranes well show the presence of polyurea composition after the interfacial polymerization process.

Also, in order to investigate the presence of κ-Carrageenan in the membrane surface modification process, FT-IR spectra related to κ-Carrageenan powder and PAN/PIP/κ-Car (0.06 w/v%) membrane in Fig. 3 are given. In the κ-Carrageenan spectrum (Fig. 3b), the strong peak in 3,426 cm^{-1} shows the OH groups in its structure. Also, peaks in 2,915; 1,640; 1,382; and 1,262 cm^{-1} represent the C–H, C–C, S=O, and C–O bonds, respectively, in the composition of κ-Carrageenan [16,23]. The spectrum of the PAN/PIP/κ-Car (0.06 w/v%) membrane (Fig. 3a) in addition to having the above-mentioned peaks, includes polyurea-indicating peaks, which in most cases have been merged.

3.2. SEM analysis

In this section, images obtained from SEM are also used to study and compare the morphology [24] of three samples of substrate, PAN/PIP, and PAN/PIP/κ-Car (0.06 w/v%) membranes in Figs. 4 and 5. Although the results of this test alone are not sufficient to prove the formation of a thin active layer, in the images obtained from the cross-section of these samples, the formation of the polyurea active layer on the substrate membrane
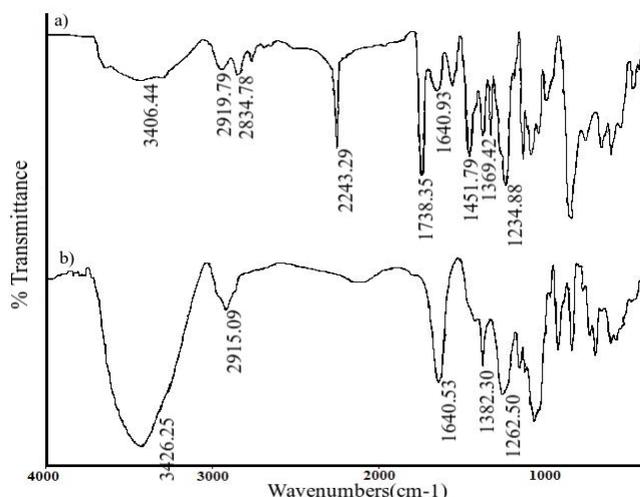
is somewhat clear. Also, the thickness of this layer is measured and shown in each image.

Fig. 5 shows the images obtained from the surface of the samples by SEM. As can be seen from the images, the polymeric substrate membrane (Fig. 5a) has a uniform surface and no pores are observed on it. However, after the interfacial polymerization reaction (Fig. 5b), the morphology of the membrane surface changes, which proves the formation of a polyurea active layer on it. At the surface of PAN/PIP/κ-Car (0.06 w/v%) membrane (Fig. 5c) there are also changes compared to the surface of the substrate membrane, but compared to the surface of PAN/PIP membrane (Fig. 5b) shows a more uniform surface.

3.3. AFM analysis

In order to investigate the surface roughness parameter of the membranes prepared during this research, images obtained from the AFM [25] have been used. Comparison of Figs. 6a and b shows that via interfacial polymerization process on the substrate membrane, the surface roughness decrease. This reduction in roughness can be attributed to the use of difunctional toluene diisocyanate monomer. Because the time of use as organic phase monomer, unlike the trifunctional and widely used trimesoyl chloride monomer, which forms a network polymer, causes the formation of a linear polymer in the polymerization reaction [14,26], thus reducing the roughness of the membrane surface.

As shown in Fig. 6c, addition of κ-Carrageenan in the interfacial polymerization process increases the roughness of the membrane surface. Although the increase in membrane permeability with the addition of κ-Carrageenan is due to the increase in hydrophilicity of the membrane surface. However, increasing the roughness of the membrane surface also increases the surface area and ultimately increases the rate of diffusion into the membrane and can increase the amount of membrane flux slightly [14].
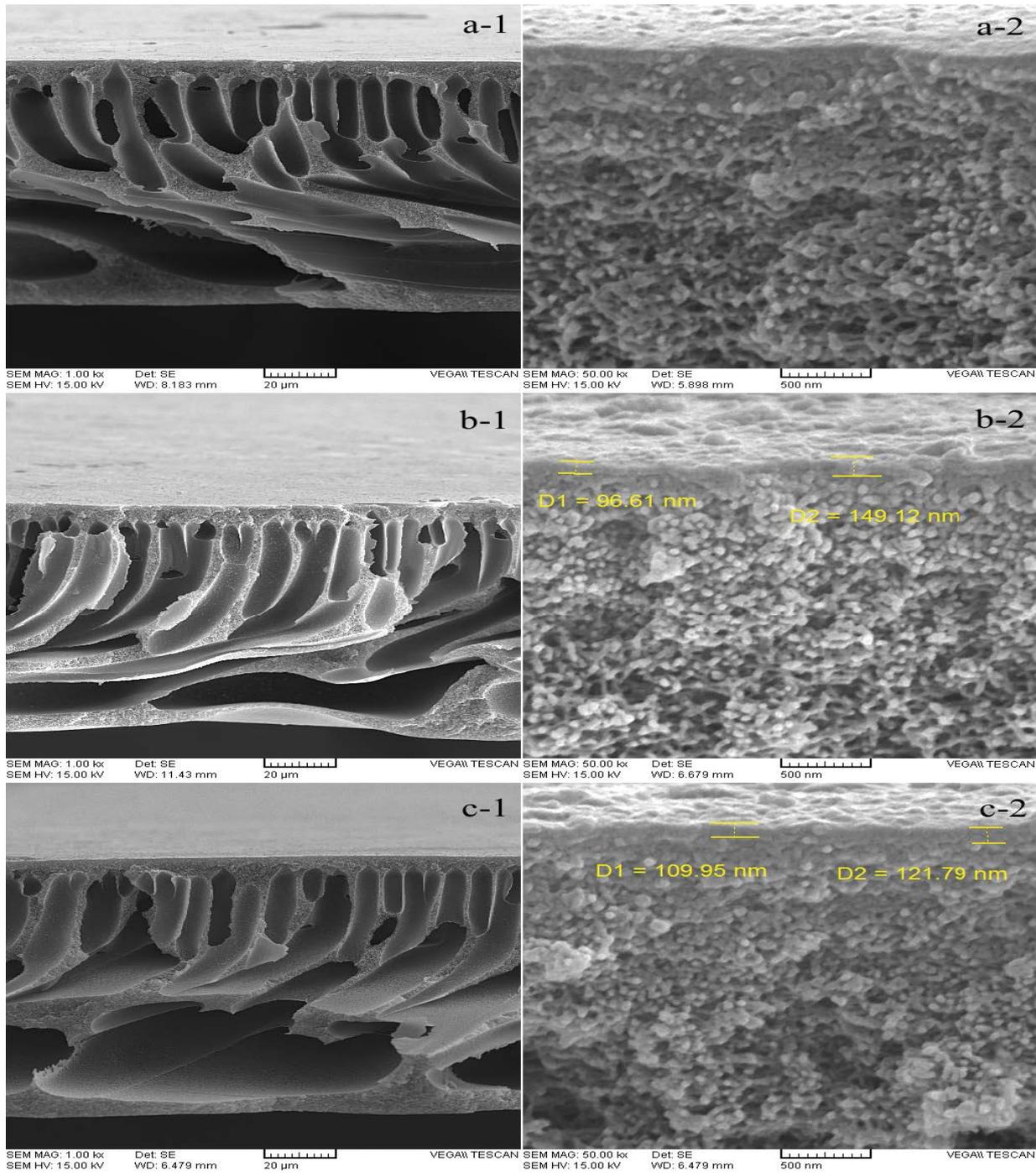
Fig. 4. Cross-section SEM images on the scale 20 μm and 500 nm of (a) substrate membrane, (b) PAN/PIP membrane, and (c) PAN/PIP/κ-Car (0.06 w/v%) membrane.

Also for better comparison of PAN/PIP/κ-Car membranes and to investigate the effect of κ-Carrageenan on surface roughness, three samples with different values (0.03, 0.06, and 0.15 w/v%) of κ-Carrageenan were analyzed (Fig. S1).

3.4. C.A. analysis

In this study, the contact angle test to measure the hydrophilicity of membrane surface [27] was performed on substrate membrane, PAN/PIP membrane and PAN/PIP/κ-Car (0.06 w/v%) membrane and its results are as follows. According to Fig. 7 via interfacial polymerization and the formation of polyurea active layer on the substrate membrane, the reduction of contact angle from 66° to 61° is observed. As expected, the presence of 0.06 w/v% κ-Carrageenan biopolymer in the membrane modification process reduced the contact angle to 48°. These results clearly show that the addition of this hydrophilic
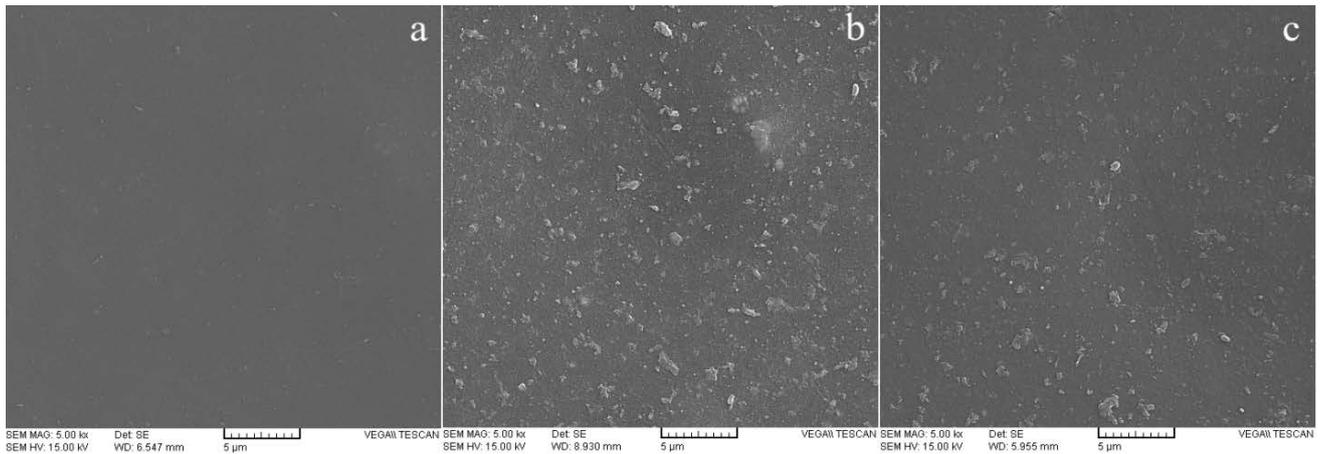
Fig. 5. Surface SEM images on the scale 5 μm of (a) substrate membrane, (b) PAN/PIP membrane, and (c) PAN/PIP/κ-Car (0.06 w/v%) membrane.

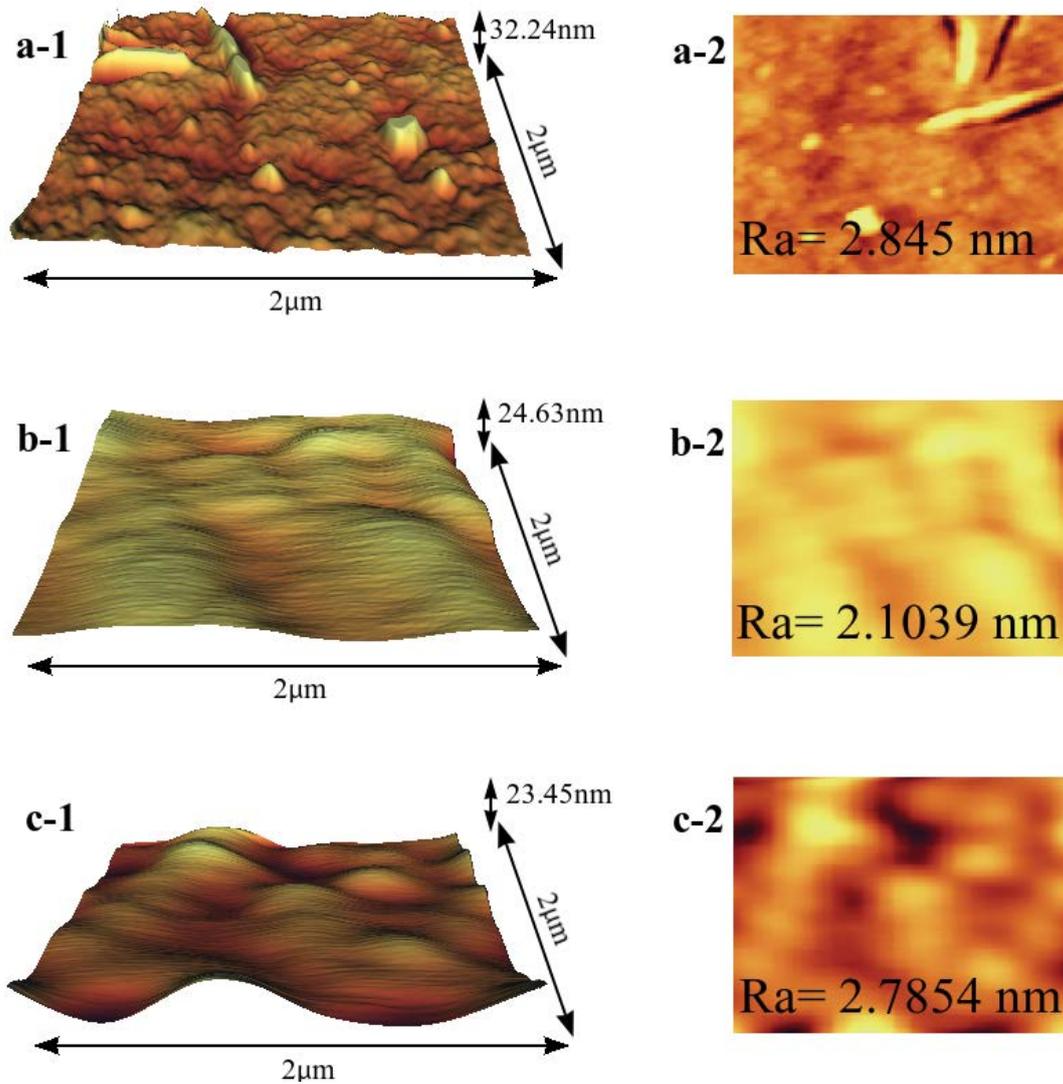Fig. 6. 2D and 3D images of AFM on the scale 2 μm of (a) substrate membrane, (b) PAN/PIP membrane, and (c) PAN/PIP/κ-Car (0.06 w/v%) membrane.
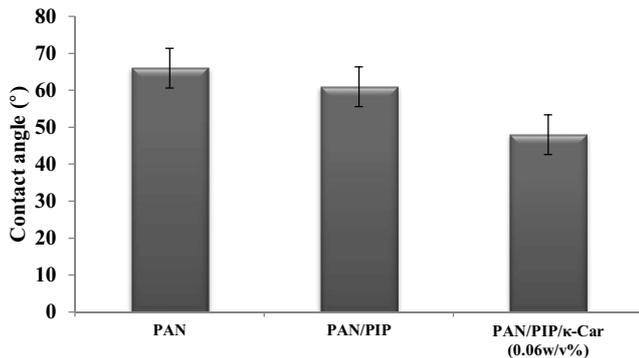
Fig. 7. Results obtained from contact angle analysis.

polymer significantly reduces the contact angle and leads to an increase in the hydrophilicity of the membrane surface [28].

In addition, to observe the effect of using different amounts of κ-Carrageenan, the contact angle test was performed on modified membranes with different percentages of additive and the results are shown in the Fig. S2.

3.5. ZP analysis

Measuring the zeta potential of nanofiltration membranes is usually performed to prove the surface charge of the membrane [21]. Since one of the purposes of using κ-Carrageenan in this study was to fabricate membranes with negative surface charge, it is necessary to use Zeta potential analysis for modified membrane without additive and modified membrane in the presence of κ-Carrageenan. Therefore, samples of the above-mentioned membranes have been analyzed and the results are presented in Table 2. The final results of the calculations indicate a negative charge on the membrane surface due to the use of κ-Carrageenan in the interfacial polymerization process.

3.6. Performance of nanofiltration membranes in the removal of anionic dyes

The purpose of using κ-Carrageenan in the modification process of nanofiltration membranes is to increase the hydrophilicity of the membrane and enhance a negative charge on the membrane surface, which increases the efficiency of removing colored contaminants, especially anionic dyes, using the Donan effect. In this study, three types of anionic dyes with molecular weights and the number of different functional groups were used to investigate the performance of modified membranes in the presence of κ-Carrageenan and their compare with non-additive membranes. Initially, feed solutions were

Table 2
Results from the measurement of zeta potential

Membrane	Zeta potential (mV)	PH
PAN/PIP	−1.87	5.60
PAN/PIP/κ-Car (0.06 w/v%)	−5.244	5.71

prepared from each sample at a concentration of 50 ppm and used for both PAN/PIP and PAN/PIP/κ-Car nanofiltration membranes for filtration process under 3 bar pressure. Since the measurement of rejection and permeability are parameters related to membrane performance, these parameters were calculated for each sample during the filtration process and the results are shown in Table 3.

As the results of Table 3 show, due to the surface charge of PAN/PIP/κ-Car membranes and the use of the Donnan repulsion mechanism, the permeability of the modified membrane in the presence of κ-Carrageenan compared to the non-additive membrane has increased more than double and in all cases, the rejection rate did not decrease, it even increased. The results also show that as the number of functional groups of samples increases – regardless of their molecular weight – the rate of rejection increases. For example, although acid blue 92 has a lower molecular weight than acid red 114, it has a higher rejection rate due to its larger number of functional groups.

One of the major problems in using membranes on an industrial scale is the phenomenon of membrane fouling. Therefore, improving the performance of the membrane and its anti-fouling property is of particular importance [29]. In this study, in order to investigate the effect of κ-Carrageenan on the anti-fouling properties of synthesized membranes, feed solutions with a concentration of 50 ppm of anionic dyes were prepared and the filtration process was performed for 4 h at 3 bar pressure and at 25°C for PAN/PIP and PAN/PIP/κ-Car (0.06 w/v%) membranes, the results of which are shown in Fig. 8.

As Fig. 8 show, at the beginning of the filtration process, the permeability of the PAN/PIP/κ-Car (0.06 w/v%) membrane is more than double the permeability of PAN/PIP membrane for all three samples. As the filtration process continues, the L_p values in both membranes decrease, and after about 2 h of filtration, this decreasing trend stops, and the graph becomes stable. It is also observed that the L_p curve of the modified membrane in the presence of 0.06 w/v% κ-Carrageenan (Fig. 8b) has a lower slope compared to the modified membrane without additive (Fig. 8a).

In the stable state, the values of the permeability of the PAN/PIP/κ-Car (0.06 w/v%) membrane for feed solutions of acid orange 7, acid red 114, and acid blue 92, were reported to be 4.3, 3.2, and 3, respectively. Also,

Table 3
Results from the filtration process under 3 bar pressure to remove anionic dyes (concentration of feed solutions: 50 ppm)

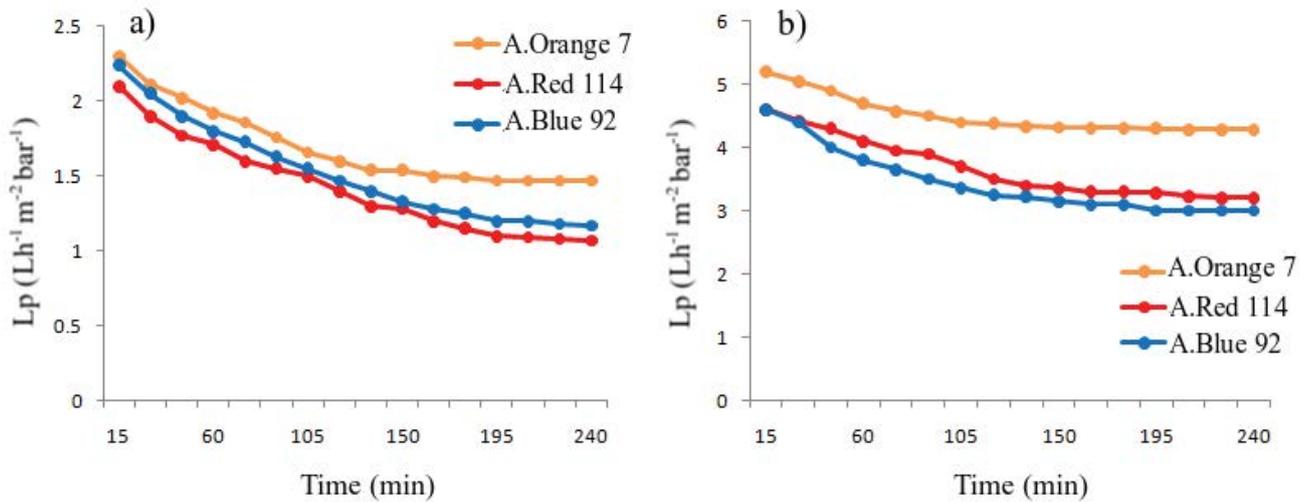| Membrane	$L_{p\text{(pure water)}}$	$\%R_{\text{A. Orange 7}}$	$\%R_{\text{A. Red 114}}$	$\%R_{\text{A.Blue 92}}$
PAN/PIP	2.7	55.2	74.4	82.9
PAN/PIP/κ-Car (0.06 w/v%)	6.1	65.4	85.6	93

Fig. 8. Changes in the permeability of feed solutions with a concentration of 50 ppm during filtration time at 3 bar pressure: (a) PAN/PIP membrane and (b) PAN/PIP/κ-Car (0.06 w/v%) membrane.

the L_p values of the PAN/PIP membrane of 1.5, 1.1, and 1.2 were obtained, respectively, which show a lower rate compared to the PAN/PIP/κ-Car (0.06 w/v%) membrane. These results indicate the improvement of membrane permeability and fouling resistance due to the use of κ-Carrageenan biopolymer in the membrane modification process, which is due to the presence of negative charge on the surface of the modified membrane and the removal of anionic dyes with the help of Donnan effect [29–31].

4. Conclusion

In the present study, interfacial polymerization method was performed using piperazine and toluene diisocyanate monomers to prepare nanofiltration membranes with negative surface charge and to investigate the effect of κ-Carrageenan biopolymer in the removal of anionic dyes. In the next step, κ-Carrageenan was used to increase hydrophilicity and enhance a surface charge on the membrane.

To investigate the performance of the synthesized membranes, filtration testing was performed for three types of anionic dyes. The results showed that the flux of the modified membrane increased in the presence of 0.06 w/v% κ-Carrageenan in comparison with the modified membrane without additive, and as a result, the hydrophilicity of the membrane increased. Also, the study of the fouling phenomenon shows better anti-fouling performance in the presence of the optimal amount of κ-Carrageenan. In addition, by measuring the rejection of anionic dyes solution, it was found that the percentage of deletion for samples increases with the number of more anionic groups. Thus, acid blue 92 had the highest rejection rate and acid orange 7 had the lowest removal rate.

Finally, by measuring the contact angle, an increase in the hydrophilicity of the membrane was well demonstrated after the addition of κ-Carrageenan to the membrane modification process. Also, the negative charge on the membrane surface was proved in the presence of additive by zeta potential analysis. In addition, FT-IR spectroscopy was used to identify the thin layer of polyurea on the surface of the substrate membrane. The SEM test also partially revealed the formation of a thin active layer during the interfacial polymerization process on the surface of the substrate membrane, and after performing AFM analysis, it was found that with the formation of this thin layer, the roughness of the membrane surface is reduced.

Symbols

L_p	—	Membrane permeability, L/m² h bar
J_w	—	Flux of water permeated through membrane L/m² h
ΔP	—	Effective pressure on the membrane bar
R	—	Rejection rate, –
C_p	—	Concentrations of permeate solution, g/L
C_a	—	Concentrations of feed solution, g/L

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Appendix

As shown in Figs. S1a–c, increasing the amount of κ-Carrageenan in the interfacial polymerization process increases the roughness of the membrane surface. This result confirms the increase in membrane permeability following the use of higher amounts of κ-Carrageenan, as described in the previous sections.

Contact angle test was performed on three samples of modified membranes in the presence of different amounts of κ-carrageenan and the results are as follows. According to Fig. S2, the presence of only 0.03 w/v% κ-Carrageenan biopolymer in the membrane modification process reduced the contact angle to 54°. In addition, a comparison the values obtained from the modified membranes with different percentages of κ-Carrageenan shows that an increase in the amount of use of this hydrophilic polymer leads to a decrease in the contact angle and thus an increase in the hydrophilicity of the membrane surface.
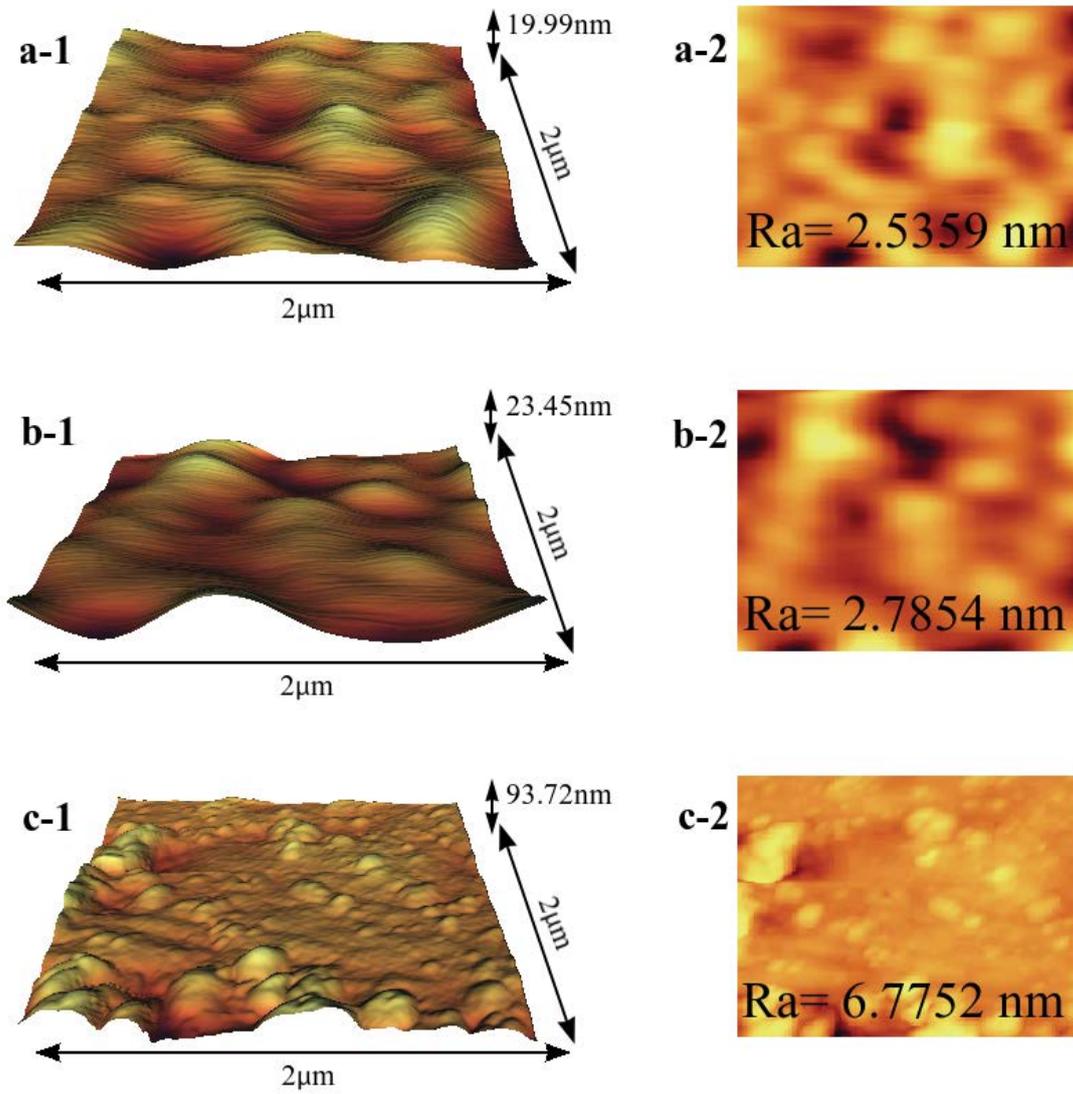
Fig. S1. 2D and 3D images of AFM on the scale 2 μm of (a) PAN/PIP/κ-Car (0.03 w/v%) membrane, (b) PAN/PIP/κ-Car (0.06 w/v%) membrane, and (c) PAN/PIP/κ-Car (0.15 w/v%) membrane.
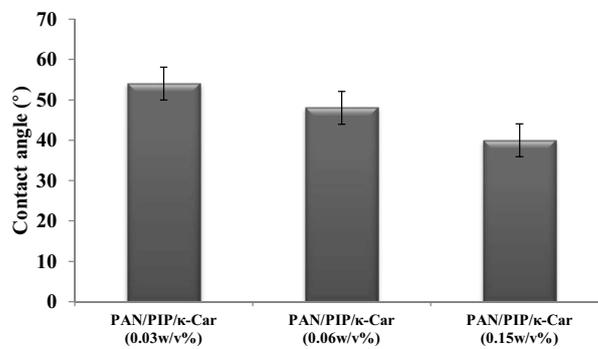

Fig. S2. Results obtained from contact angle analysis.