

http://pubs.acs.org/journal/acsodf

Recovery of Oleuropein from Olive Leaf Extract Using Zinc Oxide Coated by Polyaniline Nanoparticle Mixed Matrix Membranes

Rim Erragued, Manorma Sharma, Licínio M. Gando-Ferreira, and Mohamed Bouaziz*

Cite This: ACS Omega 2024, 9, 4762–4774



ACCESS

III Metrics & More

ABSTRACT: This study explores the integration of zinc oxide coated with polyaniline (ZnO-PANI) nanoparticles into a poly(ether sulfone) (PES) matrix to concurrently enhance permeate flux and oleuropein (OLP) rejection during the filtration of olive leaf extract (OLE). The effect of ZnO-PANI content on porosity, pore size, surface hydrophilicity, and pure water flux (PWF) was studied. The results indicate that an increase in ZnO-PANI content (0–0.2%) leads to a 3-fold increase in mean pore size, permeability (1.29–7.18 L/m² h bar), porosity (72.2–77.8%), and improved surface hydrophilicity of the prepared membranes. Membrane performance was tested for OLE permeate flux of the OLE and total phenolic compounds (TPC) rejection at various pressures (10–30 bar), the performance of the OLP rejection at 30 bar, and fouling resistance. The 0.2 wt % ZnO-



PANI membrane exhibits the highest permeate flux, while the 0.4 wt % ZnO-PANI membrane offers the highest rejection values (90–97% for TPC and 100% for OLP). Bare PES demonstrated the best fouling resistance. Strategic ZnO-PANI incorporation achieves a balance, enhancing both the flux and rejection efficiency. The 0.2 wt % ZnO-PANI membrane emerges as particularly favorable, striking a beneficial equilibrium between permeate flux and OLP rejection. Intriguingly, the use of these membranes for OLE filtration, postpretreatment with ultrafiltration (UF), results in a remarkable 100% rejection of OLP. This discovery underscores the significant and specific separation of OLP from OLE facilitated by a ZnO-PANI-based mixed matrix membrane (MMM). The study contributes valuable insights into the development of advanced membranes with enhanced filtration capabilities for high-added value phenolic compound separation.

1. INTRODUCTION

Olive tree leaves are readily available from grooves, agricultural residues, and industrial waste,¹ with the olive oil production process generating substantial amounts of about 10% of total olive weight.² Additionally, pruning contributes around 25 kg of leaves per tree annually.³ Currently disposed of through incineration or grinding, valorizing this byproduct can enhance profitability in the olive sector and mitigate its environmental impact.⁴ Researchers have explored the bioactive compounds in olive byproducts, especially in OL, which are rich in secoiridoids, flavonoids, and other phenolic compounds.^{5,6} These compounds offer diverse biological benefits, including antioxidants, anti-inflammatory, and antimicrobial effects.⁷ Industries such as pharmaceuticals, cosmetics, and food are increasingly intrigued by the potential health advantages of olive leaves.

Oleuropein, constituting 17–23% of olive leaves,⁸ demonstrates anti-inflammatory, antioxidant, antimicrobial, anticancer, and antidiabetes properties.^{2,3} The extraction and purification of oleuropein from olive leaves gain attention due to increasing demand for natural alternatives.⁹ To enhance the nutritional benefits of natural extracts and improve the added value of the final product, concentration techniques like extraction, precipitation, chromatography, electrophoresis, and osmotic distillation have been explored.^{10,11} Despite their potential, these methods are hindered by downsides, including thermosensitive compound degradation, high energy consumption, ineffectiveness, and cost intensiveness.^{9,10}

Membrane technology is a successful method for concentrating sensitive natural compounds, offering advantages such as energy savings, no additives, high removal efficiency, simplicity of operation, and environmental friendliness. In fact, a range of both polymeric and ceramic membrane processes namely microfiltration, ultrafiltration (UF), and NF

Received:October 19, 2023Revised:December 24, 2023Accepted:December 28, 2023Published:January 16, 2024





are studied for the recovery of value-added compounds, particularly phenolic compounds from different natural extracts.^{12–14} Nevertheless, there are certain limitations associated with this process, including the instability of polymeric membranes when exposed to extreme temperatures and pH conditions, limited selectivity for total phenolic compounds (TPC) separation, particularly with ceramic membranes, and potential contamination of TPC with similar molecular weight impurities.

Significant advancements in the field include the introduction of mixed matrix membranes (MMM), which show promise by integrating inorganic, organic, or hybrid nanofillers into a continuous polymeric matrix. These nanofillers can also serve as a coating layer on polymeric membranes.¹⁵

Various fillers, including titanium dioxide (TiO₂), aluminum oxide (Al₂O₃), zirconia (ZrO₂), silica (SiO₂), and graphene oxide (GO) are used in the preparation of MMMs.^{16–18} These nanomaterial additives enhance surface hydrophilicity, promote pore formation, and improve antifouling properties.¹⁶ Studies by Sharma et al.¹⁹ incorporated ZnO nanoparticles into a PSf matrix, revealing that up to 0.5% ZnO improves water flux and antifouling properties due to enhanced surface hydrophilicity. Zinadini et al.²⁰ blended GO nanoparticles into PES membranes, showing that 0.5% GO enhances pore properties, water flux, hydrophilicity, and antifouling. Wang et al.²¹ found that adding 0.01% CNTs to PES membranes improves water permeation, surface hydrophilicity, and roughness.

ZnO is a significant nanofiller with excellent properties such as commercial availability, nontoxicity, low cost, and high stability,^{16,22} making it ideal for various purposes. Despite these advantageous attributes, the incorporation of ZnO into the membrane matrix has been demonstrated to enhance the permeate flux. However, it falls short of improving the rejection efficiency.

Progressing in membrane technology science requires a careful balance between two key factors: permeate flux and rejection efficiency. Achieving a perfect harmony between these elements is crucial in membrane technology research. Researchers are dedicated to improving membrane systems, aiming not only for elevated rejection rates but also for the maximization of permeate flux. The integration of ZnO complexes with specific materials capable of adsorbing polyphenols represents a promising avenue in membrane technology. This innovative approach beckons us toward a future where membranes not only exhibit enhanced permeate flux but also attain unprecedented heights in rejection efficiency, heralding a transformative era in separation sciences. PANI is a cost-effective, environmentally stable, and highly conductive polymeric material, making it a promising adsorbent for efficient separation processes. Its notable adsorption capabilities extend to heavy metal ions and organic pollutants.²³

Therefore, incorporating nanostructured ZnO-PANI composites into the membrane matrix is considered a doubleedged sword that can enhance membrane properties and surface hydrophilicity due to the presence of ZnO in the membrane matrix and achieve a high rejection of polyphenols due to polyaniline.

In addition, PES is a promising polymeric material for membranes in separation processes due to its high rigidity, excellent thermal and chemical resistance, good mechanical stability, and commercial availability.^{24–26} These properties

make it stand out for the preparation of NF asymmetric membranes. $^{\rm 22}$

Nanostructured ZnO composites have been extensively investigated in many applications such as solar cells, chemical sensors, photocatalysis, optoelectronic, and field emission.²⁷ To the best of our knowledge, the removal of TPC has not been explored using ZnO-PANI nanocomposites. In a prior study, a simple method was used to coat PANI onto ZnO nanoparticles, creating a composite material with an enhanced adsorption capacity for phenolic compounds. Therefore, the incorporation of ZnO-PANI in MMM preparation becomes a successful candidate to enhance the membrane performance in terms of permeate flux and rejection. Hence, in this work, an innovative application of laboratory-made ZnO-PANI-based MMM to separate the OLP from the TPC was proposed. ZnO-PANI nanoparticles were chosen as the basis for creating MMM because they possess an excellent adsorption affinity for TPC and can be easily synthesized. Membranes were prepared using the nonsolvent-induced phase inversion technique, and their properties were tested by varying ZnO-PANI concentrations. The performance was evaluated through TPC rejection at various pressures (10-30 bar) and through the OLP rejection at 30 bar.

2. MATERIALS AND METHODS

2.1. Materials. Olive leaves were obtained from the Chemlali cultivar grown in Sfax (Tunisia). Following collection, the raw material was subjected to a 24 h drying process in a convection oven at 40 $^{\circ}$ C and finely ground with a blade cutter. Olive leaf powder was kept in a dark environment at room temperature (RT) until the extraction process.

2.2. Chemicals. Poly(ether sulfone) (PES, $M_w = 60,000 \text{ g} \text{ mol}^{-1}$), polyvinylpyrrolidone (PVP, $M_w = 29,000 \text{ g} \text{ mol}^{-1}$), and *N,N*-dimethylacetamide (DMAc) were purchased from Sigma-Aldrich for preparation of NF membranes. Self-synthesized zinc oxide coated with polyaniline nanoparticles (ZnO-PANI), produced through chemical oxidation polymerization, was used as an additive to prepare the membranes. For the extraction of olive leaves, ethanol from Fisher Chemical was utilized, along with distilled water obtained via the Milli-Q system from Millipore, Bedford, MA, USA. Acetonitrile high-performance liquid chromatography [(HPLC) grade] and phosphoric acid (85%) were obtained from Carlo Erba and Sigma-Aldrich, respectively, for the purpose of HPLC analysis. OLP (purity \geq 98% by HPLC), which was used as a standard, was obtained from Sigma-Aldrich.

2.3. Preparation of PES/ZnO-PANI Nanofiltration Membranes. PES/ZnO-PANI nanofiltration membranes were prepared via a nonsolvent phase inversion process using casting solutions consisting of PES (20 wt %), PVP (1 wt %), and different amounts of ZnO-PANI in DMAc as solvent. First, a desired amount of ZnO-PANI nanoparticles (0.05, 0.1, 0.2, 0.4, and 0.6 wt %) was dispersed in DMAc and kept in an ultrasonic cleaner water bath (Ultrasons, J.P. SELECTA) to achieve a suitable dispersion. The membrane identified as 0.05 wt % ZnO-PANI is the result of preparing a casting solution where the ZnO-PANI content, relative to PES + DMAC, was 0.05 wt %, etc. After dispersing ZnO-PANI in a solvent, the mixture was continuously stirred at RT for 24 h while PES and PVP were added. Afterward, the produced mixtures were ultrasonicated again for 30 min to avoid the aggregation of ZnO-PANI nanoparticles. Then, the casting solutions were left in a vacuum oven at 50 °C for 6 h to sufficiently remove the air



Figure 1. Prepared membranes with different concentrations of ZnO-PANI nanoparticles.

bubbles. Next, the homogeneous casting solutions were applied onto glass substrates by an automatic film applicator (Elcometer 4340) equipped with a 250 μ m thickness casting knife. After casting, the glass substrates were immediately submerged into a nonsolvent bath (distilled water) and then kept at 25 °C.

After initial phase separation and membrane solidification, the prepared membranes were moved to fresh distilled water containers for 24 h. Finally, the prepared membranes were kept between filter papers at RT for 1 day for drying. Figure 1 displays the membranes that have been prepared.

2.4. Characterization of Membranes. Membrane porosity was determined by gravimetric weight analysis and calculated using eq 1. The procedure entailed immersing three samples of each membrane, all with identical dimensions, in water for 24 h. Subsequently, their surfaces were dried using filter paper and promptly weighed. Following this, the membranes underwent a 24 h drying period in an oven set at 40 °C, after which they were weighed once again. To minimize errors, each experiment was conducted in triplicate. The results obtained are expressed as the average \pm the standard deviation (SD).

$$\varepsilon(\%) = \frac{\frac{m_1 - m_2}{\rho_w}}{V_m} \times 100 \tag{1}$$

where m_1 (g), m_2 (g), $\rho_{w'}$ and V_m are the wet membrane weight, dry membrane weight, water density (g/cm³), and membrane volume (cm³), respectively.¹⁵

The Guerout–Elford–Ferry eq 2 was used to assess the mean pore radius size (r_m) of the prepared membranes. This evaluation was based on the results of pure water flux (PWF) and porosity.^{33,34} Results were given as average values \pm SD.

$$r_{\rm m} = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\mu_{\rm w}lQ_{\rm w}}{\varepsilon A_{\rm m}\Delta P}} \tag{2}$$

where ε is the membrane porosity, μ_w (Pa s) is the water viscosity (8.9 × 10⁻⁴), *l* (m) is membrane thickness, Q_w (m³/

s) is the volume of water passing through the membrane per unit time, $A_{\rm m}$ (m²) is membrane active area, and ΔP (Pa) is the operating pressure.

The water contact angle measurement method was utilized to assess the hydrophilic characteristics of the prepared membrane's surface. The Theta Flex goniometer instrument (Biolin Scientific, Sweden) was employed to measure the static contact angle formed between the membrane's surface and water, using the sessile-drop method at a temperature of 25 °C. Contact angle measurements were taken at five randomly selected locations on each sample. Subsequently, the resulting average value \pm SD was calculated to minimize the experimental error.

2.5. Extract Preparation. 2.5.1. Extraction of Total Phenolic Compounds from Olive Leaves. The extraction of olive leaves was carried out as described below. Briefly, 1.2 g of olive leaves powder was immersed into 40 mL of ethanol/water, 75/25% (v/v), followed by a 90 min mixing in a shaking bath at 120 rpm and 50 °C. After extraction, the mixture was subjected to a vacuum pump using sintered glass at 0.45 μ m and then centrifuged (Sorvall ST 16 R, Thermo Scientific, Leicestershire, UK) at 4000 rpm for 15 min. The extract obtained was stored in a refrigerator until analysis.

2.5.2. Pretreatment of Olive Leaves Extract. After extraction, the olive leaf extract (OLE) underwent a UF procedure to eliminate suspended solids and, therefore, reduce the fouling phenomena during NF experiments using the prepared membranes. The filtration trials were conducted using a crossflow membrane filtration device (Sepa CF II Membrane Cell system, Sterlitech Corporation), which featured a membrane area of 140 cm², as illustrated in Figure 2. This equipment consists of a permeate and feed tank, a highpressure diaphragm pump (Hydra-Cell, Wanner Engineering, Inc.), a membrane cell system, and a pressure manometer. The UF unit was equipped with a UP005 P flat sheet membrane module (hydrophobic poly(ether sulfone), thickness between 210 and 250 μ m, typical operating pressure 5 bar, maximum operating temperature 50 °C, nominal molecular weight cutoff



Figure 2. Schematic diagram of the ultrafiltration cell in cross-flow filtration mode.

5000 Da) supplied by Microdyne Nadir (Germany advanced separation technologies). UF experiment was carried out in the batch concentration mode at an operating temperature of 25 °C and a transmembrane pressure (TMP) of about 4 bar. Permeate stream was collected and kept in a sealed glass bottle in a refrigerator until further use.

2.5.3. Determination of Total Phenolic Compounds. The analysis of TPC was performed using a modified colorimetric Folin–Ciocalteu method described by Szydłowska-Czerniak et al.³⁵ Shortly, 100 μ L of extract solution was added to 100 μ L of the Folin–Ciocalteu reagent. The mixture was then incubated at 25 °C for 5 min in the dark. Next, 300 μ L of Na₂CO₃ (0.333 g/mL) was added to the mixture. After the sample was maintained at 40 °C in the dark for 30 min, the absorbance at 765 nm was recorded using a UV/vis spectrophotometer (PG Instruments T60). A calibration curve was created using gallic

acid, and the outcomes were reported as milligrams of gallic acid equivalents (GAE) per gram of olive leaves powder (mg GAE/g_{OLP}). The results obtained are expressed as an average \pm SD of three measurements for all TPC determinations carried out in this study.

2.5.4. Analysis Using High-Performance Liquid Chromatography. The quantification of oleuropein in the different fractions of OLEs was performed in line with a method previously established by Mulinacci et al.³⁶ A HPLC system (Waters 2695 Alliance HPLC) coupled with a UV-vis multiwavelength detector was used. The separation was carried out at RT on a Brisa LC2 C18 column (250 × 4.6 mm inner diameter, 5 μ m, Spain). The mobile phase consisted of water adjusted to pH 3.20 with phosphoric acid (solvent A) and acetonitrile (solvent B). The conditions of the solvent gradient were the following: 100-89% A (0-3 min), 89-87% A (3-41 min), 87-80% A (41-55 min), 80-75% A (55-70 min), 75-100% A (70-71 min), and finishing with an isocratic elution (100% A) during 9 min. The flow rate was 1 mL/min. The chromatographic profiles were assessed at 215 and 280 nm after injecting a 10 μ L volume. Prior to injection, the samples were filtered using a 0.1 μ m microfilter. The peak of oleuropein was identified by a congruent retention time compared with a standard solution. A calibration curve was prepared at five concentration levels to quantify the amount of oleuropein. The tests were performed in duplicate, and the results are expressed as an average \pm SD.

2.6. Filtration Performance of the Prepared NF Membranes. A bench-scale, stirred dead-end filtration cell system (Sterlitech HP4750 Stirred Cell) was applied to characterize the filtration performance of the prepared membranes. The performance of PES/ZnO-PANI NF membranes was evaluated by measuring the PWF, TPC, and



Figure 3. Schematic diagram and working lab scale of the dead-end cell.

OLP rejection and analyzing the occurrence of fouling. The volume capacity and the effective membrane surface area of the module were 300 mL and 14.6 cm², respectively. The cell system was pressurized with nitrogen gas to force the liquid through the membrane. A magnetic stirrer was used to reduce the concentration polarization of the membranes. The setup of the dead-end filtration system is shown in Figure 3.

The primary aim of the water filtration test was to assess the hydraulic permeability (L_p) and resistance (R_m) of the membrane. To determine the hydraulic permeability, pure water filtration was conducted at various pressure levels (5, 10, 15, 20, 25, and 30 bar), and samples of the permeate were collected at 5 min intervals during the process.

First, each membrane was primarily immersed in distilled water for 30 min. Afterward, the membrane was fixed within the filled cell by using more distilled water. Then, the membranes were subjected to compression at 20 bar for 30 min to achieve a stable water flux. Subsequently, the pressure was adjusted to the designated working pressure. The PWF of all membranes was tested triplicate to obtain an average value \pm SD. The PWF was calculated by the following eq 3¹⁵

$$J_{\rm w} = \frac{V_{\rm m}}{tA_{\rm m}} \tag{3}$$

while J_w (L/m² h), V_w (L), t (h), and A_m (m²) stand for the permeate flux, volume of collected permeate, time for permeate collection, and effective membrane area, respectively.

The PWF values obtained were graphed against the operating TMP, yielding a linear curve. The slope of this curve was then utilized to calculate the average hydraulic permeability (as given in eq 4) within the applied TMP range.¹⁹ Permeability data were expressed as average values \pm SD.

$$L_{\rm p} = \frac{J_{\rm w}}{\Delta P} \tag{4}$$

where L_p (L/m² h bar) represents the hydraulic permeability, while ΔP (Pa) denotes the TMP.

The $R_{\rm m}$ (m⁻¹) represents the overall resistance presented by the membrane during the filtration procedure and was computed using eq 5.¹⁵

$$R_{\rm m} = \frac{1}{L_{\rm p}\mu_{\rm w}} \tag{5}$$

where μ_{w} (Pa·s) denotes the dynamic viscosity of water at the temperature employed in the filtration test.

To evaluate the performance of the membranes for concentrating TPC from UF permeate, filtration experiments at a feed temperature of 25 °C and at variable pressures (10, 20, and 30 bar) were carried out. The feed solution was stirred at a rate of 1000 rpm. Permeate samples were collected at intervals of 75 min and then analyzed for determination of TPCs and oleuropein concentrations by UV–vis spectrophotometry (Section 2.5.3) and by HPLC (Section 2.5.4), respectively, this permits the determination of rejection values for TPC and OLP as provided in eq 6.^{15,37}

Rejection
$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100$$
 (6)

where C_p and C_f represent the concentrations of TPC or OLP in the permeate and feed solutions, respectively.

2.7. Fouling Analysis. After filtration runs of OLE, the membranes underwent immediate cleaning using a 0.2 M NaOH solution at 20 bar and RT to reclaim the PWF of the membrane. The flux recovery (FR) was then determined using eq 7, allowing for an assessment of the membrane's resistance to fouling and its reusability properties.^{15,19} The FR value was expressed as the mean \pm SD for three tests.

$$FR(\%) = \frac{L_{p,f}}{L_{p,i}} \times 100$$
⁽⁷⁾

where $L_{p,i}$ and $L_{p,f}$ refer to the initial hydraulic permeability of the membrane and the hydraulic permeability restored after filtering the OLE and subsequently cleaning with a 0.2 M NaOH solution, respectively, expressed in units of (L/m² h bar).

It is important to know the amount of oleuropein adsorbed on the membrane surface. To calculate the oleuropein adsorbed on the membrane surface, permeate samples coming from the cleaning filtration using a NaOH solution were collected for 60 min and then analyzed by HPLC.

3. RESULTS AND DISCUSSION

3.1. Characterization of Membranes. *3.1.1. Porosity and Mean Pore Size.* The porosity and pore size results of the prepared mixed matrix nanofiltration membranes, calculated using eqs 1 and 2, are presented in Figure 4. The incorporation



Figure 4. Effect of ZnO-PANI nanoparticle concentration on porosity and mean pore size of prepared membranes.

of 0.05–0.2 wt % of ZnO-PANI nanoparticles in the casting solution enhances both porosity and mean pore radius compared to the bare PES membrane. This phenomenon can be elucidated by considering the impact of the speed of the precipitate phase. The presence of hydrophilic agents in the casting solution would increase the mass exchange rate between solvent and nonsolvent, resulting in bigger channels and pore size.³⁷ The membrane porosity and pore size decreased with a higher content (>0.2 wt %) of hydrophilic nanoparticles. This decrease is attributed to the increased viscosity of the casting solution.^{18,26,37,38} The rise in the casting solution viscosity can reduce the mass exchange rate, leading to the formation of a membrane with lower porosity and narrower pore size. These results align with findings from other similar studies on MMMs.^{23,26,37,39,40}

3.1.2. Membrane Surface Hydrophilicity. The hydrophilicity of a membrane's surface can impact its performance



Figure 5. Water contact angle of the prepared PES membranes.

in terms of fouling resistance, permeability, and overall efficiency. Contact angle is a common parameter used to quantify the surface hydrophilicity. A lower contact angle indicates higher hydrophilicity.¹⁸ Contact angle measurements involve placing a water droplet on the membrane surface and measuring the angle formed between the droplet and the surface. As depicted in Figure 5, it is evident that the angle between the water droplet and the membrane surface noticeably diminished by adding ZnO-PANI nanoparticles into the membrane matrix up to 0.2 wt %. This phenomenon results from the high hydrophilic nature of the incorporated nanoparticles, leading to enhanced hydrophilicity of the membrane surface.¹⁶ During the preparation of membranes by the phase inversion method, the ZnO-PANI in the ZnO-PANI/PES mixed solution tended to move to the top layer of the prepared membrane,³⁷ and after membrane formation, ZnO-PANI was fixed on the membrane surface, leading to reduced interfacial energy and improved membrane hydrophilicity.^{16,37} However, the incorporation of 0.4 and 0.6 wt % of ZnO-PANI resulted in an increase in the contact angle to $61.48^{\circ} \pm 2.1$ and $64.93^{\circ} \pm 2.2$, respectively. This might be explained by the irregular positioning of ZnO-PANI in the membrane structure at over 0.2 wt % ZnO-PANI content, which lead to aggregation and reducing the effective surface of nanotubes.¹⁸ Similar phenomena were also reported by Wang et al.²¹ and Hosseini et al.²⁴

3.1.3. Hydraulic Permeability and Resistance. The flux/ permeability of prepared membranes was analyzed to evaluate the impact of incorporating nanoparticles on the filtration efficiency. Figure 6a,b illustrates the PWF under various pressures ranging from 5 to 25 bar along with the average permeability and hydraulic resistance of the membranes.

Figure 6a distinctly illustrates that all MMMs exhibit higher flux in comparison to that of the basic PES membrane at different operation pressures. Moreover, the PWF of the synthesized membranes increases as the applied pressure increases, which is in agreement with the results reported by other researches.²⁰ As expected, the membrane with higher permeability displayed low hydraulic resistance.⁴¹ Out of all the prepared NF membranes, the bare PES membrane exhibited the highest level of hydraulic resistance, whereas the membrane containing 0.2 wt % ZnO-PANI displayed the lowest hydraulic resistance. The hydraulic resistance of 0.2 wt % ZnO-PANI was 14% lower than the bare PES membrane. By addition of the amount of ZnO-PANI nanoparticles to the polymer matrix, the prepared NF membranes showed an increase in permeability compared to bare PES membranes. At first, the permeability increased significantly when the ZnO-PANI amount was increased and then slightly reduced when the additive was further increased. The findings revealed that the highest permeability rate was observed at 0.2 wt % ZnO-



Figure 6. (a) Relationship between PWF and TMP; (b) hydraulic permeability and resistance of PES membranes that were fabricated.

PANI, with 0.1 wt % ZnO-PANI following closely in second place. The addition of ZnO-PANI until 0.2% led to an 82% increase in hydraulic permeability in comparison to the bare PES membrane.

The improvement in permeability can be related to an increase in surface hydrophilicity. It was mentioned that a strong correlation exists between water flux and the hydrophilicity of the membrane surface.¹⁶ The hydrophilic characteristic of the ZnO-PANI surface increases the hydrophilicity of the membrane surface. This increase leads to an increase in water permeability by enhancing the flow of water molecules within the membrane matrix and facilitating their passage through the membrane.^{16,26}

In addition, the membrane permeability is closely connected to morphological parameters, including porosity, and mean pore size.²³ Moreover, by addition of ZnO-PANI nanoparticles into the polymer casting solution, the interaction between the



Figure 7. Behavior of permeate flux of olive leaves extracts with time, for each TMP of prepared PES membranes: (a) bare PES, (b) 0.05% ZnO-PANI, (c) 0.1% ZnO-PANI, (d) 0.2% ZnO-PANI, (e) 0.4% ZnO-PANI, and (f) 0.6% ZnO-PANI.

polymer chain and nanoparticles may obstruct the polymer chain, thus enhancing water permeability due to the formation of additional voids, resulting from the presence of free volumes between the polymer chains and the additive interface. This results in increased porosity and subsequently increased permeability.^{18,23,26} Nevertheless, an inconsiderable decrease appears when the amount of ZnO-PANI nanoparticles increases to 0.4 wt %. This effect may be attributed to the combination of low contact angle, porosity, and pore size, resulting from the excessive addition of ZnO-PANI nanoparticles. Zinadini et al. (2017) and Bagheripour et al. (2016) both observed comparable phenomena of reduced PWF caused by high nanoparticle concentration, using ZnO/MWCNTs and PANI-*co*-MWCNT nanoparticles, respectively.^{16,23}

3.2. Nanofiltration of Olive Leaves Extract. Figure 7 illustrates the permeate flux trend over time during the filtration process of OLE using PES membranes under various pressures (10, 20, and 30 bar).

It is crucial to note that for each pressure level, a fresh membrane was employed and the filtration process was conducted continuously for a duration of 300 min. Subsequently, the membrane underwent cleaning using a 0.2 M NaOH solution, with the objective of restoring the original PWF.

As anticipated, the data presented in Figure 7 demonstrate a consistent trend of increasing flux with higher TMP values for all of the membranes tested. Furthermore, an increase in the concentration of ZnO-PANI was found to result in a corresponding increase in the initial flux of permeates from



Figure 8. Time-dependent rejection of total phenolic compounds for different TMPs of prepared PES membranes: (a) bare PES, (b) 0.05% ZnO-PANI, (c) 0.1% ZnO-PANI, (d) 0.2% ZnO-PANI, (e) 0.4% ZnO-PANI, and (f) 0.6% ZnO-PANI.

the prepared membranes. For example, at 30 bar, the initial flux of the OLE of the unfilled PES was 3.88 L/m^2 h. However, by introducing ZnO-PANI nanoparticles into the casting solution, the initial permeate flux reached 4.50, 7.00, and 7.88 L/m² h for 0.05, 0.1, and 0.2 wt % ZnO-PANI/PES membranes, respectively. This can be linked to the rise in pore size and permeability with increasing concentration of ZnO-PANI. However, at a high concentration of the nanofiller (more than 0.2 wt %), due to the phenomenon of agglomeration and plugging of the pore of membranes, the initial permeate flux was reduced to 5.58 and 3.95 L/m² h for membranes blended by 0.4 and 0.6 wt % ZnO-PANI. Concentration polarization and membrane fouling appeared to be two main factors for the flux reduction over time. It is intriguing to note that the starting flux of 0.2% ZnO-PANI was comparable to that of the 0.1% ZnO-PANI membranes. However, they exhibited a consistent decline throughout the filtration duration. In contrast, a permeate flux of 0.1% ZnO-PANI experienced a decline during the initial 75–150 min period, followed by a subsequent stabilization. Furthermore, the permeate flux of 0.6% ZnO-PANI at all pressures is low (3.95 L/m² h), then decreases very quickly and reaches 1.54 L/m² h after 300 min at 30 bar.

3.3. Total Phenolic Compounds Rejection. This study aimed to examine the nanofiltration performance of the membranes that were prepared, focusing on their ability to remove TPCs from the OLE. While the extract was filtered, permeate samples were collected and analyzed to determine the concentration of TPCs. Subsequently, the calculation of



Figure 9. Analysis of oleuropein in the feed stream, retentates, and permeates obtained after 300 min at 30 bar using different prepared membranes.



Figure 10. HPLC chromatograms of polyphenols (oleuropein) in feed; retentates (a) and permeates (b) obtained after 300 min at 30 bar using different prepared membranes.

rejection was performed. Figure 8 illustrates the correlation between the changes in phenolic compound rejection and the duration and pressure of filtration.

As displayed in this figure, the highest rejection for TPCs was obtained after 300 min from the 0.4 wt % ZnO-PANI (93.1–97.3%) and simple PES membranes, followed by 0.2,

0.1, and 0.05 wt % membranes. A low rejection was obtained by 0.6 wt % ZnO-PANI (50.2–58.2%).

Typically, membrane rejection is influenced by factors such as pore size, pore shape, and the interaction between membrane components and solute molecules.^{19,42} Although bare PES showed a relatively low flux (Figure 8a), it demonstrated satisfactory rejection capabilities for the TPCs. The reason behind this can be attributed to the presence of a small pore size in this membrane. Nevertheless, concerning the ZnO-PANI-based MMM, aside from pore size, the predominant factor influencing the removal of phenolic compounds was found to be the interaction between the membrane's constituents and phenolic molecules.

It was expected that the membranes filled with 0.05 and 0.1 wt % ZnO-PANI would exhibit superior rejection compared to the 0.4 wt % ZnO-PANI membrane because of their reduced pore size. However, these membranes displayed lower values across all pressures.

This can be related to their containing a low amount of ZnO-PANI nanoparticles and therefore less adsorption capacity.

Figure 8b-e demonstrates an increase in the rejection of phenolic compounds using the prepared NF nanocomposite membranes with the increase of ZnO-PANI nanoparticles amount into the casting solution. As a conclusion, the removal of phenolic compounds is primarily governed by the adsorption mechanism, with the performance of the synthesized membranes being influenced significantly by the concentration and dispersion of ZnO-PANI nanoparticles.⁴³ The declined rejection, which appeared using 0.6 wt % ZnO-PANI/PES membrane (Figure 8f), may be attributed to the critical agglomeration of nanoparticles at high ZnO-PANI density in the casting solution. Therefore, the amount of adsorptive active sites/active surface area decreased, causing a decrease of TPCs adsorption by nanoparticles, leading to increased transport of phenolic compounds throughout the membrane matrix. Among the prepared membranes, the modified membrane containing 0.4 wt % ZnO-PANI composite nanoparticles showed the highest rejection of phenolic compounds (about 97.3%) at 30 bar. In Figure 8, it can also be seen that all membranes indicated a linear trend for membrane rejection toward TPC with pressure and time. This result is in close agreement with the literature.^{44–47}

Solute transfer across the membrane is essentially described as being the result of diffusion or convection which are due, respectively, to a concentration and a pressure gradient across the membrane. At low pressure, the contribution of the diffusive transport is dominant, so that the concentration in the permeate fraction increases; consequently, the retention coefficient decreases. Contrariwise, with increasing pressure, the transport became convective, resulting in a lower concentration of permeate, and hence the retention coefficient is higher. In addition, the increase in the rejection coefficient with the extract filtration time extends can be explained by the solute's adsorption onto the membrane pore walls and its deposition on the membrane surface, resulting in narrower pores on the membrane surface with time.^{15,48,49} This phenomenon can be described as follows: as the filtration process continues, the feed becomes enriched with larger solute molecules that cannot readily traverse through the pores of the membrane. Consequently, these molecules begin to build up on the membrane's surface, resulting in decreased flux and an intensified rejection phenomenon. Nevertheless, these cannot be considered universal laws as various other factors may come into play, such as the intrinsic features of each membrane and the type and composition of the feed being filtered, which also play a significant role.⁴⁵

3.4. Oleuropein Rejection. To more deeply study the performance of the prepared membranes, the retentates and permeates fractions obtained after 300 min at 30 bar were

analyzed by HPLC to determine oleuropein concentration. Figure 9 illustrates the concentration of oleuropein in the feed, retentate, and permeate streams, corresponding to the various prepared membranes. Chromatographic profiles of feed, retentates, and permeates are displayed in Figure 10. Results in Figure 10 show the dominant polyphenol in the original OLE to be oleuropein, with a concentration of 44.61 mg/g_{OLP}.

NF-prepared membranes exhibited varying rejection values for oleuropein (molecular weight = 540 g mol⁻¹), ranging from 67 to 100%. From Figures 9 and 10, it is clearly observed that the rejection of oleuropein increases with the addition of adsorptive ZnO-PANI nanoparticles, and the highest rejection was obtained with 0.4 wt % ZnO-PANI membrane (100%). The reason behind this behavior may be attributed to the greater adsorption capacity of phenolic compounds exhibited by ZnO-PANI nanoparticles. Consequently, as the amount of ZnO-PANI in the membrane rises, more active sites become accessible for the adsorption of oleuropein.

However, only 67% rejection of oleuropein was achieved with 0.6 wt % ZnO-PANI membrane. This reduction may be attributed to the critical agglomeration of nanoparticles at high ZnO-PANI concentrations in the casting solution. In addition, the 100% rejection of oleuropein was attained by bare PES as a result of its small pore size and the polar interactions (van der Waals interactions and hydrogen bonds) that occur between membrane components and polyphenols such as oleuropein.⁹ However, as mentioned above, this membrane exhibits a very low permeate flux. In this work, the main goals were first to prepare MMMs of polyaniline-coated zinc oxide nanoparticles and second to obtain a hydroethanolic extract enriched with oleuropein from olive leaves. Based on the results obtained, the membrane with 0.4 wt % ZnO-PANI demonstrated excellent performance regarding the concentration of oleuropein. It successfully produced a retentate fraction that was enriched in oleuropein, reaching a content of 118.22 mg/ g_{OLP} .

3.5. Membrane Cleaning and Fouling Analysis. Membrane fouling is widely recognized as an inherent phenomenon in membrane filtration, stemming from the inevitable formation of a cake on the membrane surface or within its pores. In this study, fouling phenomena predominantly resulted from the adsorption and deposition of phenolic compounds onto the membrane surface, as well as the entrapment of these compounds within the pores.

As previously mentioned, after each pressure cycle, a fresh membrane was employed, and subsequently, the membrane underwent cleaning using a 0.2 M NaOH solution in an effort to restore the initial PWF.

To examine membrane fouling, the PWF was measured at 20 bar after the cleaning step. This was done to compare the changes in the permeability values. The calculation of the FR was then expressed as a percentage. Table 1 presents the FR

 Table 1. Flux Recovery Ratio of the Membranes That Were

 Prepared

membrane type	FR (%)
bare PES	74.3
0.05 wt % ZnO-PANI	65.3
0.1 wt % ZnO-PANI	52.2
0.2 wt % ZnO-PANI	45.1
0.4 wt % ZnO-PANI	39.2
0.6 wt % ZnO-PANI	42.2

Table 2. Oleuropein Amount in Membrane Permeate after Cleaning for Each Membrane

	/	, ,
oleuropein	(mg/	gOID

			(0.00LL)		
bare PES	0.05 wt % ZnO-PANI	0.1 wt % ZnO-PANI	0.2 wt % ZnO-PANI	0.4 wt % ZnO-PANI	0.6 wt % ZnO-PANI
1.1 ± 00	1.5 ± 00	1.9 ± 00	2.0 ± 00	2.3 ± 00	2.1 ± 00

values obtained for both simple and nanocomposite NF membranes. The incorporation of nanoparticles into the membrane matrix significantly influenced the membrane's antifouling ability, as evidenced by the prominent impact of the fouling factor FR, which is considered the most crucial in this context. The FR for the bare PES membrane which was recorded at 74.3% was higher than the blended membranes (45.1-39.2%) filled with 0.2 and 0.4 wt % ZnO-PANI nanoparticles. The decrease in FR is explained by the adsorptive effect of the used nanoparticles, which produce a thin layer cake formed by the adsorption of phenolic compounds on the membrane surface. Therefore, membranes blended with a high concentration of ZnO-PANI nanoparticles have an enhanced capability to adsorb phenolic compound molecules on their surface. The rise in FR observed in the membrane, when incorporating 0.6 wt % ZnO-PANI, could be explained by the agglomeration of nanoparticles at higher concentrations. This agglomeration may lead to a reduction in the effective surface area of the nanoparticles, subsequently resulting in a decrease in fouling occurrences.

In addition, the collected samples of cleaner permeate (0.2 M NaOH solution) from the cleaning step were subjected to analysis via HPLC to determine the membrane most affected by oleuropein deposition either within the membrane or in its pores. Table 2 presents the obtained results. All cleaner samples showed evidence of oleuropein adsorption on their surfaces, as it was present in each of them. The 0.4 wt % ZnO-PANI membrane demonstrated the highest oleuropein adsorption, as anticipated due to its superior TPC and oleuropein rejection rates compared to other membranes, followed by membranes with 0.2, 0.1, 0.05, and 0.6 wt % ZnO-PANI and, finally, by bare PES membranes.

The level of oleuropein in the cleaner sample for each membrane appears to align with the findings presented in Section 3.4.

4. CONCLUSIONS

In conclusion, this study illuminates the significant impact of ZnO-PANI on both the structure and the performance of the prepared membranes, along with their consequential effects on separation performance. The incorporation of ZnO-PANI within the developed MMMs resulted in notable enhancements in PWF, hydrophilicity, porosity, and mean pore radius. The membrane filled with 0.2 wt % ZnO-PANI emerged as the optimal choice, outperforming the bare PES membrane by striking a delicate balance between permeate flux and achieving an impressive 95% oleuropein rejection for OLE pretreated by UF at 30 bar. However, it is imperative to acknowledge the limitations highlighted in fouling studies, revealing an incomplete recovery of the original PWF for ZnO-PANIbased membranes, while the bare PES membrane exhibited superior fouling resistance. Moving forward, future investigations should prioritize the development and implementation of robust fouling mitigation strategies tailored specifically to ZnO-PANI-based membranes. Potential avenues include exploring surface modifications, integrating antifouling agents, and devising innovative cleaning protocols to bolster the

recovery of PWF postfouling events. By addressing these challenges, this study not only contributes valuable insights into membrane technology but also sets the stage for advancements that can enhance efficiency and longevity in a variety of separation applications.

AUTHOR INFORMATION

Corresponding Author

Mohamed Bouaziz – Laboratory of Electrochemistry and Environment, National School of Engineers of Sfax, University of Sfax, Sfax 3038, Tunisia; orcid.org/0000-0001-9107-7027; Email: mohamed.bouaziz@isbs.usf.tn

Authors

- Rim Erragued Laboratory of Electrochemistry and Environment, National School of Engineers of Sfax, University of Sfax, Sfax 3038, Tunisia; Department of Chemical Engineering, University of Coimbra, CIEPQPF, Coimbra 3030-790, Portugal
- Manorma Sharma Department of Chemical Engineering, University of Coimbra, CIEPQPF, Coimbra 3030-790, Portugal
- Licínio M. Gando-Ferreira Department of Chemical Engineering, University of Coimbra, CIEPQPF, Coimbra 3030-790, Portugal; © orcid.org/0000-0003-0739-1238

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.3c08225

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for support from the Strategic Research Centre Project UIDB/00102/2020, funded by the Fundação para a Ciência e a Tecnologia (FCT) and the Ministry of Higher Education and Scientific Research Tunisia (Program contract LR14ES08). The Project inpactus-innovative products and technologies from eucalyptus, project no. 21874 funded by Portugal 2020 through the European Regional Development Fund (ERDF) in the frame of COMPETE 2020 no. 246/AXIS II/2017 is also gratefully acknowledged.

REFERENCES

(1) Markhali, F. S.; Teixeira, J. A.; Rocha, C. M. R. Olive tree leaves-A source of valuable active compounds. *Processes* **2020**, *8*, 1177.

(2) Lama-Muñoz, A.; Contreras, M. d. M.; Espínola, F.; Moya, M.; Romero, I.; Castro, E. Optimization of oleuropein and luteolin-7-oglucoside extraction from olive leaves by ultrasound-assisted technology. *Energies* **2019**, *12*, 2486.

(3) Kashaninejad, M.; Sanz, M.; Blanco, B.; Beltrán, S.; Niknam, S. Freeze dried extract from olive leaves: Valorisation, extraction kinetics and extract characterization. *Food Bioprod. Process.* **2020**, *124*, 196–207.

(4) Contreras, M. d. M.; Lama-Muñoz, A.; Espínola, F.; Moya, M.; Romero, I.; Castro, E.; Castro, E. Valorization of olive mill leaves through ultrasound-assisted extraction. *Food Chem.* **2020**, *314*, 126218. (5) Cruz, R. M. S.; Brito, R.; Smirniotis, P.; Nikolaidou, Z.; Vieira, M. C. Extraction of bioactive compounds from olive leaves using emerging technologies. *Ingredients Extraction by Physicochemical Methods in Food*; Elsevier: Amesterdam, 2017; Chapter 11, pp 441–461.

(6) Cifá, D.; Skrt, M.; Pittia, P.; Di Mattia, C.; Poklar Ulrih, N. Enhanced yield of oleuropein from olive leaves using ultrasound-assisted extraction. *Food Sci. Nutr.* **2018**, *6*, 1128–1137.

(7) Irakli, M.; Chatzopoulou, P.; Ekateriniadou, L. Optimization of ultrasound-assisted extraction of phenolic compounds: Oleuropein, phenolic acids, phenolic alcohols and flavonoids from olive leaves and evaluation of its antioxidant activities. *Ind. Crops Prod.* **2018**, *124*, 382–388.

(8) Yateem, H.; Afaneh, I.; Al-Rimawi, F. Optimum conditions for Oleuropein extraction from olive leaves. *Int. J. Appl. Sci. Technol.* **2014**, *4*, 153–157.

(9) Erragued, R.; Braga, M. E. M.; Bouaziz, M.; Gando-Ferreira, L. M. Integration of solvent extraction and membrane processes to produce an oleuropein extract from olive leaves. *Sep. Purif. Technol.* **2022**, *299*, 121751.

(10) Pereira, D. T. V.; Marson, G. V.; Barbero, G. F.; Tarone, A. G.; Cazarin, C. B. B.; Hubinger, M. D.; Martínez, J. Concentration of bioactive compounds from grape marc using pressurized liquid extraction followed by integrated membrane processes. *Sep. Purif. Technol.* **2020**, 250, 117206.

(11) Khemakhem, I.; Gargouri, O. D.; Dhouib, A.; Ayadi, M. A.; Bouaziz, M. Oleuropein rich extract from olive leaves by combining microfiltration, ultrafiltration and nanofiltration. *Purif. Technol.* 2017, *172*, 310–317.

(12) Tundis, R.; Loizzo, M. R.; Bonesi, M.; Sicari, V.; Ursino, C.; Manfredi, I.; Conidi, C.; Figoli, A.; Cassano, A. Concentration of Bioactive Compounds from Elderberry (Sambucus nigra L.) Juice by Nanofiltration Membranes. *Plant Foods Hum. Nutr.* **2018**, *73*, 336– 343.

(13) Conidi, C.; Cassano, A.; Drioli, E. Recovery of phenolic compounds from orange press liquor by nanofiltration. *Food Bioprod. Process.* **2012**, *90*, 867–874.

(14) Mudimu, O. A.; Peters, M.; Brauner, F.; Braun, G. Overview of membrane processes for the recovery of polyphenols from olive mill wastewater. *Am. J. Environ. Sci.* **2012**, *8* (3), 195–201.

(15) Manorma; Ferreira, I.; Alves, P.; Gil, M. H.; Gando-Ferreira, L. M. Lignin separation from black liquor by mixed matrix polysulfone nanofiltration membrane filled with multiwalled carbon nanotubes. *Sep. Purif. Technol.* **2021**, *260*, 118231.

(16) Zinadini, S.; Rostami, S.; Vatanpour, V.; Jalilian, E. Preparation of antibiofouling polyethersulfone mixed matrix NF membrane using photocatalytic activity of ZnO/MWCNTs nanocomposite. *J. Membr. Sci.* **2017**, *529*, 133–141.

(17) Guo, J.; Kim, J. Modifications of polyethersulfone membrane by doping sulfated-TiO2 nanoparticles for improving anti-fouling property in wastewater treatment. *RSC Adv.* **2017**, *7*, 33822–33828. (18) Rahimi, Z.; Zinatizadeh, A. A. L.; Zinadini, S. Preparation of high antibiofouling amino functionalized MWCNTs/PES nanocomposite ultrafiltration membrane for application in membrane bioreactor. *J. Ind. Eng. Chem.* **2015**, *29*, 366–374.

(19) Sharma, M.; Alves, P.; Gil, M. H.; Gando-Ferreira, L. M. Fractionation of black liquor using ZnO nanoparticles/PES ultrafiltration membranes: Effect of operating variables. *J. Clean. Prod.* **2022**, 345, 131183.

(20) Zinadini, S.; Zinatizadeh, A. A.; Rahimi, M.; Vatanpour, V.; Zangeneh, H. Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates. *J. Membr. Sci.* **2014**, 453, 292–301.

(21) Wang, L.; Song, X.; Wang, T.; Wang, S.; Wang, Z.; Gao, C. Fabrication and characterization of polyethersulfone/carbon nanotubes (PES/CNTs) based mixed matrix membranes (MMMs) for nanofiltration application. *Appl. Surf. Sci.* **2015**, 330, 118–125.

(22) Nasrollahi, N.; Aber, S.; Vatanpour, V.; Mahmoodi, N. M. The effect of amine functionalization of CuO and ZnO nanoparticles used

as additives on the morphology and the permeation properties of polyethersulfone ultrafiltration nanocomposite membranes. *Composites, Part B* **2018**, *154*, 388–409.

(23) Bagheripour, E.; Moghadassi, A.; Hosseini, S. M. Preparation of mixed matrix PES-based nanofiltration membrane filled with PANIco-MWCNT composite nanoparticles. *Korean J. Chem. Eng.* **2016**, *33*, 1462–1471.

(24) Hosseini, S. M.; Bagheripour, E.; Hamidi, A. R.; Moghadassi, A. R.; Madaeni, S. S. Fabrication of PES-based nanofiltration membrane modified by composite PAA-co-PMMA-g-ZnA nanoparticles. *J. Iran. Chem.* **2016**, *13*, 1749–1758.

(25) Rahimpour, A.; Jahanshahi, M.; Khalili, S.; Mollahosseini, A.; Zirepour, A.; Rajaeian, B. Novel functionalized carbon nanotubes for improving the surface properties and performance of polyethersulfone (PES) membrane. *Desalination* **2012**, *286*, 99–107.

(26) Vatanpour, V.; Madaeni, S. S.; Moradian, R.; Zinadini, S.; Astinchap, B. Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO2 coated multiwalled carbon nanotubes. *Sep. Purif. Technol.* **2012**, *90*, 69–82.

(27) Beek, W. J.; Wienk, M. M.; Janssen, R. A. Efficient hybrid solar cells from zinc oxide nanoparticles and a conjugated polymer. *Adv. Mater.* **2004**, *16*, 1009–1013.

(28) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Conjugated polymer-based organic solar cells. *Chem. Rev.* **2007**, *107*, 1324–1338. (29) Yousefi, R.; Jamali Sheini, F.; Muhamad, M. R.; More, M. A. Characterization and field emission properties of ZnMgO nanowires fabricated by thermal evaporation process. *Solid State Sci.* **2010**, *12*, 1088–1093.

(30) Huang, J.; Xia, C.; Cao, L.; Zeng, X. Facile microwave hydrothermal synthesis of zinc oxide one-dimensional nanostructure with three-dimensional morphology. *Mater. Sci. Eng., B* **2008**, *150*, 187–193.

(31) Khan, A. A.; Khalid, M. Synthesis of nano-sized ZnO and polyaniline-zinc oxide composite: characterization, stability in terms of DC electrical conductivity retention and application in ammonia vapor detection. J. Appl. Polym. Sci. **2010**, 117, 1601–1607.

(32) Xu, F.; Lu, Y.; Xie, Y.; Liu, Y. Synthesis and photoluminescence of assembly-Controlled ZnO architectures by Aqueous Chemical growth. *J. Phys. Chem. C* **2009**, *113*, 1052–1059.

(33) Xu, Z.; Zhang, J.; Shan, M.; Li, Y.; Li, B.; Niu, J.; Zhou, B.; Qian, X. Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes. *J. Membr. Sci.* **2014**, *458*, 1–13.

(34) Ghaemi, N.; Madaeni, S. S.; Daraei, P.; Rajabi, H.; Shojaeimehr, T.; Rahimpour, F.; Shirvani, B. PES mixed matrix nanofiltration membrane embedded with polymer wrapped MWCNT: Fabrication and performance optimization in dye removal by RSM. *J. Hazard. Mater.* **2015**, *298*, 111–121.

(35) Szydłowska-Czerniak, A.; Łaszewska, A. Effect of refining process on antioxidant capacity, total phenolics and prooxidants contents in rapeseed oils. *LWT-Food Sci. Technol.* **2015**, *64*, 853–859.

(36) Mulinacci, N.; Romani, A.; Galardi, C.; Pinelli, P.; Giaccherini, C.; Vincieri, F. F. Polyphenolic content in olive oil waste waters and related olive samples. *J. Agric. Food Chem.* **2001**, *49*, 3509–3514.

(37) Wang, W.; Zhu, L.; Shan, B.; Xie, C.; Liu, C.; Cui, F.; Li, G. Preparation and characterization of SLS-CNT/PES ultrafiltration membrane with antifouling and antibacterial properties. *J. Membr. Sci.* **2018**, 548, 459–469.

(38) Hosseini, S.; Afshari, M.; Fazlali, A.; Koudzari Farahani, S.; Bandehali, S.; Van der Bruggen, B.; Bagheripour, E. Mixed matrix PES-based nanofiltration membrane decorated by (Fe3O4–polyvinylpyrrolidone) composite nanoparticles with intensified antifouling and separation characteristics. *Chem. Eng. Res. Des.* **2019**, *147*, 390– 398.

(39) Sengur, R.; de Lannoy, C.-F.; Turken, T.; Wiesner, M.; Koyuncu, I. Fabrication and characterization of hydroxylated and carboxylated multiwalled carbon nanotube/ polyethersulfone (PES) nanocomposite hollow fiber membranes. *Desalination* **2015**, *359*, 123–140. (40) Silva, T. L. S.; Morales-Torres, S.; Figueiredo, J. L.; Silva, A. M. T. Multi-walled carbon nanotube/PVDF blended membranes with sponge- and finger-like pores for direct contact membrane distillation. *Desalination* **2015**, 357, 233–245.

(41) Sharma, M.; Alves, P.; Gando-Ferreira, L. M. Effect of activated carbon nanoparticles on the performance of PES nanofiltration membranes to separate kraft lignin from black liquor. *J. Water Process. Eng.* **2023**, *52*, 103487.

(42) Hosseini, S. M.; Amini, S. H.; Khodabakhshi, A. R.; Bagheripour, E.; Van der Bruggen, B. Activated carbon nanoparticles entrapped mixed matrix polyethersulfone based nanofiltration membrane for sulfate and copper removal from water. *J. Taiwan Inst. Chem. Eng.* **2018**, *82*, 169–178.

(43) Daraei, P.; Madaeni, S. S.; Ghaemi, N.; Salehi, E.; Khadivi, M. A.; Moradian, R.; Astinchap, B. Novel polyethersulfone nanocomposite membrane prepared by PANI/Fe3O4 nanoparticles with enhanced performance for Cu (II) removal from water. *J. Membr. Sci.* **2012**, 415–416, 250–259.

(44) Diawara, C. K.; Diop, S. N.; Diallo, M. A.; Farcy, M.; Deratani, A. Performance of Nanofiltration (NF) and Low Pressure Reverse Osmosis (LPRO) Membranes in the Removal of Fluorine and Salinity from Brackish Drinking Water. *J. Water Resour. Protect.* **2011**, *03*, 912–917.

(45) Todisco, S.; Tallarico, P.; Gupta, B. B. Mass transfer and polyphenols retention in the clarification of black tea with ceramic membranes. *Innovative Food Sci. Emerging Technol.* 2002, *3*, 255–262.

(46) Cassano, A.; Cabri, W.; Mombelli, G.; Peterlongo, F.; Giorno, L. Recovery of bioactive compounds from artichoke brines by nanofiltration. *Food Bioprod. Process.* **2016**, *98*, 257–265.

(47) Bunani, S.; Yörükoğlu, E.; Sert, G.; Yüksel, Ü.; Yüksel, M.; Kabay, N. Application of nanofiltration for reuse of municipal wastewater and quality analysis of product water. *Desalination* **2013**, *315*, 33–36.

(48) Van.Gestel, T.; Vandecasteele, C.; Buekenhoudt, A.; Dotremont, C.; Luyten, J.; Leysen, R.; Van der Bruggen, B.; Maes, G. Salt retention in nanofiltration with multilayer ceramic TiO2 membranes. *J. Membr. Sci.* **2002**, *209*, 379–389.

(49) Schaep, J.; Vandecasteele, C.; Peeters, B.; Luyten, J.; Dotremont, C.; Roels, D. Characteristics and retention properties of a mesoporous γ -Al2O3 membrane for nanofiltration. *J. Membr. Sci.* **1999**, *163*, 229–237.