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Diazonium-Based Surface Functionalization of PES Nanofiltration Membranesto Improve Antifouling Properties and Heavy Metal Removal

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ABSTRACT

In this study, Nano filtration (NF) membranes, composed of polyethersulfone (PES) modified with titanium dioxide (TiO_2) nanoparticles, were fabricated using the phase inversion method. By grafting aniline oligomers onto the surface of the modified membrane, the final membrane with the structure of PES NF/TiO_2/AO was fabricated. The morphology of the final membrane was investigated using FESEM, EDX and FTIR analyses. The membrane separation performance was evaluated through measuring the contact angle and pure water flux (PWF), flux recovery ratio (FRR%), and salt rejection tests using Na_2SO_4 and $MgSO_4$ solutions. The highest PWF (3.66 $\frac{kg}{m^2.h}$) was obtained with the final modified membrane compared to the initial membrane at an operating pressure of 4.5 bar, which can be attributed to the increased hydrophilicity caused by the surface modification of the initial membrane. The removal efficiencies for heavy metals Pb and Cu using the pristine membrane were measured to be 28.2% and 43%, respectively, while the optimized membrane showed the significantly improved rejection rates of 99.97% and 94%. Furthermore, the total fouling rate of the original membrane was approximately 70.4%, which was reduced to 47.4% in the modified membrane. The irreversible fouling was reduced from 44.5% in the original membrane to 32.6% in the optimized membrane, indicating an improvement in the antifouling performance of the modified membrane. The results suggest that the PES NF/TiO_2/AO modified membrane can be considered an effective approach for enhancing the physical and chemical properties of membranes, as well as their separation performance, particularly for the removal of heavy metals.

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1. Introduction

Water pollution is a serious concern in the twentieth century, primarily attributed to population explosion, industrialization, and urbanization. The World Health Organization (WHO) has reported that by 2050,

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approximately one billion people will lack access to safe drinking water, and water scarcity may affect up to four billion individuals [1,2]. Nowadays, access to freshwater is gradually decreasing, and to produce potable water, chemical, microbial, and hazardous contaminants must be removed. Therefore, researchers have focused extensively on developing efficient and cost-effective water treatment methods.

On the other hand, with the advancement of modern industries, environmental pollution has significantly increased. These industries, either directly or indirectly, discharge wastewater containing heavy metals, contributing to environmental contamination. Toxic pollutants such as chromium (Cr), mercury (Hg), arsenic (As), and copper (Cu) adversely affect human health and agriculture due to their environmental stability and bioaccumulation. To mitigate this growing problem, cost-effective and efficient technologies for the pre-concentration and removal of heavy metals are being investigated [3]. Conventional methods for removing heavy metal ions include ion exchange, chemical oxidation/reduction, reverse osmosis, ultrafiltration, and other effective techniques; however, these methods face limitations such as harsh operating conditions, lower efficiency, and potential secondary pollution [4].

Membrane processes have found widespread applications in separation industries. Key advantages of membrane technology include selective separation capabilities, simplicity of mass transfer processes, high process speed, and lower energy consumption compared to those of other methods.

In particular, the use of nanofiltration (NF) membranes, with pore sizes of approximately 0.2 to 0.5 nm, demonstrates higher separation efficiency for organic compounds, moderate retention of inorganic ions, and superior performance compared to other commonly used separation methods, making them increasingly important in water purification and reuse.Polyethersulfone (PES) membranes are widely used in the fabrication of commercial NF membranes due to their environmental tolerance, high toughness, thermal resistance, mechanical stability, miscibility, and potential for improved antifouling and enhanced permeability properties [5].

In the present study, the focus is on modifying the surface properties of PES membranes to enhance antifouling characteristics and improve the removal efficiency for dyes and heavy metal ions. Titanium dioxide (TiO_2) has attracted significant attention due to its high chemical stability, non-toxicity, low cost, commercial availability, and ease of preparation. Additionally, TiO_2 possesses features such as strong oxidizing power, high hydrophilicity, long-term photo stability, high transparency in the visible range, good thermal and chemical stability, and non-toxicity, making it an excellent catalyst for water treatment applications [6]. Owing to the hydrophilic nature of TiO_2, incorporation of these nanoparticles into membrane structures enhances the affinity of composite materials for water, thereby increasing the water permeability of membranes [7]. For preparing membranes in this study, surface coating with aniline oligomers, resulted from diazonium bonding on TiO_2-modified membranes, was employed.

In a similar research work, Parvizián et al. designed NF membranes using polyvinylidene fluoride (PVDF) composite membranes modified with Titania/polyvinyl alcohol nanoparticles via surface coating for heavy metal separation [8]. Additionally, Zeineddini et al. synthesized PES membranes modified with 4, 4-diaminodiphenyl sulfone, as a precursor, using an efficient coupling method

and fabricated membranes with five different compositions via classic phase inversion. Their study demonstrated that surface coupling modification is a cost-effective, simple, and feasible method with great potential for producing membranes with exceptional flux, fouling resistance, and superior dye rejection for separating heavy metals. In that work, electrochemical reduction of aryl diazonium salts was used to covalently graft aromatic layers onto silicon, metal, and carbon surfaces [9]. Rahimi et al. focused on modifying the surface properties of PES membranes by adding functionalities to enhance the antifouling properties, dye removal efficiency, and heavy metal ion rejection. They used tetrathioterephthalic acid as a sulfur-based cross linker to form polymer membranes. Subsequently, diazonium bonding and tetrathioterephthalic acid coating were applied to prepare aniline oligomer-coated membranes. The sulfur species (S=C-S) in tetrathioterephthalic acid participated in complexing with heavy metal ions, enhancing heavy metal ion removal [10]. Pinson et al. employed electrochemical reduction of aryl diazonium salts to covalently bond aromatic layers onto silicon, metals, and carbon surfaces, using iron powder as a chemical reducing agent for aryl diazonium salt reduction [11].

Considering all these studies, in this research, a simple and practical chemical reduction method for aryl diazonium salts was employed, using hypophosphorous acid (H_3PO_2) as a reducing agent to form C–C bonds between aryl radicals and the PES membrane surface. This grafting method introduced NH_2 groups onto the PES membrane surface, which subsequently interacted with hydroxyl groups formed on the membrane via hydrogen bonding. Moreover, this grafting approach is expected to significantly enhance the hydrophilicity of the membrane. The reason for choosing this topic is to improve the performance of the designed membranes and to overcome common problems and obstacles in the surface modification stage. The combination of two-stage surface modification on the PES membrane and the use of two simultaneous surface modifications by TiO_2 nanoparticles and the use of covalent bonding of diazonium radicals on the surface increased the membrane efficiency and reduced fouling and improved the hydrophilicity and long-term stability of the designed membrane, which has not been used in any paper so far. In the final stage of the chemical process of producing diazonium radicals, iron filings are used in most articles, which in many cases has caused membrane rupture, which is one of the reasons why researchers are reluctant to use diazo radicals in the surface modification of Nano filtration membranes. After extensive studies, the use of hypophosphorous acid as a suitable replacement for the metal ligand in the diazonium reaction has solved the problem of membrane rupture during the surface modification process [12]. This combination of surface modification methods has not been used in any article so far.

The PES membrane modified with TiO_2 nanoparticles and coated with aniline oligomers will be characterized in terms of surface hydrophilicity, surface morphology, overall porosity, active pore radius, pore size distribution, and active layer thickness. Additionally, the membrane's performance will be evaluated regarding pure water flux, heavy metal ion removal (Pb^{2+} and Cu^{2+}), dye rejection (methylene blue), and antifouling properties.

2. Materials and methods

2.1. Materials used

Hypophosphorous acid (H_3PO_2, MW = 66 g/mol, density = 1.21–1.26 g/cm^3), aniline

($C_6H_5NH_2$, MW = 93.13 g/mol), sodium nitrite ($NaNO_2$, MW = 68.9953 g/mol), hydrochloric acid (HCl, 37%, MW = 36.50 g/mol), lead nitrate ($Pb(NO_3)_2$, MW = 331.2 g/mol), copper nitrate ($Cu(NO_3)_2$, MW = 187.56 g/mol), polyvinylpyrrolidone (PVP, MW = 25,000 g/mol), and dimethylacetamide (DMAC, MW = 87.12 g/mol) were purchased from Merck. Polyethersulfone (PES, MW = 58,000 g/mol) polymer was supplied by BASF, Germany. Additionally, methylene blue (≥95% MB, MW = 319.85 g/mol) and sodium chloride (NaCl, MW = 58.44 g/mol) were obtained from Sigma-Aldrich. Throughout all laboratory procedures and filtration tests, deionized water was used.

To modify the membrane, rutile titanium dioxide (TiO_2) Nano powder was provided by the knowledge-based company Novavaran Nano Maqyas Borhan.

2.2. Preparation of Polyethersulfone Membrane modified with TiO_2 nanoparticles

To enhance the properties of the membrane, polyethersulfone (PES) membranes modified with TiO_2 nanoparticles were fabricated using the phase inversion method assisted by immersion in an anti-solvent bath. For this purpose, a homogeneous solution of PES polymer, PVP, and TiO_2 nanoparticles with the weight percentages listed in Table 1 was prepared in the dimethylacetamide (DMAC) solvent.

To prepare the solution, TiO_2 nanoparticles were first dispersed in the DMAC solvent and sonicated in an ultrasonic bath for 15 minutes. Then, 1 wt% of the pore-forming agent polyvinylpyrrolidone (PVP) was added to the solution. After achieving a homogeneous solution, 20 wt% of PES polymer was added in the third step. The final solution was sonicated for 30 minutes to ensure complete homogenization. The homogeneous polymer solution was left at room temperature for one day, and then cast onto a clean glass plate with a thickness of 140 micrometers using a manual film applicator.

Subsequently, the cast polymer film was immersed into an anti-solvent bath (containing ion-free water). After phase separation occurred, the formed membrane was washed and soaked in deionized water for one day to extract any remaining solvent. Finally, the membranes were dried by placing them between two filter papers for one day until completely dry.

Table 1.
Composition of membranes used in this study

membrane	membrane number (Mn)	PES (Wt. %)	PVP (Wt. %)	DMAc (Wt. %)	Rutile titanium oxide Nano powder (Wt. %)
PES	M0	20	1	79	0
PES NF/TiO_2/0.1	M1	20	1	78.9	0.1
PES NF/TiO_2/0.25	M2	20	1	78.75	0.25
PES NF/TiO_2/0.5	M3	20	1	78.5	0.5

2.3. Polyethersulfone membrane modified with TiO_2 nanoparticles and Functionalized with aniline oligomers

To prepare the Nano filtration polyethersulfone membrane modified with TiO_2 nanoparticles and coated with aniline oligomers, first the PES membrane modified with TiO_2 nanoparticles was fabricated using the phase inversion method. The membrane surface was then modified by covalently

bonding branched aniline oligomers. For the surface modification, the chemical reduction of aryl diazonium salts and their covalent attachment to the membrane surface were performed using the following experimental procedure:

Initially, 0.93 g of oxidized aniline was dissolved in 37 mL of deionized water. Then, 70 mL of a 0.5 M hydrochloric acid solution was slowly added to the solution, which was subsequently placed in an ice bath to reach a temperature of 5 °C. Separately, a solution containing 1.45 g of sodium nitrite dissolved in 10 mL of distilled water was prepared and cooled in an ice bath. After the sodium nitrite solution reached 5 °C, it was slowly added to the aniline solution to form aryl diazonium salts. To generate oligomer radicals, 10 mL of hypophosphorous acid was slowly added to the solution to chemically reduce the aryl diazonium salts and produce oligomer radicals [13].

Then, a PES NF/TiO_2 membrane (8 × 8 cm) was immersed in the prepared solution for 4 hours. The PES NF/TiO_2 membrane bonded with aniline oligomers was soaked in distilled water and ethanol for 5 minutes, and then dried in an oven at 80 °C. The final membrane, consisting of polyethersulfone modified with TiO_2 nanoparticles and functionalized with aniline oligomers, was used for measuring pure water flux, heavy metal ion removal (Pb^{2+} and Cu^{2+}), and dye rejection (methylene blue), and antifouling properties.

For simplicity, the structure of the final membrane in this study will be referred to as PES NF/TiO_2/AO.

Figure 1. View of the dead-end laboratory system and the structure of the modified PES NF/TiO_2/AO membrane.

Surface modification via the reductive grafting of aryl-diazonium salts is recognized as a versatile and multifunctional strategy, as it enables the incorporation of a broad spectrum of chemical groups onto the membrane surface. This approach allows the precise tuning of surface properties, meaning that numerous interfacial characteristics can be systematically altered or optimized. Beyond improving specific functional attributes, such modifications also offer valuable insights into the intrinsic structure–property relationships of membranes, as the induced chemical and physicochemical changes can be directly correlated with the filtration behavior, hydrophilicity/hydrophobicity, and surface charge.

In this study, the feasibility of modifying the PES/TiO_2 membrane surface using a simple yet highly adaptable covalent-bonding-based method was investigated. The flexibility of this technique enabled by aryl-diazonium salts bearing different functional groups is illustrated in Figure 2. According to the results obtained, the chemical functionalities introduced during the diazonium reaction led to a pronounced enhancement in surface hydrophilicity, along with the development of a positive surface charge. These changes are considered essential for improving the separation efficiency and promoting more favorable interfacial interactions.

A set of complementary characterization techniques was employed to verify the success of the surface modification and to assess the resulting changes in the membrane performance. Finally, the influence of the chemical grafting on transport properties was evaluated by comparing the experimental results of the pristine PES membrane with those of the modified membrane. The findings confirm that the surface modification significantly improves the overall separation efficiency of the membrane and enhances its suitability for water treatment applications.

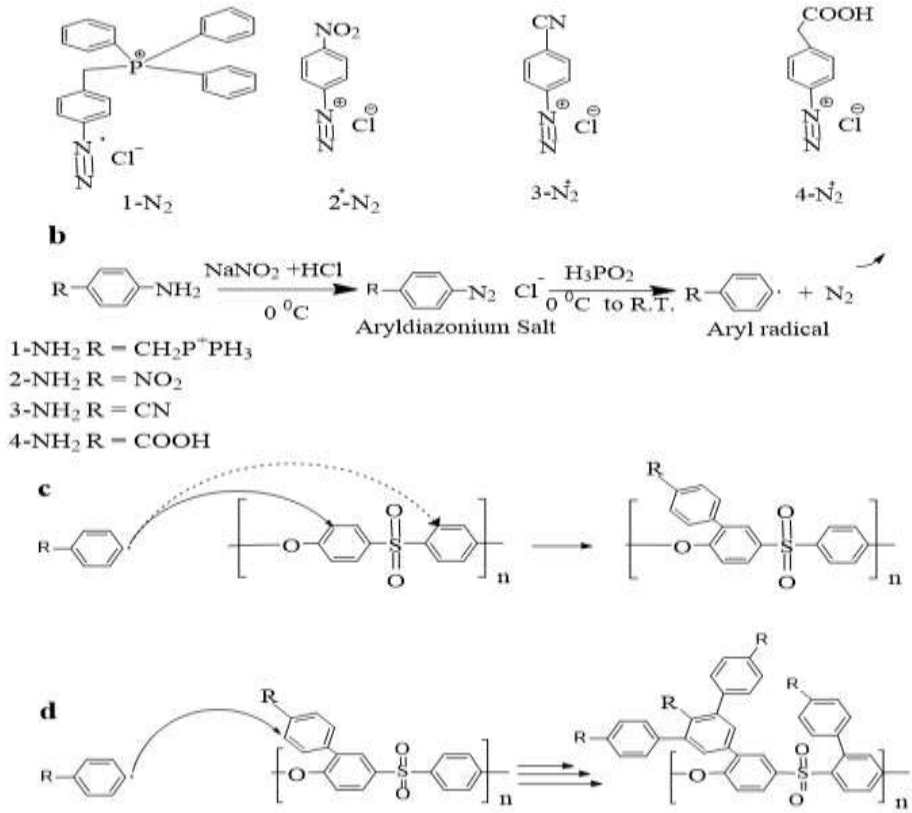

Figure 2. (a) Structures of the in situ generated aryl diazonium salts used to functionalize membranes. (b–d) Schematic of the PES surface modification mechanism, illustrating the reduction of diazonium by hypophosphorous acid, the formation of aryl radical, and subsequent covalent grafting onto the polymer backbone [13].

2.4. Characterization tests for the surface properties and morphology of membranes

The field-emission scanning electron microscopy (FESEM, CamScan MV2300), Fourier-transform infrared spectroscopy in

ATR mode (FTIR-ATR, Bruker Alpha), and energy-dispersive X-ray analysis (EDX), including both the point and bulk elemental assessment, were employed to characterize the PES NF/TiO_2/AO membrane and the prepared membrane series, including pristine PES NF, TiO_2-functionalized PES NF/TiO_2, and the final PES NF/TiO_2/AO membrane. These techniques were utilized to investigate the surface morphology, chemical composition, and elemental distribution of the membranes.

To evaluate surface wettability, water contact angles were measured at ambient temperature. For each sample, 5-µL droplets of deionized water were deposited at randomly selected positions on the membrane surface, and the average contact angle was recorded over a 60-second period.

The overall porosity was quantified for the PES membrane, the TiO_2-functionalized PES NF/TiO_2 membrane, and the final PES NF/TiO_2/AO membrane, using a gravimetric method, as described in references [14].

For this purpose, a membrane sample measuring 1 × 1 cm² was prepared and soaked in deionized water at room temperature for 24 hours. Then, the membrane was removed from the water, placed between two filter papers to remove the excess surface water, and the wet weight was measured. This procedure was repeated for six samples, and the average value was reported.

$$(\%)Prosity = \frac{(W_{wet} - W_{dry})}{A \times L \times d_w} \times 100 \quad (1)$$

In this equation: W_{dry} represents the weight of the dry membrane, W_{wet} is the weight of the wet membrane, A is the effective membrane area, L is the membrane thickness and d_w is the density of water at room temperature (1 $(\frac{g}{cm^3})$).

Additionally, the water content of the membrane can be calculated using Equation 2 [14].

$$\%\text{Water content} = \frac{W_{wet} - W_{dray}}{W_{dray}} \times 100 \quad (2)$$

To calculate the average surface pore size, the results from porosity and pure water flux data can be used. The average pore radius is calculated using Equation (3) [15].

$$R_m = \sqrt{\frac{(2.9 - 1.5\ prosity) 8\eta LQ}{prosity \times A \times \Delta P}} \quad (3)$$

In the above equation: λ is the viscosity of water (4×10^{-3} to $9/8 \times 10^{-4}$), L is the membrane thickness (m), A is the effective membrane area, ΔP is the operating pressure, equal to 4.5 bar and Q is the pure water flux $(\frac{m^3}{s})$.

2.5. Membrane Flux and Rejection

To measure the flux and rejection rate, a stirred separation system with a closed-end stainless steel chamber of 150 mL volume was used. The nitrogen gas from a reservoir with a pressure regulator valve was applied as the driving force. For uniformity and increased accuracy in measurements, the membranes were compacted for 15 minutes, after which the volume of permeate collected from the membrane at specific time intervals was recorded. The membrane flux was calculated based on the volume of the permeate per unit time and the membrane area in contact with the feed solution [16].

$$J = \frac{Q}{A \times t} \quad (4)$$

In this equation, J is the membrane flux $(\frac{L}{m^2 \cdot h})$, Q is the volume of the permeate (L), A is the membrane area in contact with the feed (m²), and t is the time (h).

Additionally, to measure the membrane separation efficiency, sodium sulfate and magnesium sulfate salt solutions with the

concentration of 1000 ppm were used. To evaluate the separation performance of the prepared membranes, tests for removing heavy metals and colors, and salt rejection were conducted. The removal efficiency of each contaminant was calculated using equation (5). In this equation, C_p represents the concentration of the solution permeate and C_f is the concentration of the initial feed [16].

$$\%R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (5)$$

Furthermore, to evaluate the performance of the optimized membrane in removing heavy metals, a 20 ppm copper and lead salt solution (relative to metal ions) was prepared. The conductivity measurement was used to determine the concentration of the salt, and the atomic absorption spectroscopy was employed to determine the concentration of heavy metal ions.

2.6. Fouling resistance performance

Resistance to fouling is one of the most important properties of membranes. In this experiment, a milk powder solution was used to investigate the antifouling properties of the membrane. Initially, the pure water flux of the membranes was measured, followed by measuring the flux of the milk powder solution. Next, the membrane was washed with water for 15 minutes and the pure water flux was measured again. This process was repeated continuously for ten consecutive cycles, and the average values were reported. The total fouling, reversible fouling, and irreversible fouling were calculated using the following equations [16]:

$$\%R_t = \left(1 - \frac{J_p}{J_{w,1}}\right) \times 100 \quad (6)$$

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

$$\%R_r = \left(\frac{J_{w,2} - J_p}{J_{w,1}}\right) \times 100 \quad (8)$$

In these equations, $J_{W,1}$, $J_{W,2}$, and J_p represent the initial pure water flux, secondary pure water flux, and milk powder solution flux respectively.

The composition of the salt and milk powder solutions used for evaluating the membrane performance is listed in Table 2. For the analysis and statistical comparison of the experimental data, a t-test analysis was employed, and a p-value < 0.05 was considered statistically significant.

Table 2.
Composition of salt and milk powder solutions used to evaluate membrane performance.

Name of the substance under investigation	Concentration (PPM)
Na_2SO_4	1000
$MgSO_4$	1000
Cu_2SO_4	20
$PbSO_4$	20
Powdered milk	1000

3. Results and discussion

3.1. Surface morphology analysis

To obtain a comprehensive understanding of the effects of chemical and structural modifications on the membrane surface, three membrane types—including the pristine PES-NF membrane, the modified PES-NF/TiO_2 membrane, and the final PES-NF/TiO_2/AO membrane were systematically examined. A set of advanced surface-characterization techniques was employed to precisely elucidate the changes introduced by each modification step.

The FTIR spectroscopy was used to analyze alterations in functional groups and to confirm the formation of covalent bonds between aniline oligomers, generated via the diazonium reaction, and the membrane surface. This analysis provided insights into the extent to which the chemical structure of the membrane was altered by surface modification. In parallel, the EDX analysis was carried out to

detect and map the elemental distribution of Ti across the membrane surface, enabling the evaluation of nanoparticle immobilization, distribution uniformity, and the verification of covalent interactions between aniline oligomers and the membrane surface. The SEM imaging, as a powerful tool for visualizing surface morphology, was utilized to reveal nanoparticle embedding and spatial distribution within the polymeric matrix.

Additionally, water-contact-angle measurements were performed to assess the changes in surface hydrophilicity following grafting, the incorporation of TiO_2, and the diazonium-based surface reaction. This parameter provided a direct link between the chemical modification and interfacial wettability. Collectively, these complementary techniques offered a multidimensional and detailed depiction of the chemical, elemental, and physical evolution of the membrane surface.

The analysis of the FTIR spectra of the three samples: the pristine PES membrane, the PES/TiO_2 membrane, and the PET/TiO_2/AO membrane, revealed distinct and quantifiable variations in the intensity of characteristic peaks. In all three samples, the carbonyl band appeared around 1700 cm^{-1}; however, its depth decreased from 0.069 in the pristine membrane to 0.051 in the TiO_2 containing sample, and then increased to 0.064 in the chemically modified membrane. This trend reflects the interaction of diazonium-derived species with the carbonyl groups of PET.

Aromatic bands near 1600 cm^{-1} exhibited the most pronounced relative changes: the peak depth decreased from 0.138 in the pristine membrane to 0.123 in the TiO_2 deposited membrane, and subsequently increased to 0.166 in the modified membrane. This increase indicates the formation of new aromatic structures resulting from the radical-mediated grafting of diazonium salts onto the membrane surface.

The peak at 1240 cm^{-1}, associated with C–O stretching vibrations, remained prominent in all samples, but its depth rose from 0.626 in the pristine membrane and 0.645 in the PES/TiO_2 membrane to 0.653 in the modified membrane, confirming successful surface grafting. The peak around 600 cm^{-1}, attributed to TiO_2 vibrations, showed a slight but meaningful increase in depth in the modified sample (0.100 compared to 0.089), indicating the enhanced interfacial interactions of TiO_2 following chemical modifications.

Overall, these numerical changes in the intensity of peaks directly confirm the presence of a TiO_2 deposition layer and the stable chemical fixation of diazonium-derived aromatic groups on the membrane surface. The attachment of diazo radicals to the surface is covalent and cannot be attributed to the chain scission or a secondary reaction. The FTIR spectrum of the final PET/TiO_2/AO membrane showed clear changes in the chemical structure of its surface. In the initial membrane, characteristic PET bands such as C=O extending around 1715 cm^{-1}, aromatic C-O-C vibrations in the region of 1240–1100 cm^{-1} and benzene ring bands in the range of 1600–1400 cm^{-1} were dominant. The increase in the intensity of the peak at 1240 cm^{-1} is due to the change in the dipole moment of the C-O bonds due to the electronic interactions between diazonium radicals and the aromatic rings of polyether sulfone, as well as the surface interactions with TiO_2 nanoparticles. The lack of a decrease in the intensity of the peaks of the main aromatic rings and the absence of peaks related to broken end groups (such as C=O or O-H) indicate the stability of the chain skeleton and the absence of the chain scission during the modification process.

Following the incorporation of TiO_2 and the diazonium reaction, a significant enhancement of O–H stretching bands in the 3500–3200 cm^{-1} region, along with intensified nitrogen-containing bands (N=N and C–N) at 1500–1400 cm^{-1}, was observed. These spectral changes confirm the introduction of new polar functionalities and the formation of stable surface-grafted structures, which align well with the increased hydrophilicity and reduced contact angle of the modified membrane [17–19].

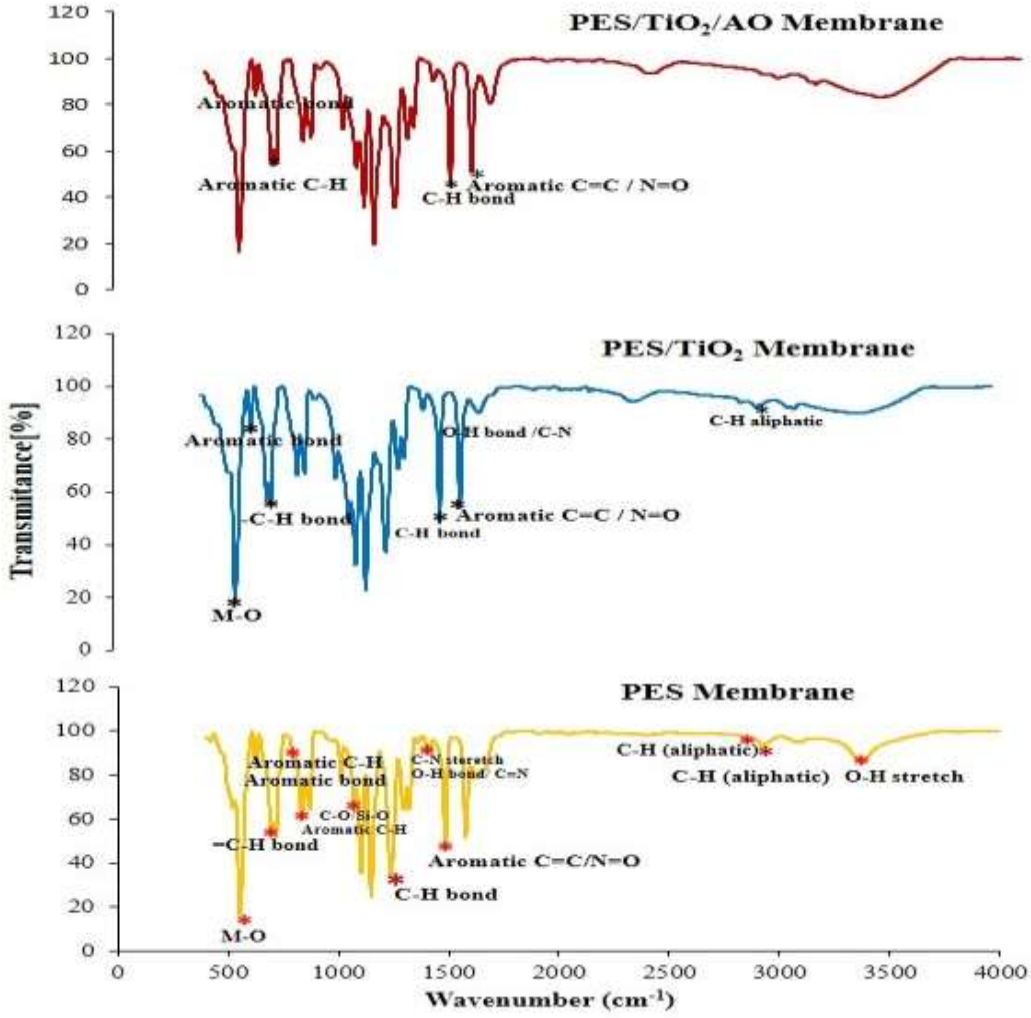

Figure 3. FTIR spectra of the three membranes—pristine PES, PES/TiO_2, and PES/TiO_2/AO—depict the characteristic absorption bands corresponding to the functional groups present in each structure. A comparative assessment of these spectra provides valuable insight into the chemical similarities and differences among the samples, the nature of the involved bonding, and the potential structural modifications introduced during the process of preparing membranes and surface-modification.

The SEM micrographs of the membrane samples were fabricated via the phase-inversion technique and subsequently modified using aniline oligomers, which are presented in Figure 4. The images clearly demonstrate the presence of nanoparticles embedded within the membrane structure, and it is evident that increasing the concentration of nanoparticles leads to more noticeable agglomeration on the membrane surface. The

detailed examination of the micrographs revealed that the nearly spherical bright spots correspond to TiO_2 nanoparticles, while the appearance of micro-cracks reflects the high porosity of the membrane.

To estimate pore size and surface porosity, 93 surface pores were analyzed. The abundance of pores with relatively uniform dimensions indicates a homogeneous pore distribution, which is essential for ensuring consistent membrane performance across the entire surface. By increasing the nanoparticle content, the pore diameter decreased slightly, whereas the number of pores increased. This structural modification effectively lowers the back-diffusion flux while simultaneously enhancing pure-water permeation. Such morphological changes originating from the interaction of TiO_2 nanoparticles with the polymer during phase inversion enhance the hydrophilicity of the casting solution, promote water uptake, and facilitate faster solvent nonsolvent exchange. The increased hydrophilicity results in higher water influx during demixing, ultimately generating a membrane with greater overall porosity.

The SEM images of the membrane cross-section show fundamental changes in the phase separation kinetics due to the presence of TiO_2 nanoparticles. These nanoparticles, acting as nucleation sites, lead to a structure with a more spongy porosity and a more uniform distribution of pores, which prevents the formation of macrovoids and increases the mechanical stability of the membrane. In the surface analysis, the membrane modified with diazonium radicals shows significant morphological changes at the nanoscale. The increase in surface roughness and the change in texture from smooth to rough are due to the covalent attachment of new functional groups to the aromatic rings of PES. These changes lead to an increase in the effective surface area and improved surface properties (e.g. wettability and fouling resistance).The absence of the thick or separate layers of diazonium materials confirms the covalent nature of the attachment and the deep penetration of radicals into the membrane surface, rather than physical coating. This two-step combination (TiO_2 in the matrix + diazonium on the surface) has resulted in a membrane with a smart structure that simultaneously offers mechanical stability and optimal surface performance.

The SEM micrographs of the final PET/TiO_2/AO membrane show that surface morphology undergoes clear alterations following surface functionalization. TiO_2 nanoparticles appear as bright, well-distributed domains, while the presence of small nanoparticle clusters is consistent with the typical behavior of metal-oxide nanostructures on polymer matrices. The observed increase in surface roughness after modification may further enhance hydrophilicity, in agreement with wetting models reported in previous studies [20–22].

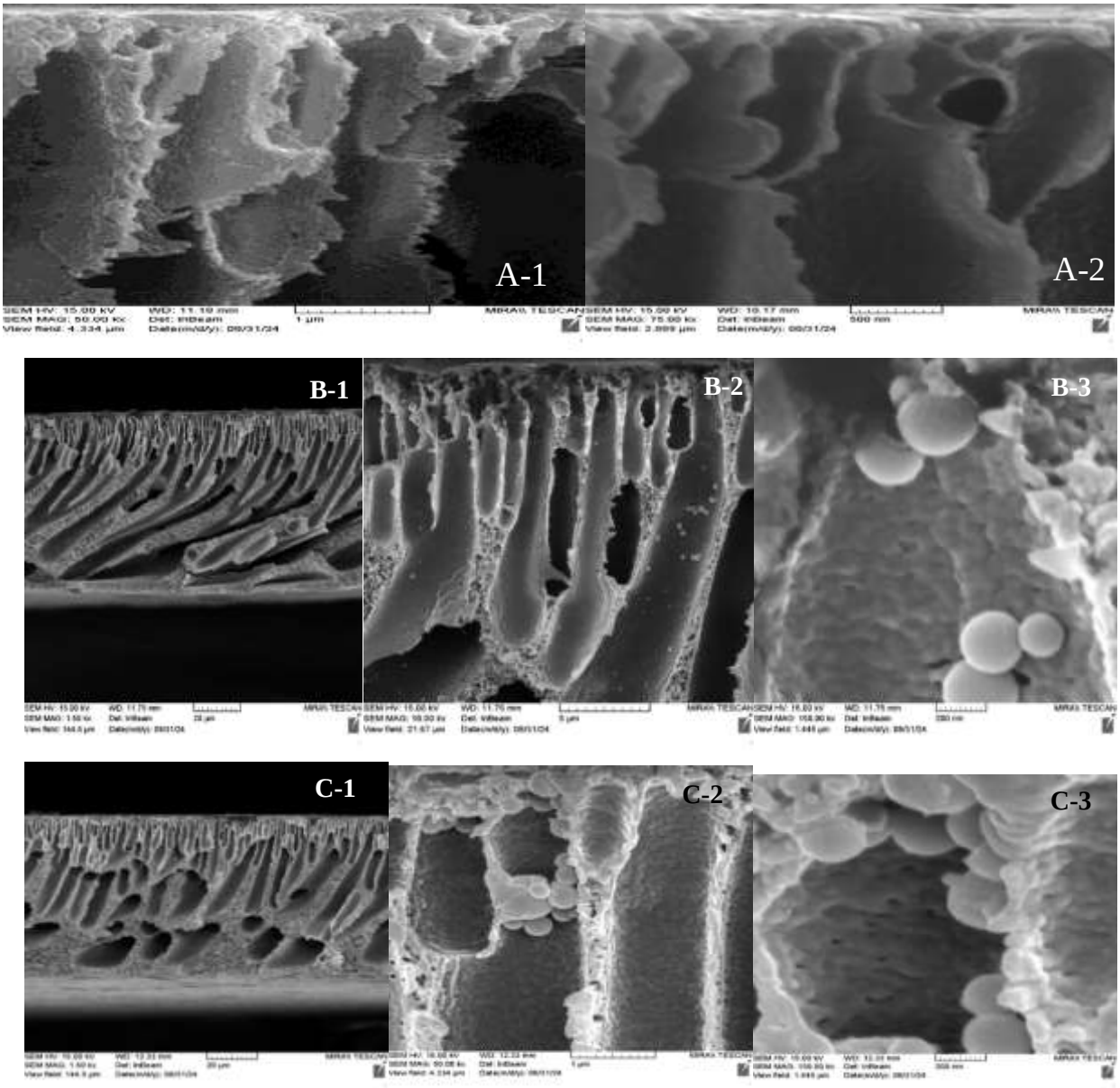

Figure 4. SEM images of the surface of the optimized membrane used the: A) PES-TiO_2 membrane and B) surface-modified PES-TiO_2-AO membrane

The EDX results obtained for the final PET/TiO_2/AO membrane confirm the presence of C, O, S, N, P, and a very small yet definite amount of Ti. The elemental weight composition consists of 67.43 wt% carbon, 31.26 wt% oxygen, 0.46 wt% nitrogen, 0.78 wt% sulfur, 0.04 wt% phosphorus, and 0.03 wt% titanium. Despite the low concentration of Ti, the appearance of a distinct Ti Kα peak at approximately 4.5 keV provides clear evidence of the incorporation of TiO_2 nanoparticles.

The low content of Ti is attributed to the extremely thin surface deposition of TiO_2 combined with the relatively high penetration depth of the electron beam in the EDX technique, which leads to the significant dilution of the Ti signal within the PET matrix. Such behavior is typical and has been frequently reported in studies involving ultrathin surface modifications [23–25].

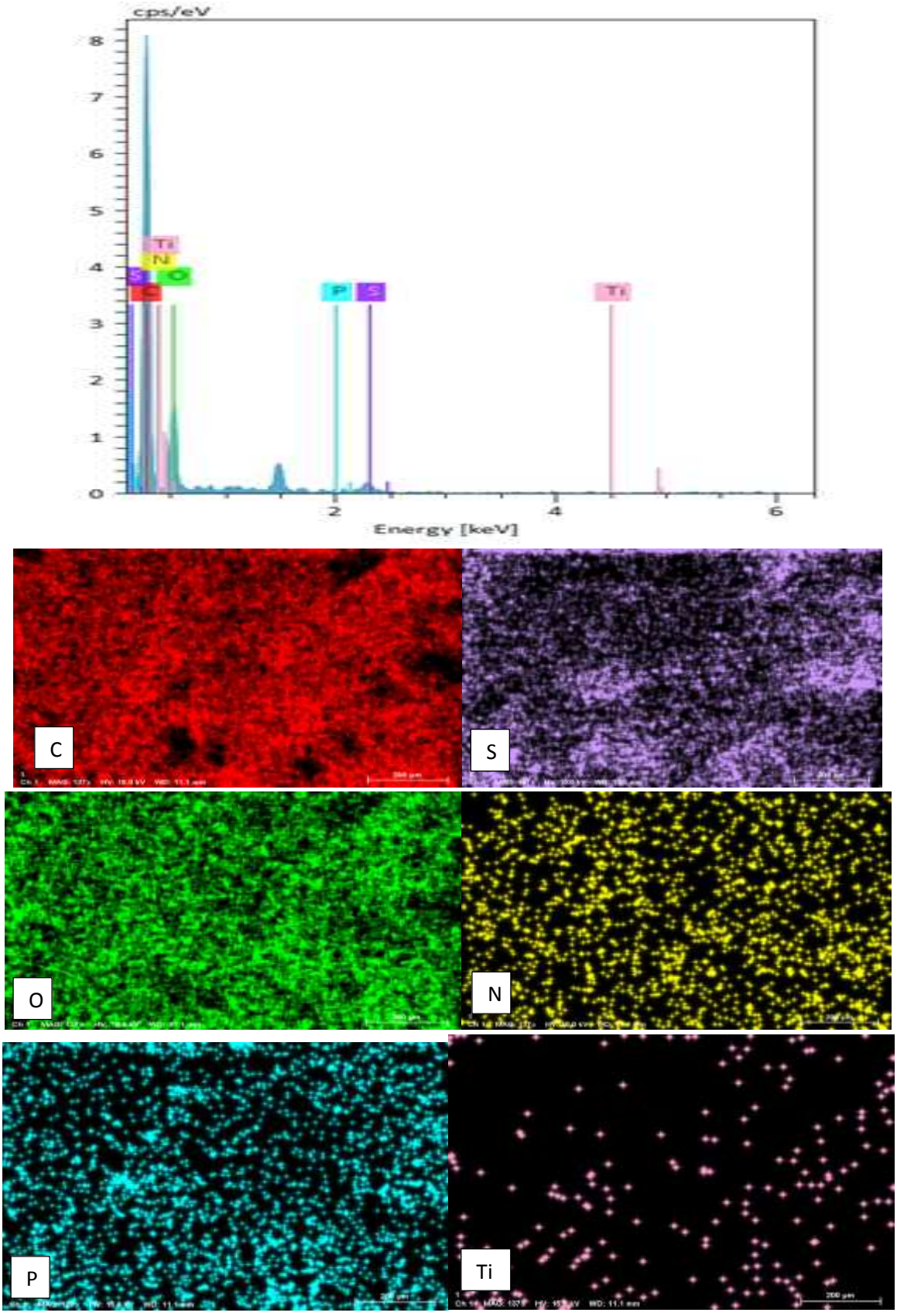

Figure 5. (A) Energy-dispersive X-ray spectroscopy (EDX) spectra of the modified PET/TiO_2/AO membrane, displaying the characteristic peaks corresponding to the detected elements. (B) Elemental composition spectra illustrating the relative intensity and distribution of the elements present on the membrane surface.

Table 3.
Mass and atomic percentages of the elements identified by the EDX analysis.

Element	At.No.	Lines.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs.error [%] (1sigma)	abs.error [%] (2sigma)	abs.error [%] (3sigma)	rel.error [%] (1sigma)	rel.error [%] (2sigma)	rel.error [%] (3sigma)
Carbon	6	K-Serie	2185	67.43	67.43	73.61	12.54	25.08	37.61	18.59	37.19	55.78
Oxygen	8	K-Serie	498	31.26	31.26	25.62	8.76	17.51	26.27	28.01	56.02	84.04
Sulfur	16	K-Serie	77	0.78	0.78	0.32	0.13	0.25	0.38	16.33	32.65	48.98
Nitrogen	7	K-Serie	2	0.46	0.46	0.43	1.26	2.51	3.77	275.46	550.92	826.38
Phosphorous	15	K-Serie	4	0.04	0.04	0.02	0.02	0.04	0.06	50.42	110.83	151.25
Titanium	22	K-Serie	1	0.03	0.03	0.01	0.03	0.06	0.10	92.91	185.82	278.74
			Sum	100.00	100.00	100.00						

The measurement of water contact angle provides a reliable indication of the hydrophilicity or hydrophobicity of the membrane surface. As presented in Table 4, the surface modification significantly decreased the water contact angle, thereby enhancing the hydrophilicity of the modified membranes. This improvement in hydrophilicity can be attributed to the reduced surface roughness resulted from the surface deposition layer, as well as to the presence of carboxyl and hydroxyl functional groups introduced by diazonium-derived radicals.

The slight increase in the contact angle observed in some of the modified samples, compared with thed same in the unmodified membrane, can be explained by the surface roughness variations induced by the diazonium reaction and the incorporation of TiO_2 nanoparticles, both of which contribute to the overall increase in surface hydrophilicity.

Table 4.
Water content and water contact angle values for the prepared membranes.

Sample	Water content Percentage (%)	Contact angle (˚)	Porosity (%)
PES	63.67	64.79	7.1428
PES/TiO_2	113.793	53.44	11.7857
PES NF/TiO_2/AO	125	49.45	14.2857

3.3. Water content percentage

The results indicate that the pure water flux of the TiO_2-modified membranes is markedly higher than that of the pristine polyethersulfone (PES) membrane. This enhancement in hydraulic performance is fully consistent with the structural and surface changes observed in the modified membranes, including the higher overall porosity, larger mean pore size, and reduced water contact angle reflecting an increase in surface hydrophilicity.

The reduction in contact angle enhances interfacial wettability and decreases the entry resistance of water into the pore channels, allowing water to penetrate and pass through the membrane more readily. Similar hydrophilicity driven improvements in flux have been widely reported for PES–TiO_2 mixed-matrix membranes [26]. Moreover, the increase in the mean pore size has a

pronounced effect on permeation, as predicted by classical hydraulic models based on the Darcy Poiseuille relationship, where the volumetric flow rate is proportional to the fourth power of the effective pore radius [27]. Consequently, even a moderate increase in pore radius leads to a substantial rise in water flux. The concomitant increase in the total porosity also provides additional transport pathways, further facilitating water permeation [28].

Among all fabricated membranes, the highest pure water flux was obtained for the membrane containing 0.5 wt% TiO_2. This membrane exhibited the greatest degree of surface hydrophilicity along with an optimized pore size and porosity profile, resulting in the lowest overall hydraulic resistance and the maximum flux. This behavior aligns with the well-known concept of the "optimal nanoparticle loading," where the low to moderate concentrations of TiO_2 improve hydrophilicity and pore architecture, while higher loadings may cause particle aggregation, partial pore blockage, and consequently performance deterioration[29].

3.4. Porosity and pore size

Figure 6 presents the variations in the porosity and mean pore radius of the fabricated membranes following different modification stages. As observed, the incorporation of TiO_2 nanoparticles into the membrane matrix significantly decreases the overall porosity, which can be attributed to the penetration of nanoparticles into the polymer network and partial blockage of pore pathways. The subsequent surface modification through the diazonium-aniline reaction leads to a renewed increase in porosity, primarily due to the formation of structural heterogeneity, an increased density of surface-active groups, and an enhancement of the effective surface area. The mean pore radius analysis further reveals that TiO_2 initially reduces pore size, whereas diazonium-based radical grafting causes a temporary increase followed by a secondary decline. This behavior results from the formation of an aromatic organic layer, localized rearrangement of polymer chains, and increased surface layer thickness [30-32].

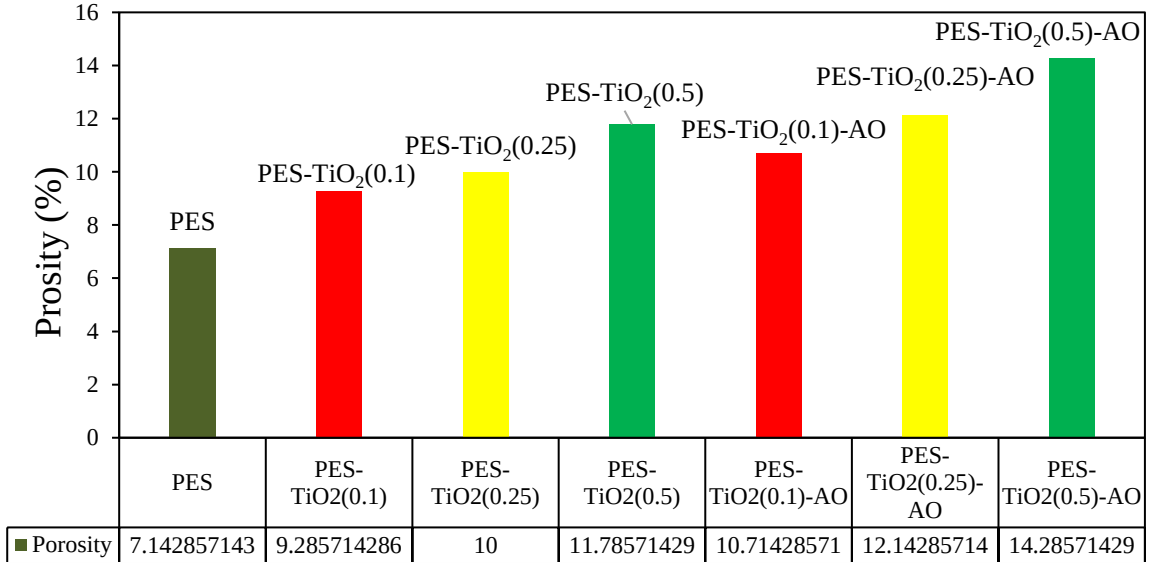

Figure 6. Investigation of the effect of the membrane modification by TiO_2 particles and the membrane surface modification by diazonium reaction (in this study, measurements were performed at a temperature of 27°C, a pressure of 4.5 bar, and an average pore size).

3.5. Permeate flux

The permeation flux of pure water was evaluated to assess the hydraulic performance of the membranes after each modification step. As illustrated in Figure 7, the surface modification process leads to a noticeable decline in flux. This reduction can be attributed to a combination of factors, including the constriction of surface pores, the alterations in the morphology of the active layer, and the formation of a supplementary coating that increases the overall mass transfer resistance. Since permeation flux is strongly influenced by the surface hydrophilicity, the pore size distribution, the pore geometry, and the effective thickness of the selective layer, the incorporation of a new functional coating significantly elevates the hydraulic resistance, ultimately resulting in a substantial reduction in flux.

Moreover, the decreased flux can also be linked to the partial blockage of transport pathways and the potential formation of non-connected or tortuous channels following surface modification. Experimental findings further reveal that the addition of TiO_2 nanoparticles to the casting solution leads to a noticeable decrease in the overall hydraulic resistance, which can be associated with structural rearrangement within the sublayer and improved uniformity of the pore network. The operational stability of the PES/TiO_2/AO modified membrane was examined over three consecutive fouling–cleaning cycles. As summarized in the table, the flux recovery ratio (FR) progressively decreased by increasing the cycle number for both the pristine and modified membranes. Nevertheless, after the third cycle, the composite membrane maintained an antifouling resistance and improved structural resilience during repeated operations. It was also observed that increasing the content of TiO_2 to up to 1 wt% results in a slight decline in the pure water flux. This reduction is likely caused by a moderate decrease in hydrophilicity and effective porosity, which has also been reported in previous studies involving the incorporation of metal-oxide nanoparticles into polymeric membranes. Overall, these findings indicate that while TiO_2 contributes to the structural refinement and fouling resistance, its concentration must be carefully optimized to avoid the excessive suppression of water permeability the higher FR, compared to that of the unmodified membrane, indicate correct optimization. [34-37].

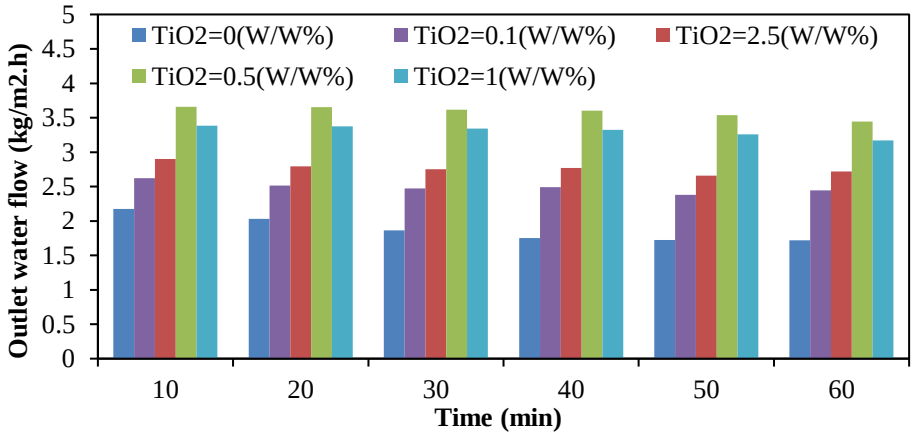

Figure 7. Investigation of the effect of the membrane modification by TiO_2 particles and the membrane surface modification by diazonium reaction (in this study, measurements were performed at a temperature of 27°C, a pressure of 4.5 bar, and an average pore size).

3.6. Salt rejection

The performance of the surface-modified PES NF/TiO_2/AO membrane in rejecting inorganic salts (Na_2SO_4 and $MgSO_3$) was tested at a feed concentration of 1000 ppm, under ambient conditions and operating pressure of 4.5 bar. The rejection results revealed that R (Na_2SO_3) > R ($MgSO_4$), which aligns with the typical behavior of negatively charged Nano filtration membranes.

This trend can be rationalized by considering two dominant rejection mechanisms: steric exclusion and dielectric / Donnan exclusion. Although the hydrated ionic radius of Mg^{2+} (~0.43 nm) exceeds those of Na^+ (~0.36 nm) or SO_4^{2-} (~0.38 nm), which would conventionally favor higher Mg^{2+} rejection via steric hindrance, the presence of a negatively charged surface (introduced by the incorporation of TiO_2 and surface functionalization) strengthens electrostatic repulsion toward the divalent anion SO_4^{2-}. As a result, the salt containing sulfate (Na_2SO_3)(Fig 8) is rejected more efficiently than those containing $MgSO_4$.(fig 9)

In effect, the negative surface charge of the membrane significantly enhances the rejection of multivalent and negatively charged ions. The overall salt retention performance is thus governed by a delicate balance between size-based sieving and electrostatic/dielectric exclusion. Accurate control over the pore size distribution and surface charge density is therefore critical to achieving high salt rejection in modified NF membranes [38-40].

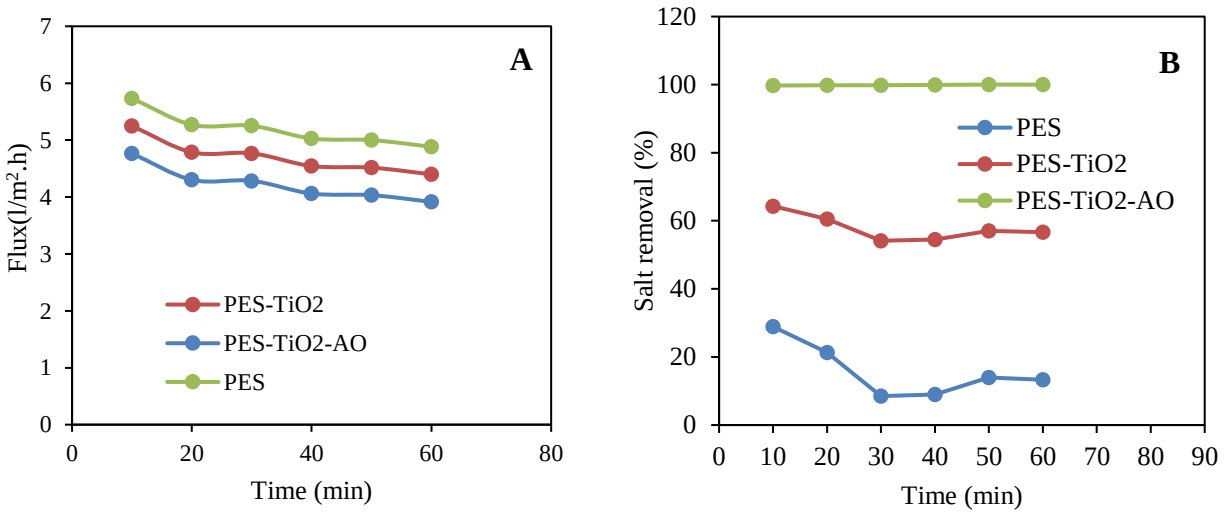

Figure 8. Value of the sodium sulfate salt rejection for the modified membrane prepared at 4.5 bar pressure and ambient conditions, the positive effect of surface modifications on salt rejection (P value > 0.05).

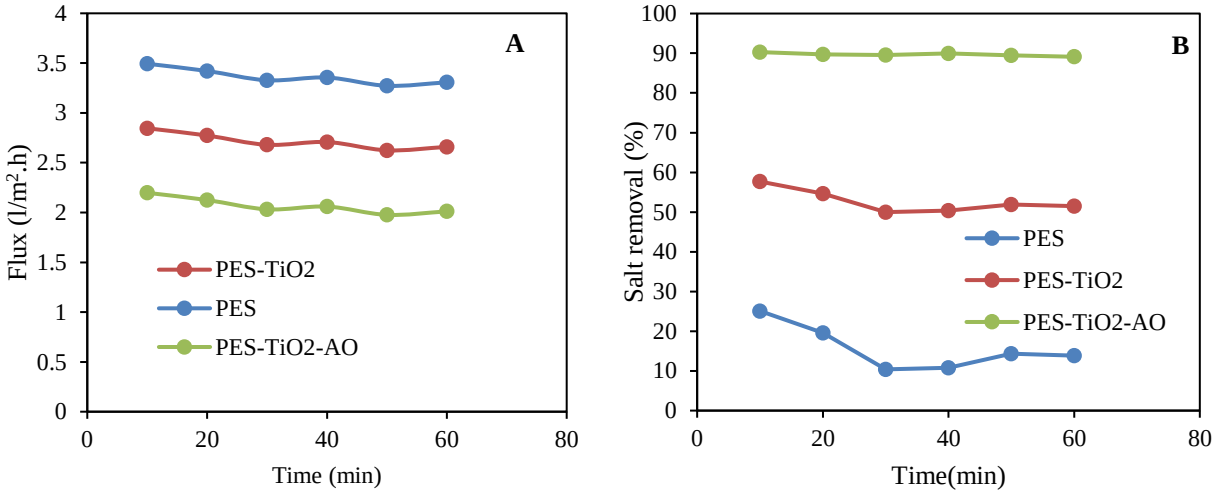

Figure 9. Value of the magnesium sulfate salt rejection for the modified membrane prepared at 4.5 bar pressure and ambient conditions, the positive effect of surface modifications on salt rejection (P value > 0.05).

3.7. Dye removal

The separation performance and permeability of the modified PES NF/TiO_2/AO membrane were evaluated using a closed-system setup for pollutant removal tests. Specifically, the removal efficiency of the cationic dye methylene blue (MB) at an initial concentration of 30 mg/L and an operating pressure of 4.5 bar was investigated.

As shown in Figure 10, the permeate flux for the dye solution was approximately the same for all membranes tested. The permeate flux of the MB solution through the pristine membrane was measured to be 2.03 kg/m²·h, whereas the flux through the surface-modified membrane was 1.92 kg/m²·h. The higher flux of the modified membrane is attributed to its enhanced hydrophilicity compared to that of the base membrane.

Furthermore, the dye removal efficiency of the modified membrane was higher than that of the pristine membrane, measured to be 99.9% and 99.29% respectively. The dye rejection by charged membranes is mainly governed by charge exclusion and size exclusion mechanisms.

Due to the presence of TiO_2 nanoparticles and the diazonium surface modification, the modified membrane possesses a higher negative surface charge compared to the pristine membrane. This results in the improved rejection of the cationic dye by the modified membrane. Additionally, the average pore size of the modified membrane is smaller than that of the pristine membrane due to the incorporation of TiO_2, which enhances size exclusion and further contributes to the increased dye rejection.

The increased hydrophilicity of the polyethersulfone membrane, achieved through surface modification, plays a crucial role in methylene blue removal. The higher membrane surface hydrophilicity reduces interactions between the dye-containing solution and the membrane, thereby minimizing dye fouling [41-43].

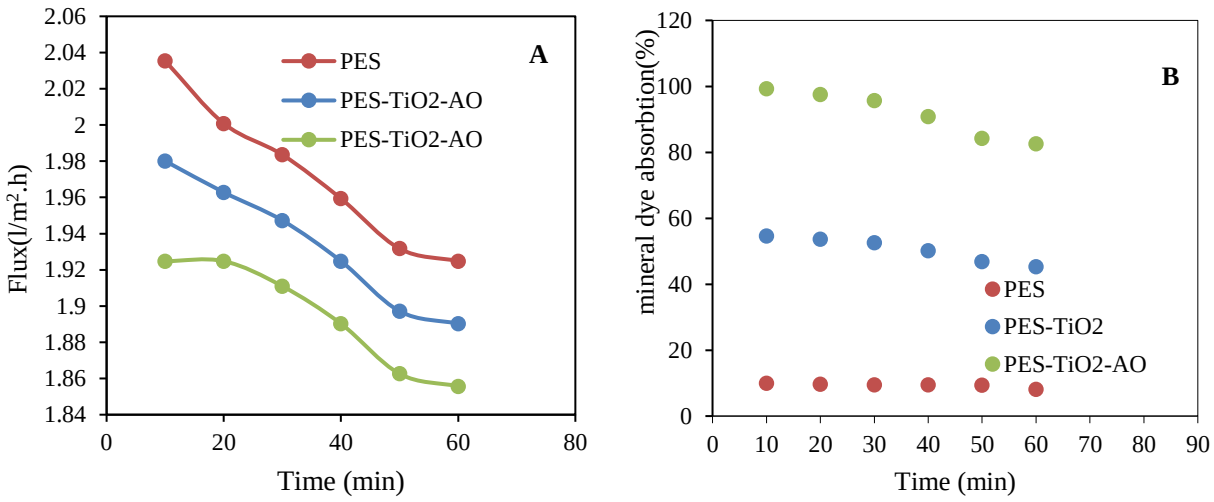

Figure 10. Value of the methylene blue dye removal for the basic and modified membranes prepared under 4.5 bar pressure and ambient conditions (Pvalue>0.05).

3.8. Heavy metal separation

The removal performance of heavy metal ions Cu(II) and Pb(II) was evaluated using both the pristine PES membrane and the surface-modified PES-NF/TiO_2/AO membrane. The feed solutions containing an initial concentration of 20 mg/L of each metal ion were prepared for the filtration experiments. As illustrated in Figures 11 and 12, the instantaneous permeate flux for both membranes exhibited maximum values at the initial stages of filtration, followed by gradual declines over time. This flux reduction can be attributed to concentration polarization and progressive membrane fouling, which increase mass-transfer resistance and reduce the effective permeability of the membrane. Such behavior is widely reported in the literature on membrane filtration and is considered a characteristic response of Nano filtration systems under the ionic load [44].

The optimized membrane demonstrated superior removal efficiencies, achieving 97.99% for Cu(II) and 94% for Pb(II). These results clearly indicate that surface modification significantly enhances purification performance by strengthening surface adsorption mechanisms, electrostatic interactions, and steric hindrance effects. The incorporation of TiO_2 nanoparticles together with aryl diazonium (AO) functional layers into the polymer matrix introduces dual functionality: (i) the increased surface hydrophilicity and negative surface charge, and (ii) a higher density of active binding sites capable of coordinating metal ions. These enhancements are consistent with prior findings on TiO_2/PES composite membranes and functionalized polymeric membranes containing metal-binding groups [45].

With the introduction of TiO_2 nanoparticles and diazonium-based functional layers, the Cu(II) rejection increased substantially from 43.2% for the pristine PES membrane to 97.99% for the modified membrane (fig 11). Similarly, Pb(II) rejection improved from 28.2% to 94%.(fig 12) This remarkable enhancement can be primarily attributed to (i) the higher density of adsorption sites originating from TiO_2 and AO functionalities, (ii) the stronger electrostatic repulsion of positively charged ions due to the more negatively charged membrane surface, and (iii) the improved hydrophilicity, which facilitates the formation of a stable hydration

layer that enhances selectivity toward metal ions.

Nevertheless, evidence in the literature indicates that excessive loading of nanoparticles may induce severe agglomeration on the membrane surface, leading to pore blockage, the reduction of effective surface area, and a decrease in the number of available adsorption sites. Such structural drawbacks ultimately reduce both ion removal efficiency and permeate flux [46]. Therefore, optimizing the nanoparticle loading and ensuring uniform dispersion within the polymer matrix are essential for achieving the maximum membrane performance.

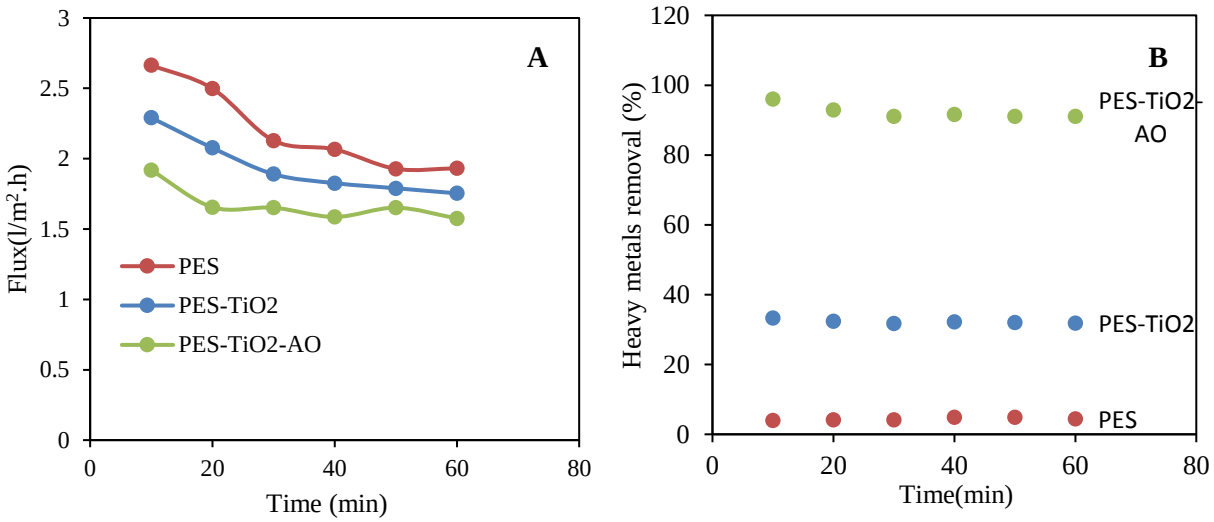

Figure 11. Cu (II) separation study for the basic membrane and the optimized membrane. A) Flux of the Cu (II) solution passing through the membrane. B) Percentage of Cu (II) removal in a time period of 60 minutes, under ambient conditions and 4.5 bar pressure.

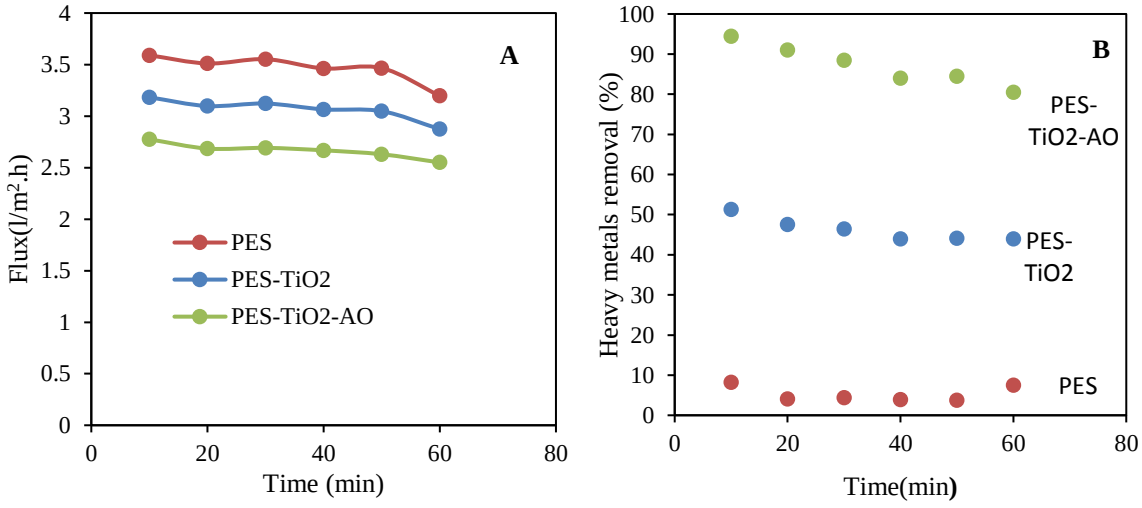

Figure 12. Investigation of Pb(II) separation for the basic membrane and the optimized membrane. A) The flux of Pb(II) solution passing through the membrane. B) The percentage of Pb(II) removal in a time period of 60 minutes, under ambient conditions and a pressure of 4.5 bar.

3.9. Membrane fouling test results

The antifouling performance of the surface-modified PES NF/TiO_2/AO membrane was evaluated through a five-cycle filtration test using a nonfat dry milk solution over a period of 300 minutes, and after each 60-minute

filtration cycle, the membrane was soaked in deionized water for 15 minutes to evaluate the ease of the fouling removal and structural stability of the modified surface. The reaction was repeated several times and the results are presented as averages. The results revealed that the modified membrane exhibited a remarkably high flux recovery ratio (FRR) without the use of any chemical cleaning agents, whereas the pristine PES membrane showed only 34% recovery. This substantial difference clearly demonstrates the superior antifouling capability of the surface-engineered membrane [47].

The enhanced FRR of the modified membrane is primarily attributed to the increased surface hydrophilicity imparted by TiO_2 nanoparticles and aryl-diazonium functionalities. These hydrophilic groups facilitate the formation of a stable and tightly bound hydration layer through hydrogen bonding with water molecules. This hydration layer acts as an effective steric and energetic barrier, mitigating hydrophobic interactions and preventing the adhesion of organic foulants such as proteins. Similar mechanisms have been widely reported as key contributors to the antifouling behavior in hydrophilic polymeric membranes [48].

As illustrated in Figures 10 and 11, the irreversible fouling ratio dramatically decreased from 34% for the pristine membrane to 2.89% for the modified PES NF/TiO_2/AO membrane. Conversely, the reversible fouling ratio increased from 32.6% to 44.5%, indicating that most foulants accumulated on the modified surface can be readily removed through simple hydraulic cleaning. This shift from irreversible to reversible fouling highlights the crucial role of the hydration layer in preventing the permanent adsorption of foul ants [49].

Overall, the findings confirm that the incorporation of TiO_2 nanoparticles and diazonium-based functional layers significantly enhances membrane hydrophilicity, promotes the formation of a protective hydration film, and markedly improves the antifouling resistance. Thus, the PES NF/TiO_2/AO membrane shows great potential for industrial applications involving highly fouling feed streams [50].

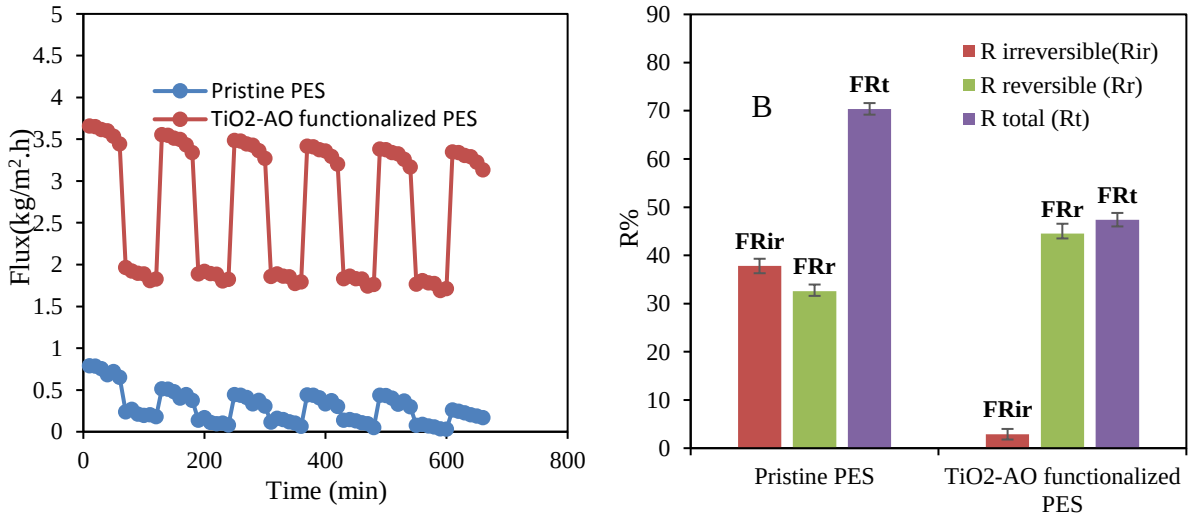

Figure 13. Evaluation of fouling parameters for the initial base membrane and the effect of membrane modification (at 27°C and 4.5 bar pressure). Positive effect of surface modifications on the fouling resistance of the modified PES NF-TiO_2-AO membrane, compared to that of the base membrane (P value >0.5).

Based on the obtained results and comparing them with those of previous studies, employing the surface-modified PES NF/TiO_2/AO membrane can be considered a viable approach for enhancing the physicochemical properties of the membrane and improving its separation performance particularly for heavy metal ion removal. All experiments were repeated across three independent cycles spaced one month apart, and observations indicated that the removal efficiency and membrane properties remained essentially unchanged; this suggests that the functional coating exhibits strong long-term stability and that the modified membrane is suitable for extended use.

Such operational durability aligns well with prior reports on mixed-matrix PES/TiO_2 membranes, which demonstrate enhanced hydrophilicity, structural stability, and fouling resistance after multiple filtration cycles [51]. Likewise, the long-term performance examinations of TiO_2-implanted PVC ultrafiltration membranes show that TiO_2 nanoparticles significantly extend membrane lifespan and preserve filtration efficacy over prolonged operation [52].

Therefore, the combined surface modification using TiO_2 nanoparticles and active chemical functionalization (AO) not only improves the morphological and surface properties of the membrane but also ensures the sustained performance and reusability in heavy metal separation applications. This makes the PES NF/TiO_2/AO membrane a promising candidate for industrial-scale water treatment and wastewater remediation.

Table 5.

Comparison between the membranes studied in this study and some other studies.

Membrane	Water flux	Heavy metals removal (%)	Ref.
PES NF-TiO_2-AO	3.66 (kg/m^2h)	Cu(II)<95.9% - Pb(II)<94.5%	This study
PES /OA-TiO_2	1.826 (kg/m^2.h)	Cu(II)<79%	51
T-AO functionalized PES	1.7506 (kg/m^2h)	Cu(II)<99% -Pb(II)<98%	10
PES-PMMA/GO	2-3% (kg/m^2.h)	Cr >81%, Cu >75%	52

4. Conclusions

In this study, the influence of the surface modification of a polyethersulfone (PES)-based nanofiltration membrane using TiO_2 nanoparticles and anilinium diazonium oligomers was systematically investigated. The surface functionalization was carried out through a dip-coating process. The combined evidence obtained from the FTIR spectroscopy, SEM imaging, and EDX elemental analysis confirmed the successful deposition of TiO_2 and the effective grafting of diazonium-based functional groups onto the membrane surface. The emergence of characteristic O–H and N related bands, the homogeneous distribution of TiO_2, the favorable morphological alterations, and the substantial decrease in water contact angle collectively demonstrated that the modification significantly enhanced the physicochemical properties and hydrophilicity of the membrane that are directly associated with the improved antifouling behavior and separation performance.

The separation experiments revealed a remarkable enhancement in the membrane's capability to remove heavy-metal ions. While the pristine PES membrane achieved only 4.3% and 2.8% rejection of Cu(II) and Pb(II) respectively, the optimized modified membrane exhibited the removal efficiency of 97.99% for Cu(II) and 94% for Pb(II). This substantial improvement is attributed to the introduction of additional active binding sites, elevated surface hydrophilicity, strengthened electrostatic interactions, and enhanced steric hindrance effects induced by the TiO_2

nanoparticles coupled with diazonium-derived functional groups.

The fouling analysis further confirmed the advantages of the surface modification. The total fouling ratio of the pristine membrane was approximately 70.4%, whereas it decreased significantly to 47.4% for the modified membrane. Moreover, the irreversible fouling fraction dropped from 44.5% to 32.6%, while the reversible fouling fraction increased correspondingly. This shift indicates that the deposition of foulants on the modified surface became less adhesive and more easily removable by simple water rinsing, reflecting the formation of a stable, hydration-rich interfacial layer that resists hydrophobic interactions. Such behavior aligns with the well-established antifouling mechanisms of hydrophilic functional layers.

Overall, the results clearly demonstrate that the PES-NF/TiO_2/AO modified membrane offers a robust and effective strategy for improving the physicochemical characteristics, antifouling resistance, and separation performance of PES-based membranes, particularly in the removal of heavy-metal ions from aqueous media. Additionally, the reproducibility tests conducted over three independent cycles within a three-month interval revealed negligible variations in performance, confirming the long-term stability of the deposited modification layer and its suitability for practical applications.

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