

## Preparation of polyethersulfone membrane with copper oxide nanoparticle for hydroquinone removal from waste water

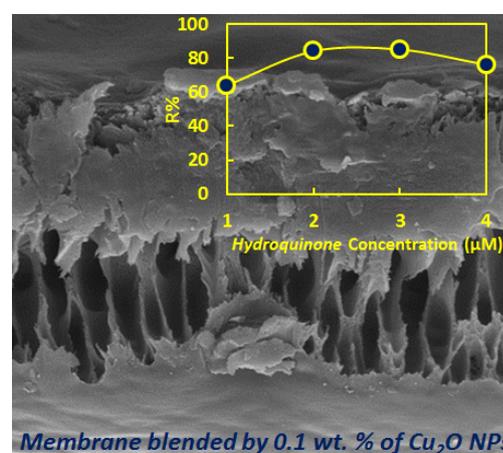
Safora Ghiasi, Hamideh Roshanfekar \*, Hossein Peyman

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Department of Chemistry, Ilam branch, Islamic Azad University, Ilam, Iran

### Abstract

The hydrophobicity of the surface of polyethersulfone causes negative effects on membrane performance. One of the applicable and suitable methods to improve the performance of the polymeric membrane is the addition of nanoparticles. Here, copper oxide nanoparticles (Cu<sub>2</sub>O NPs) were used to modify the surface of the membrane. Nanofiltration membrane based on polyethersulfone polymer was prepared by dimethylacetamide as a solvent, polyethylene glycol as pore-maker, and Cu<sub>2</sub>O NPs as a modifier of the membrane properties, using the reverse-phase technique. The membranes were structurally studied by FTIR, SEM, EDX, AFM techniques. Results have shown that the membranes with different concentrations of nanoparticles perform differently. Modified membranes with higher amounts of Cu<sub>2</sub>O NPs showed improved pure water flux, porosity, and antifouling property due to increased hydrophilicity. The modified membrane containing 0.5 wt.% Cu<sub>2</sub>O showed the best results. In higher concentrations like 1 wt.%, the agglomeration of nanoparticles fills the pores, reduces the porosity, and decreases the flux. Nanofiltration performance was also examined by removal of hydroquinone.



Membrane blended by 0.1 wt. % of Cu<sub>2</sub>O NPs

**Keywords:** Membrane, Polyether sulfone, Nanofiltration, Copper oxide, Nanoparticles.

### Introduction

Providing sufficient healthy water for beverage, industrial, and agricultural purposes is one of the important factors for the sustainable development of societies. In recent years, the lack of rains and pollution of water resources with urban and industrial wastewaters have forced humans to purify urban and industrial wastewater. In this way, from one side we will be able to stop the high pollution of water resources and on the other hand, can employ the purified wastewater for other non-drinking purposes.

In every society, more than 70% of the consumed water has been converted to wastewater. Furthermore, more than 99.9% of urban wastewater is constructed of water and the rest is solid material.<sup>1</sup> Wastewater could be counted as a potential water source. For the utilization of wastewater, the purification methods must be improved to convert it to applicable non-drinking water.<sup>2,3</sup>

In advanced wastewater treatment, different methods such as sand filtration, reverse osmosis, membrane, surface

adsorption, advanced oxidation, natural treatment, and other techniques are employed to reuse wastewater for non-urban applications. One of the most common methods of wastewater preparation for reusing is filtration.<sup>4</sup> In recent years, membranes and membrane processes have improved and expanded from research areas to industrial applications. Membranes and membrane processes have various applications such as chemical, medicinal, food, biotechnology, and environmental (e. g. water treatment, drinking water production) industries. They have significant advantages such as energy-saving, simple and clean technology, high-purity product, and flexibility in system design. The key features of membranes are controllable diffusion of species and types of chemical species.<sup>5</sup> Membrane technologies were first used for drinking water filtration of Germany army.<sup>5</sup>

Researches for extended use of this technology were granted by the United States of America and finally were exploited by Millipore Company, the first and largest producer of microfilters. In past, the largest application of microfiltration was in beverage

\*Corresponding authors: Hamideh Roshanfekar, Email: [roshanfekarhamide@gmail.com](mailto:roshanfekarhamide@gmail.com)

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industries (0.45  $\mu\text{m}$ ), commercial cold sterilization for medicinal purposes (0.2  $\mu\text{m}$ ), and supplying pure water in semiconducting processes (0.1  $\mu\text{m}$ ). Until 1960, despite the fundamental principles of modern membranes, no important industries have existed in this area. Later, by fixing some disadvantages such as high price, time-consuming processes, non-selective, etc. the membranes have transferred from laboratory to industry.

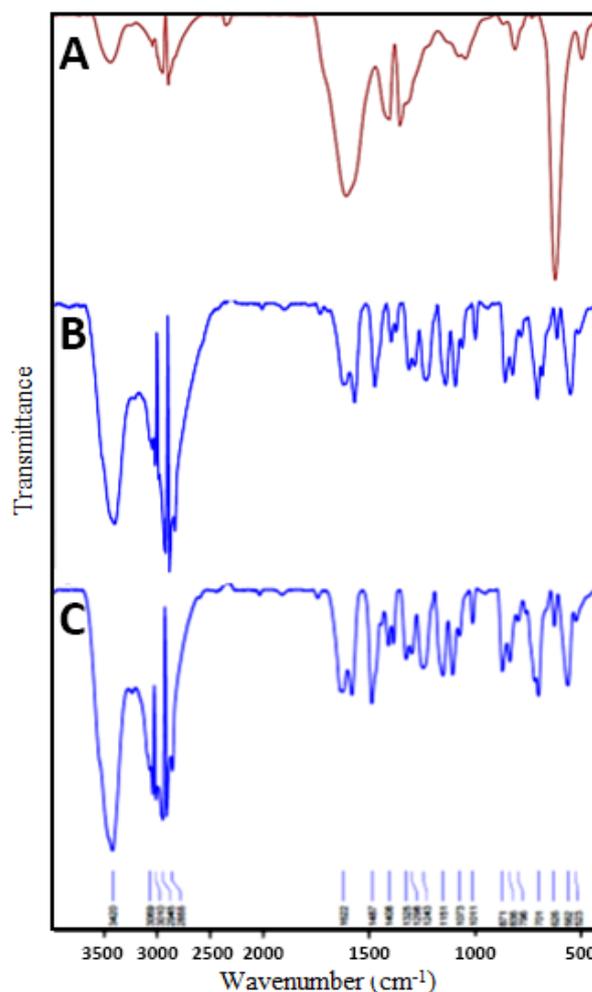
Common polymers for the fabrication of nanofiltration (NF) membrane are aromatic polymers such as polyamides, polysulfones, polyimides, or other copolymers. Lately, the highly cross-linked polymers have been used because using them may cause high strength and stability of the polymer in high or low pH values, high temperatures, and organic solvents. Fabrication of ceramic NF membranes is also possible, however, even now the pore size of these membranes is rather large.

In phenolic compounds, one or multiple hydroxyl groups are bonded to a benzene ring. Aromatic hydrocarbons with the production rate of millions of tones, yearly, are the highest volume of produced chemicals. One of the most important compounds is hydroquinone with the molecular formula of  $\text{C}_6\text{H}_4(\text{OH})_2$  (with the names of dihydroxy benzene, 1,4-benzoicidyl, 1,4-dihydroxy benzene, p-benzoicidole) which is highly soluble in water and very applicable in photography, cosmetic, rubber manufacturing, antioxidant production, and chemical and agricultural compounds industries. Due to the presence of wastewater in the mentioned industries and hazardous effects, using an efficient purification system is urgent for environmental protection.<sup>6</sup>

Hydroquinone (HQ) have extensively used as a dyeing agent in cosmetics, medicines, the environment, and the human diet. This compound could be oxidized to benzoquinone, which is potentially one of the blood and gene poisoning compounds and carcinogenic. Every gram of hydroquinone in aqueous media can make 1 g 5-day biochemical oxygen demand (BOD5) and 1.83 g chemical oxygen demand (COD). Phenol, hydroquinone, and benzene are very carcinogenic. There is potential exposure to hydroquinone through inhalation, digestion, and skin contact. If being contacted with the eye may cause irritation, serious damage to the eye, and a skin allergic reaction. Due to the presence of hydroquinone in the wastewater of the mentioned industries and its toxic effect, its removal is so urgent. Various studies for the removal of these compounds have been done with different physical, chemical, and biological methods.<sup>7</sup>

Some of the most important non-biologic methods in the removal of cyclic and hydroquinone-type compounds are Fenton, chemical oxidation, electrochemical, adsorbents, and enzymatic treatment procedures.<sup>8</sup> Advanced oxidation procedures are one of the most efficient processes in the decomposition of resistant compounds. Today, the advanced oxidation processes have achieved so many interests due to their high efficiency for the removal of resistant organic pollutants. Advanced oxidation methods have based the production of oxidizing agents such as hydroxyl radicals. They can effectively and selectively oxidize a large number of pollutants.

In this study, a pure sulfone polyether membrane with a certain percentage of polyether sulfone and four membranes modified with copper oxide ( $\text{Cu}_2\text{O}$ ) nanoparticles with a 4% difference of copper oxide nanoparticles were prepared. After membrane preparation, several membrane functional tests were performed. The effect of adding different concentrations of nanoparticles in a polymer solution on the performance and structure of membranes is investigated. Results showed the membranes with different concentrations of nanoparticles perform differently.



**Figure 1.** The FTIR spectra of (A)  $\text{Cu}_2\text{O}$  NPs, (B) pure polyethersulfone membrane, and (C) the modified polyethersulfone membrane with  $\text{Cu}_2\text{O}$  NPs.

## Experimental

### Materials and methods

Polyethersulfone was purchased from the SEF Company. Other chemicals including dimethyl acetamide, polyethylene glycol 400, sodium dodecyl sulfate, ascorbic acid, copper(II) acetate dihydrate, cow serum, deionized water, NaOH, and hydroquinone were purchased from Merck without further purification. In this research, a pure polyethersulfone membrane with a specific amount of polyethersulfone and modified four membranes with copper oxide ( $\text{Cu}_2\text{O}$ ) nanoparticles with four different amounts of copper oxide nanoparticles were prepared. After preparation, many membrane performance experiments were done.

### Synthesis of copper oxide nanoparticle

The solution of  $\text{Cu}(\text{AC})_2 \cdot \text{H}_2\text{O}$  (copper(II) acetate) was mixed with the aqueous solution of NaOH and stirred. The blue precipitant of  $\text{Cu}(\text{OH})_2$  was instantly formed. Then, ascorbic acid was added to the solution. The solution was stirred in room condition for 5 minutes. During this process, the color of the solution was changed from blue to dark yellow and then orange, which shows the formation of  $\text{Cu}_2\text{O}$ . Finally, the precipitants were centrifuged from the solution at 4000 rpm for 5 minutes. They were rinsed well by pure water and pure ethanol and dried in an oven for multiple hours.<sup>9</sup>

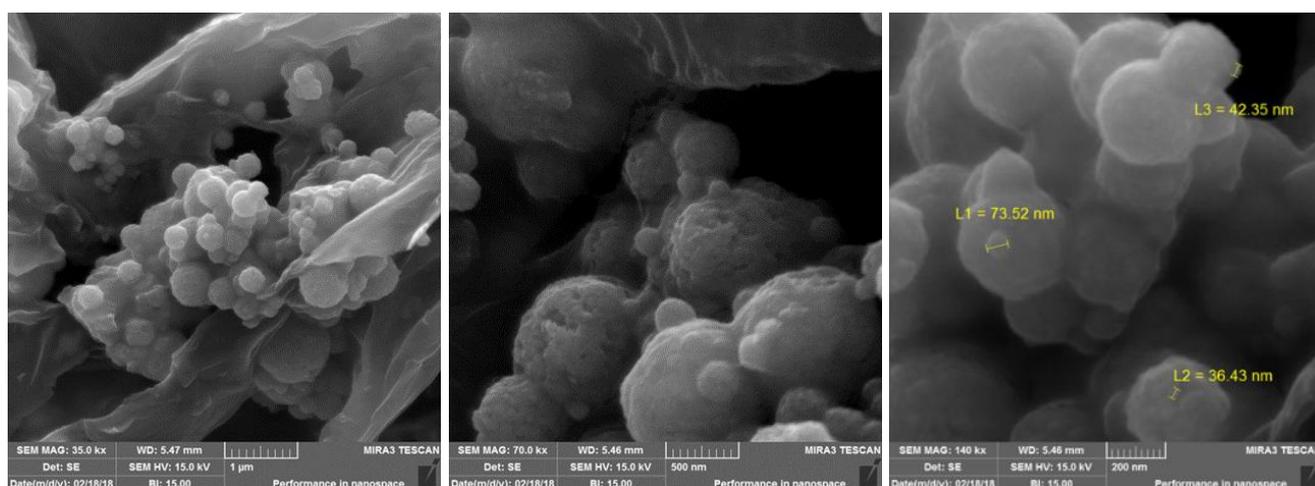


Figure 2. The SEM images of  $\text{Cu}_2\text{O}$  NPs.

### Membrane preparation

For the preparation of the membrane solution, the needed amount of the polymer was weighted and was dried in the oven at  $60\text{ }^\circ\text{C}$  for removal of moistures. Then, the dimethylacetamide solvent and polyethylene glycol additive were weighted according to the weight of the polymer. All membranes were prepared by the reverse-phase method. In the first step, a solution was prepared for the membrane. Before preparing the solution, the nanoparticles were prepared. According to Shen et al., if the nanoparticles have added to the impure solution, it would not be effective. Therefore, to increase dispersion, the inorganic nanoparticle was prepared as a following method.<sup>10</sup>

### Inorganic nanoparticle preparation

The pH value of 1000 mL deionized water was reduced to 4. The aqueous solution of 1.24 wt.% sodium dodecyl sulfate (SDS) was prepared. 0.355 g of inorganic nanoparticles was added to them and stirred for 8 hours. Then, the solution was centrifuged and the inorganic nanoparticle was collected. It was dried for 8 hours at  $60\text{ }^\circ\text{C}$  to remove the remained water amount. After drying, the particles are ready to be added to the membrane.

### Preparation of pure membrane solution

Half of the calculated dimethylacetamide was added to a volumetric flask and stirred fast. The calculated polyethersulfone (PES) was slowly added. After adding the whole PES, the rest of the dimethylacetamide was added to the solution and stirred in a  $60\text{ }^\circ\text{C}$  water bath for 6-8 hours to solve all PES. Later, the solution was kept away for 24 hours, so that the bobbles exit from the solution. Then, the solution was sonicated for 30 min in  $35\text{ }^\circ\text{C}$ .<sup>11</sup>

### Preparation of the modified membrane solution

The half of calculated dimethylacetamide (DMAC) was added to a beaker and stirred fast. Then the nanoparticle was slowly added. The solution was stirred for 10 min. Then, PES was slowly added, and after the addition of the whole PES, the rest of DMAC and PEG was added. The solution was stirred in a water bath at  $60\text{ }^\circ\text{C}$  for 6-8 hours till the whole PES is dissolved. Then, the solution was sonicated for 30 minutes at  $35\text{ }^\circ\text{C}$ .

### Making thin films

The membranes were fabricated by a reverse-phase method. A specific amount of the prepared solution was dropped on a glass plate and it was uniformly coated with the thickness of 160 nm on

the surface of the plate using a thin film-maker. Then, the coated plate was kept for 30 seconds in the atmosphere to exit the bubbles. Later, it is floated in a water bath for 2 minutes so that the reverse phase process happened and the coagulated membrane was separated from the glass plate. With the increase of solvent interaction, its solubility in polymeric solution has reduced and the phase separation was faster. In this step, the reverse phase happens so that a single phase has converted to two phases; polymer-rich and polymer-free phases. After that, the separated membrane was kept in another bath for 24 hours to complete the phase change process and exit the water-soluble organic solvent from the polymeric film. Finally, the membrane is ready for the characterization test.

Table 1. The amount of needed material for preparation of 15 g polymeric solution with 18 wt.% PES.

Material	Amount
PES	2.7 g
DMAC	11.4 g
PEG 400	0.9 g

Table 2. The amount of needed material for preparation of polymeric solution with 18 wt.% PES and 0.05 wt.%  $\text{Cu}_2\text{O}$

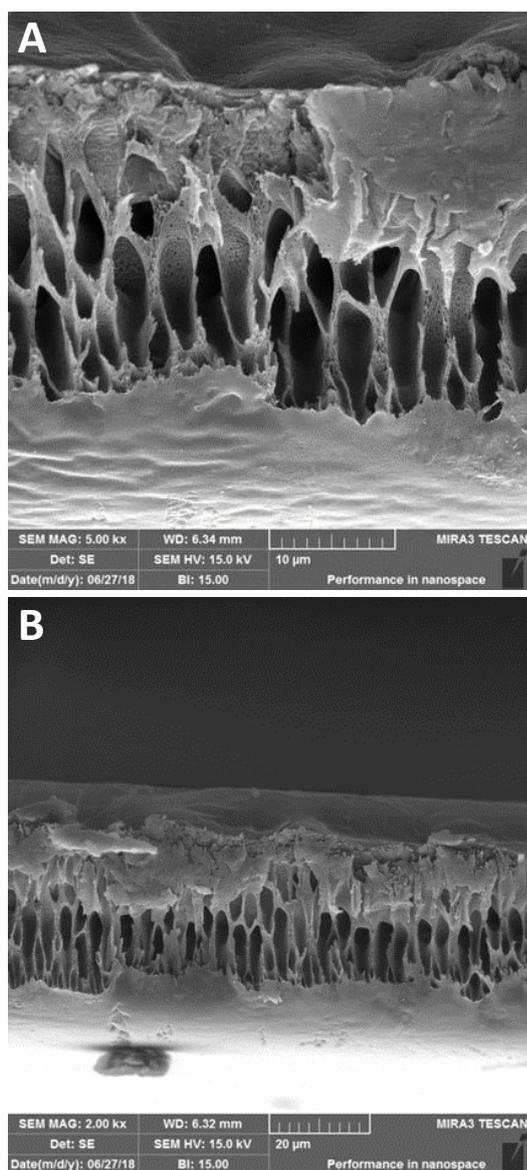
Material	0.05 wt.%	0.1 wt.%	0.5 wt.%	1.0 wt.%
PES	2.7 g	2.7 g	2.7 g	2.7 g
DMAC	11.392 g	1.385 g	11.325 g	11.25 g
PEG	0.9 g	0.9 g	0.9 g	0.9 g
$\text{Cu}_2\text{O}$	0.007 g	0.015 g	0.07 g	0.105 g

### Permeation test procedure

To measure the permeation of membrane samples, each prepared membrane was positioned in a specific place. After positioning the membrane in the pore and modulus stiffening, the inlet hose was positioned in the solution and the outlet hose was positioned in another vessel. The permeation hose was also positioned in a graduated cylinder. Finally, the volume of the permeation solution was measured or the amount of analyte on that was measured by UV-Vis spectrophotometer.

### Pure water flux

After membrane preparation, the first step is soaking each of them in distilled water for 30 min and then compacting of membranes at 6 bar for 30 min. After that, the pressure was decreased to the operating pressure value of 4 bar.



**Figure 3.** Scanning electron microscopy images from the cross section of membranes: (A) bare, (B) containing 0.05 wt.% Cu<sub>2</sub>O NP.

The flux is determined by equation 1 through the penetration volume that passes a membrane in the membrane area unit and passing time unit.

$$J = \frac{M}{A \times t} \quad (1)$$

Where J is the passing flux of the membrane (kg m<sup>-2</sup> h<sup>-1</sup>), M is the permeate quantity (kg), A is the surface area of the membrane (m<sup>2</sup>), and t is the passing time from the membrane (h). Flux is an important parameter in membrane performance. Higher flux is due to the faster filtration and therefore reduces the implementation and operation costs.

#### The membrane pore size

To measure the average size of the membrane pores (rm), Guerout-Elford-Ferry (GEF) equation (equation 2) was employed. In this equation, Q is the volume of penetrated pure water in time unit (m<sup>3</sup> s<sup>-1</sup>), η is the water density (8.9 × 10<sup>-4</sup> Pa s), and ΔP is the applied pressure.

$$rm = \sqrt{\frac{(2.9-1.75) \times 8 \eta L Q}{\epsilon \times 8 \times \Delta P}} \quad (2)$$

#### Porosity

For calculating the porosity (the volume of empty spaces in the membrane sample), first, the weight of the wet membrane has measured. Then, the membrane was dried for 8 hours at 60 °C and was weighed after drying. This experiment was applied for 3 samples of each membrane type and the average value of porosity was measured according to equation 3.

$$\epsilon = \frac{W_1 - W_2}{A \times L \times d_w} \quad (3)$$

In this equation, W<sub>1</sub> is the wet membrane weight, W<sub>2</sub> is the dried membrane weight, A is the cross section of the membrane, L is the thickness of the membrane, and d<sub>w</sub> is the water density.

#### Membrane Antifouling Property Tests

To study the membrane antifouling properties, the flux recovery ratio parameter was obtained by equation 4. Bovine Serum Albumin (BSA), as a good fouling agent, was used to evaluate membrane antifouling characteristics at a concentration of 1000 ppm. At first, the pure water flux of membranes was measured for 60 min (j<sub>w,1</sub>). Then flux of BSA solution was estimated based on the water quantity permeated through the membranes at 4 bar for 90 min. After filtration of the BSA solution, the membranes were washed with deionized water for 20 min, and after that, the water flux of washed membranes (j<sub>w,2</sub>) was obtained.

$$FRR = \left( \frac{j_{w,2}}{j_{w,1}} \right) \times 100 \quad (4)$$

Various ratio for description of the antifouling properties of the prepared membranes were defined. One of them is R<sub>t</sub>, which was calculated by equation 5. J<sub>p</sub> shows the flow containing BSA.

$$R_t (\%) = \left( 1 - \frac{j_p}{j_{w,1}} \right) \times 100 \quad (5)$$

In equation 6, R<sub>t</sub> is the lost flux due to the precipitation of BSA on the membrane surface.

$$R_r (\%) = \left( \frac{j_{w,2} - j_p}{j_{w,1}} \right) \times 100 \quad (6)$$

In equation 7, R<sub>ir</sub> is irreversible flow.

$$R_{ir} (\%) = \left( \frac{j_{w,1} - j_{w,2}}{j_{w,1}} \right) \times 100 \quad (7)$$

#### Pollutant removal and removal rate calculations

The pollutant which have used in this study, is hydroquinone. To investigate the hydroquinone removal, its 0.01 M stock solution was prepared and used for the preparing different concentrations.

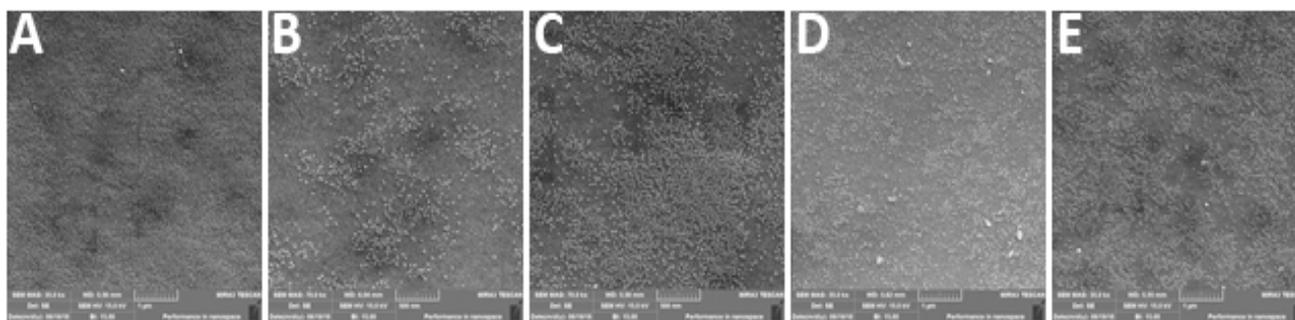
To measure the removal ratio of hydroquinone, equation 8 was used.

$$R\% = \left( 1 - \frac{C_1}{C_0} \right) \times 100 \quad (8)$$

In this equation, C<sub>0</sub> is the hydroquinone concentration on the inlet feed to membrane, C<sub>1</sub> is the hydroquinone concentration in the permeated solution from the membrane, and R is the removal ratio of hydroquinone removal.

#### Investigating the effective parameters on hydroquinone removal

To optimize the conditions of hydroquinone removal, the removal ratio was studied by varying pH, temperature, and pollutant concentration effects. The effect of pH was studied by preparing a solution of 0.01 mM hydroquinone solution with different pH values of 3, 5, 9, and 11 and passing it through the optimized membrane. The pollutant removal ratio was calculated by equation 8. The effect of temperature on the pollutant removal was investi-



**Figure 4.** Scanning electron microscope images from the surface of membranes: (A) pure, (B) containing: 0.05 wt.%  $\text{Cu}_2\text{ONPs}$ , (C) 0.1 wt.%  $\text{Cu}_2\text{ONPs}$ , (D) 0.5 wt.%  $\text{Cu}_2\text{ONPs}$ , and (E) 1 wt.%  $\text{Cu}_2\text{ONPs}$ .

gated by preparing a 0.01 mM hydroquinone solution at pH=9 and passing it through the membrane at different temperatures of 25, 30, 35, and 40 °C. The effect of the pollutant concentration was measured by different concentrations of  $10^{-3}$ ,  $5 \times 10^{-4}$ ,  $10^{-4}$ ,  $5 \times 10^{-5}$ ,  $10^{-5}$ ,  $5 \times 10^{-6}$  M of the pollutant in the optimized temperature of 35 °C and optimized pH value of 9.

## Results and discussion

### FTIR analysis

One of the techniques to study and modify the membrane is FTIR. This technique was used to study the structure of the formed membrane and the presence of the added nanoparticles. The FTIR spectra were obtained from copper oxide nanoparticles, pure polyethersulfone membrane, and the modified membrane, see Figure 1.

FTIR spectroscopy was used to determine the functional groups on the surface of the membrane. The FTIR results of  $\text{Cu}_2\text{O}$  NPs, pure polyethersulfone membrane, and the modified polyethersulfone membrane with  $\text{Cu}_2\text{O}$  NPs are shown in Figure 1.  $\text{Cu}_2\text{O}$  NPs show two main peaks at  $3443 \text{ cm}^{-1}$ ,  $502 \text{ cm}^{-1}$  (and  $628 \text{ cm}^{-1}$ ) which refers to the stretching vibrations of O-H group and methyl-oxygen. In Figure 1B, the pure membrane constructed of polyethersulfone contains O-H groups at the end of the polymeric chain, as well as C-O, C=C, C-H, aromatic ring, and sulfone groups. The stretching vibration at  $3427 \text{ cm}^{-1}$  is related to the O-H group at the end of the polymeric chain and the appeared peak at  $3070 \text{ cm}^{-1}$  refers to the stretching vibration of the aromatic ring. The presence of a double peak at around  $1634$  and  $1581 \text{ cm}^{-1}$  belongs to the stretching vibrations of C=C bond. The peak at  $1244 \text{ cm}^{-1}$  is due to the stretching vibrations of C-O group in the polyethersulfone. Furthermore, the peaks at  $1298$  and  $1151 \text{ cm}^{-1}$  refer to the sulfone group and the peaks at  $718$  and  $871 \text{ cm}^{-1}$  denote the p-benzene structure.<sup>12</sup> In Figure 1C, the modified membrane with the  $\text{Cu}_2\text{O}$  NPs shows a peak at  $523 \text{ cm}^{-1}$  which does not exist in the spectrum of the pure membrane. This approves the presence of the copper oxide nanoparticle in the membrane. The rest of the spectrum is the same with a negligible shift or difference.

### The results of scanning electron microscopy (SEM)

#### The SEM results of copper oxide nanoparticle

According to the Figure 2, the nanoparticles have the spherical morphology and the average size of the nanoparticles are about 55 nm.

#### The SEM results of the pure membrane and the modified membrane with the copper oxide nanoparticle

In the membranes which have been prepared with the reverse phase method, two different phase separation phenomena are

expected. One is the immediate solvent-non solvent exchange, which forms a capillary tube-type structure and the other is the late solvent-non solvent exchange, which forms a sponge-type structure inside the membrane.<sup>13</sup> The late phase separation process of the polymeric solution in the non-solvent bath forms the membrane with a denser separating layer.<sup>14</sup> In the immediate phase separation, the produced membrane contains a highly porous surface layer.<sup>15</sup>

Immediate separation happens when the rate of the solvent exit from the polymeric film is high. The addition of the hydrophilic nanoparticles to the polymeric solution affects the rate of the non-solvent to the polymeric film and the solvent exit. Faster solvent exit, forms the active layer faster, which causes an additional resistance toward the mass transfer, and the duration of transfer between solvent and non-solvent increases in the sublayer. Therefore, the pores in the sublayer of the sponge structure convert into the finger-type structure.<sup>16</sup> Figure 3 shows the scanning electron microscopic images from the cross-section of bare and modified membrane, prepared by the revers phase method. As can be seen, all samples contain an asymmetrical structure with a dense top layer and a porous sublayer. According to the figure, the structure of the membrane without nanoparticles is close to the sponge type and the top layer (separation layer) is denser than that in other membranes. This structure reduces the passing flux from the membrane. By adding 0.05 wt.% nanoparticles, the membrane structure has not changed compared to the non-modified membrane with nanoparticles. Only some pores have filled with nanoparticles. Such a phenomenon might be due to an insufficient number of nanoparticles. This number of nanoparticles do not play any role in the phase separation process and the solvent exit rate due to their low amount. Filling of the pores with nanoparticles also reduces the porosity. Therefore, not only the passing flux value has not improved, but also it has been reduced. The addition of nanoparticles up to 0.1 wt.% to the polymeric solution forms the membrane with a thinner separation layer and thicker sublayer. The membrane scaffold is more expansive and the porosity in the sublayer is higher.

Moreover, the pores in the separating layer are larger compared to the membrane with 0.05 wt.% nanoparticles. Such structure was made because the higher affinity between water and nanoparticles compared to polyethersulfone has increased the rate of water diffusion into the as-forming membrane and the diffusion of solvent from membrane to water, which caused the immediate phase separation and the finger-type pores have made. As well, in the sample with 0.5 wt.% nanoparticles, the size of pores in the membrane surface was increased, which increased the flux. By increasing the nanoparticles concentration up to 1

wt.%, the size and the number of pores has decreased and the thickness of the separating layer has increased. It seems that, in this concentration, the agglomeration of nanoparticles and their low distribution may reduce the membrane porosity.<sup>17</sup>

For evaluation of the nanoparticle dispersion on the membrane surface, the SEM images captured from the surface of the membrane have been used. As shown in Figure 3, the membranes with 0.1 and 0.5 wt.% copper oxide nanoparticles are containing uniform distribution of nanoparticle on the membrane surface. However, other membranes contains relative aggregation on the surface. The aggregation of nanoparticle on the sample with 1 wt.% copper oxide nanoparticle may be due to the high concentration of the used nanoparticle in the sample.

#### Contact angle measurements

The hydrophilicity of the membrane is one of the most important factors to improve the flux and reduce fouling. The fouling on the surface of the membrane may be controlled by increasing the hydrophilicity. The measured contact angles are shown in Table 3. There is an inverse relationship between the contact angle and membrane hydrophilicity. This means the larger the membrane contact angle is, the membrane is more hydrophobic and the smaller the contact angle is, the membrane would be more hydrophilic. This angle varies by different concentrations of nanoparticles. By increasing the nanoparticles concentration up to 0.5 wt.%, the contact angle has decreased, which signifies the enhancement of the membrane hydrophilicity. In a membrane with 1 wt.% nanoparticle, the contact angle has increased since the aggregation of nanoparticles in the top layer decreases the water adsorption on the surface of the membrane.<sup>18-20</sup>

**Table 3.** The effect of the concentration of Cu<sub>2</sub>O NPs on the membrane contact angle.

Cu <sub>2</sub> O NPs (wt.%)	Contact angle (degree)
0 (pure membrane)	55.08
0.05	49.34
0.1	45.65
0.5	40.55
1	47.87

#### Experimental parameters of membrane

The prepared membranes were examined by a permeation measurement system using a circular membrane with 5 cm diameter. The following tests were done to approve the membrane permeation performance.

#### Membrane permeability

In the flux experiments for different membranes, the volume of the passed water from the membrane is a flux criterion. The pure flux of the membrane is calculated by equation 1 and the corresponding results for the pure membrane and the membrane containing copper oxide nanoparticles are listed in Table 4.

**Table 4.** The calculated flux for pure water transfer

Membrane	Flux
Pure membrane	145.22
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	198.00
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	203.82
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	216.50
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	149.22

According to these results, the pure water flux was increased by the addition of nanoparticles to the membrane solution. In the membrane with 0.05 wt.% nanoparticles, the pure water flux was the lowest which was due to the significant reduction in the size of the superficial pores. Since the low number of nanoparticles did not

affect the membrane hydrophilicity and only filled the superficial pores. In concentrations of 0.1 and 0.5 wt.%, the flux of passed pure water has increased. This is due to the enhancement of hydrophilicity and increasing the size of the superficial pores compared to the pure membrane. The presence of nanoparticles in the polymeric solution with similar non-solvent properties (deionized water), may facilitate the exchange of solvent and non-solvent and the rapid phase separation happens. This phenomenon increases the size of the superficial pores.

#### The membrane antifouling measurement

Permeation and anti-fouling are two important factors for the determination of membrane performance. The presence of the nanoparticles in the polymeric solutions causes variation in the passing flux of the membrane and the anti-fouling property, and therefore in the appropriate concentrations enhances the membrane performance. The results of the antifouling study of BSA protein are presented in Table 5. The flux recovery ratio (FRR) test is known for investigating the fouling capacity of the membrane pores.

**Table 5.** The calculation of flux for transferring the solution containing BSA with different concentrations of 0.05, 0.1, 0.5, and 1 wt.%.

Membrane	Flux
Pure membrane	53.5
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	163.05
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	178.34
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	193.6
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	107

The reason that the anti-fouling has increased although the flux increased and the membrane structure expanded might be the increase of surface hydrophilicity and the presence of more water on the membrane surface, which causes lower aggregation of ions on the surface, lower absorption on the surface, and a higher selectivity. All these may lead to a higher decline. In the membrane with 0.5 wt.% Cu<sub>2</sub>O NPs, the flux has increased up to 216.5 L m<sup>-2</sup> h<sup>-1</sup>, which is due to the expansion of the membrane structure due to the rapid phase inversion and improved hydrophilicity. Concentration polarization is an unwilling issue during protein filtration. The presence of BSA polarizes the membrane surface, therefore the transferring and flux reduces. To overcome this, the membrane was stirred for 20 minutes in a solution containing deionized water, so the membrane pores were emptied from BSA. Table 6 shows the calculated flux after the membrane washing with water.

**Table 6.** Calculation of the flux after soaking the membrane on water.

Membrane	Flux
Pure membrane	47.4
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	178.3
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	204.3
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	226.7
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	127.38

As can be seen, during one hour, the flux has reduced. This phenomenon might be due to the concentration polarization. Therefore, during the solution flow, some components have passed through the membrane propulsion, and some others have declined by the membrane prevention. The aggregation of the declined components by the membrane increases the concentration on the membrane surface compared to the solution concentration. The range in which the concentration on the surface or inside the membrane is slowly increases compared to the solution concentration is called the boundary layer. In this range the returned penetration takes place. However, in the worst case, the

concentration polarization forms a cake on the membrane surface. The passing flux has a reverse relation with the cake thickness. This signifies, by increasing the cake thickness, the flux reduces. By concentration polarization, the molecules on the surface of the membrane may precipitate and produce fouling. By the creation of fouling, the flux has more reduced.<sup>21</sup>

As the results show, during the transfer of BSA from the membrane, the membrane flux has more reduced which is due to the polarization of the membrane surface by the protein. By soaking the membrane in the deionized water, constant stirring, and re-measuring the passing pure water, the flux increased. Finally, the decline of membrane was calculated by equation 4, see Table 7.

**Table 7.** The calculated FRR for different membranes

Membrane	FRR
Pure membrane	32.64
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	90.05
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	100.00
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	104.70
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	85.30

To interpret the membrane fouling, various ratios have determined and calculated for the membrane fouling; the first ratio is  $R_T$  which is the degree of flow reduction compared to the fouling which has calculated by equation 5, see Table 8.

**Table 8.** The  $R_t$  value for different membranes

Membrane	$R_t$ %
Pure membrane	63.15
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	17.56
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	12.50
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	10.60
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	28.29

The other ratios for fouling calculations are  $R_f$  and  $R_{if}$ , which were calculated by equations 6 and 7, respectively. The results are presented on Tables 9 and 10.

**Table 9.** The  $R_f$  value for different membranes.

Membrane	$R_f$
Pure membrane	5.00
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	7.70
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	12.70
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	15.30
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	13.56

**Table 10.** The value of  $R_{if}$  for different membranes

Membrane	$R_{if}$ %
Pure membrane	63.15
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	17.56
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	12.50
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	10.60
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	28.22

The flux results for different membranes did not have any uniform routine. The decline of BSA was increased by increasing the nanoparticle concentrations. According to the copper oxide properties, its adoption property facilitates the decline. As well, its adsorption property increases the filtration on the surface and depth of the membrane during the filtration. Also, the hydrophilicity of copper oxide nanoparticles increases the rate of receiving water to the membrane compared to BSA particles. Finally, this phenomenon has improved the BSA decline by increasing the concentration of nanoparticles in the membrane.<sup>22</sup>

#### Investigating the porosity of the membrane

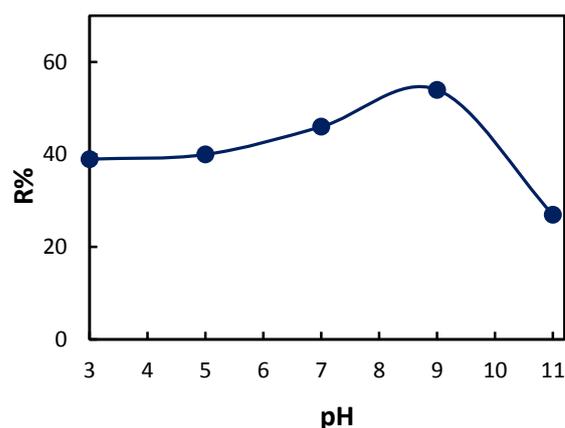
The porosity of the membrane was calculated by equation 3 and the results are presented in Table 11. The amount of water in the membrane is a measure of membrane hydrophilicity and expansion, which has a relation with the membrane porosity.<sup>23</sup> Adding nanoparticles up to 0.05 wt.% did not change the porosity and water amount. Since the low amount of nanoparticles did not vary the membrane hydrophilicity neither phase separation nor porosity. By increasing the number of nanoparticles, the porosity and water amount have increased. This is almost due to the hydrophilic properties of nanoparticles and the enlargement of pores in the sublayer. The hydrophilic nanoparticles accelerate the solvent exit from the polymeric film and the expansion of the membrane structure. The presence of components with non-solvent properties (deionized water), accelerates the exchange between solvent and non-solvent. On the other hand, the formation of polymer-nanoparticles bonds decreases the polymeric interactions and makes the casted film more unstable. Therefore, the phase separation happens sooner in the coagulation bath. Thus, the porosity has increased and the membrane may store more water.<sup>24</sup>

**Table 11.** The porosity calculations

Membrane	Porosity
Pure membrane	0.346
Membrane containing 0.05 wt.% Cu <sub>2</sub> O NPs	0.347
Membrane containing 0.1 wt.% Cu <sub>2</sub> O NPs	0.393
Membrane containing 0.5 wt.% Cu <sub>2</sub> O NPs	0.426
Membrane containing 1 wt.% Cu <sub>2</sub> O NPs	0.555

#### Pollution removal

Six pure PES membranes were prepared with different concentrations. The best concentration for the preparation of pure membrane was 18 wt.% with the thickness of 160  $\mu\text{m}$  which shows the flux of 270.063 ( $\text{kg m}^{-2}\text{h}^{-1}$ ) in the optimum pressure of 4 bar. According to the results of SEM, AFM, fouling, and porosity analyses, the membrane with 0.5 wt.% copper oxide nanoparticles was chosen as the optimum modified membrane. The optimum membrane was used for the removal of hydroquinone in the aqueous solution. The conditions and parameters for the hydroquinone removal were investigated.

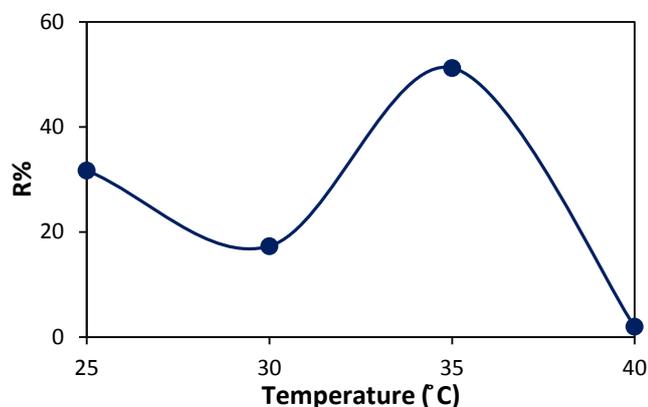


**Figure 5.** The effect of pH on the hydroquinone removal by the modified membrane with Cu<sub>2</sub>O NPs.

#### The effect of pH on the hydroquinone removal by the modified membrane with Cu<sub>2</sub>O NPs

To study the effect of pH on the hydroquinone removal by the membrane, a hydroquinone solution was prepared in different pH values which was used for UV-Vis spectroscopy before and after

passing the membrane. The percentage of hydroquinone removal was calculated and the results are shown in the chart of Figure 5. According to Figure 5, between pH=3 and pH=12, due to the unchanged charge on the membrane surface, the pH value did not change significantly. However, at pH=9, the removal percentage has increased. By increasing the pH, at high alkaline media, the removal percentage has decreased.



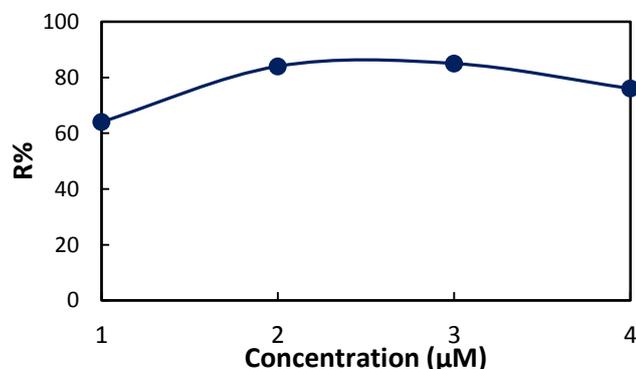
**Figure 6.** The effect of temperature on the hydroquinone removal by the modified membrane with Cu<sub>2</sub>O NPs.

#### The effect of temperature on the hydroquinone removal by the modified membrane with Cu<sub>2</sub>O NPs

Considering the sensitivity of the polymeric membrane to temperature, the membrane pores in low temperatures have shrunk due to the tightening of the polymeric membrane. Therefore the solution transfer faces issues and reduces. By increasing the temperature, the membrane pores have expanded and the transfer increases. However, in high temperatures, due to the softening of the membrane by temperature, the removal percentage has hugely reduced. According to Figure 6, the optimum temperature for the membrane is 35 °C.

#### The effect of concentration on the hydroquinone removal by the modified membrane with Cu<sub>2</sub>O NPs

To study the effect of the pollutant concentration on the removal by the membrane, six different concentrations of 10<sup>-3</sup>, 5 × 10<sup>-4</sup>, 10<sup>-4</sup>, 5 × 10<sup>-5</sup>, 10<sup>-5</sup>, 5 × 10<sup>-6</sup> M were studied and the results are presented in Figure 7. The results show that the membrane modified by Cu<sub>2</sub>O NPs can remove hydroquinone. By increasing the hydroquinone concentration, the removal percentage has also increased. However, in the concentration of 10<sup>-4</sup>, the removal percentage has reduced since the membrane surface has saturated and the pores has fouled.



**Figure 7.** The effect of hydroquinone concentration on the removal by the modified membrane with Cu<sub>2</sub>O NPs.

As shown in Figure 7, by increasing the concentration up to 2.5 µM, the removal percentage has increased. However, by increasing the concentration more than this point, the removal percentage has reduced due to the membrane saturation by hydroquinone and the pores fouling.

## Conclusion

In this study, the membrane blended by 0.5 wt. % of Cu<sub>2</sub>O NPs was considered as the chosen membrane (based on results obtained from SEM images, water contact angle measurements and permeability) to remove hydroquinone from aqueous solutions. The hydroquinone removal capacity of the chosen membrane was investigated at different pH, temperatures, and hydroquinone concentrations. According to the results, the maximum removal efficiency of hydroquinone was found at optimum conditions of pH 9, T= 35 °C and 2.5 µM of hydroquinone.

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