Enhanced Photocatalytic and Filtration Performance of TiO\(_2\)-Ag Composite-Coated Membrane Used for the Separation of Oil Emulsions

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Abstract: Polyvinylidene fluoride (PVDF) membranes were coated with TiO\(_2\) and TiO\(_2\)-Ag to enhance their efficiency for oil-in-water emulsion separation. The photocatalytic activities of the two modified membranes and their filtration performances were compared in detail. The significantly enhanced photocatalytic activity of the TiO\(_2\)-Ag composite was proved using a methyl orange (MO) solution (c = 10\(^{-5}\) M) and a crude oil emulsion (c = 50 mg L\(^{-1}\)). The TiO\(_2\)-Ag-coated membrane reduced the MO concentration by 87%, whereas the TiO\(_2\)-modified membrane reached only a 46% decomposition. The photocatalytic reduction in the chemical oxygen demand of the emulsion was also ~50% higher using the TiO\(_2\)-Ag-coated membrane compared to that of the TiO\(_2\)-coated membrane. The photoluminescence measurements demonstrated a reduced electron/hole recombination, achieved by the Ag nanoparticle addition (TiO\(_2\)-Ag), which also explained the enhanced photocatalytic activity. A significant improvement in the oil separation performance with the TiO\(_2\)-Ag-coated membrane was also demonstrated: a substantial increase in the flux and flux recovery ratio (up to 92.4%) was achieved, together with a notable reduction in the flux decay ratio and the irreversible filtration resistance. Furthermore, the purification efficiency was also enhanced (achieving 98.5% and 99.9% COD and turbidity reductions, respectively). Contact angle, zeta potential, scanning electron microscopy (SEM), and atomic force microscopy (AFM) measurements were carried out to explain the results. SEM and AFM images revealed that on the TiO\(_2\)-Ag-coated membrane, a less aggregated, more continuous, homogeneous, and smoother nanolayer was formed due to the ~50% more negative zeta potential of the TiO\(_2\)-Ag composite compared to that of the TiO\(_2\). In summary, via Ag addition, a sufficiently hydrophilic, beneficially negatively charged, and homogeneous TiO\(_2\)-Ag-coated PVDF membrane surface was achieved, which resulted in the presented advantageous filtration properties beyond the photocatalytic activity enhancement.

Keywords: polyvinylidene fluoride; membrane filtration; TiO\(_2\); silver nanoparticles; oil emulsion; zeta potential

1. Introduction

As population and consumption increase, industrial production and water usage also grow significantly. Inadequate wastewater treatment can impose a considerable burden on environmental resources, such as the water supply. For instance, the water generated during oil and gas extraction amounts to over 2.5 billion cubic meters just in the United States [1]. In
addition to the petroleum industry, various other sectors also contribute to the release of oily wastewater, such as pharmaceutical, food, and metallurgical industries, and vehicle wash stations [2–4]. This type of wastewater consists of dissolved oils, emulsified oil droplets (<5–20 µm), easily removable dispersed (20–150 µm), and floating oil (>150 µm), which cannot be effectively removed through conventional treatment methods. Improperly treated oily wastewater can damage water resources and disrupt ecosystems. This is because it contains toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals [5,6], which can bioaccumulate in living organisms and lead to biomagnification through the food chain [2,7,8]. Given the potential risks associated with these contaminants, it is essential to explore novel approaches that can effectively eliminate them.

Conventional techniques for treating oily wastewater include skimming, flotation, and sand filtration, which can eliminate floating oil with high efficiency. Moreover, chemical destabilization (coagulation/flocculation) methods are also widely used to enhance the efficiency of the previously mentioned techniques. However, for the efficient elimination of dissolved and emulsified oil droplets, advanced methods are required, such as adsorption [9], advanced oxidation processes [10], or membrane filtration [11]. These methods can be employed as a complement to conventional wastewater treatment techniques or independently to enhance treatment efficacy.

As water quality regulations tighten, membrane filtration has become popular for wastewater treatment as it can be used to demulsify and disrupt the oil–water interface in oil emulsions [12]. Membrane technology is known for its simplicity, non-chemical properties, and exceptional cleaning efficiency. However, its widespread use is hindered by rapid flux reduction, which occurs when the treated wastewater contains hydrophobic contaminants. Such wastewater leads to significant fouling of the pores, diminished lifespan, and increased energy requirement. It is necessary to develop membranes that can resist the impact of fouling and limit the interaction between pollutants and their surface.

Nowadays, an actively investigated research area of membrane separation is to improve the filtration properties of membranes by using hydrophilic and photocatalytically active nanoparticles (Al₂O₃, MgO, ZnO, SiO₂, ZrO₂, Fe₂O₃, and TiO₂) [13–18]. They cannot only reduce the pore fouling and increase the water permeability of the membranes but also potentially make them self-cleaning [19,20]. The extent of membrane fouling is primarily determined by the chemical and physical properties of the pollutants and the membrane surface. In general, low surface roughness [21], high hydrophilicity [22], and negative surface charge [23] can reduce the adhesion of oil droplets, making these properties beneficial for membranes applied for oil-in-water emulsion separation. All these factors are significantly affected by the properties of the nanomaterials used for membrane modification. Pure TiO₂, as a superhydrophilic nanomaterial, already proved to be beneficial for membrane modification [18]. However, TiO₂-based composites with higher photocatalytic activity and/or more negatively charged surfaces [13] offer further benefits. For example, carbon nanotube–TiO₂ composite-coated membranes have demonstrated increased fluxes and reduced fouling due to more negatively charged surfaces compared to solely TiO₂-coted membranes [24].

Ag deposition on TiO₂ nanoparticles is a potential solution to improve photocatalytic activity by trapping photogenerated electrons and reducing charge recombination. This has already been proven for Rhodamine B [25], tetracycline [26], sulfamethoxazole [26], metronidazole [27], oxytetracycline [28], and various endocrine disturbing compounds [29]. This effect can also be beneficial in the case of photocatalytic membranes used for the filtration of oil-in-water emulsions. Moreover, several studies show that the zeta potential of silver nanoparticles can be sufficiently negative [30–34], so the modification of TiO₂ nanoparticles with silver can potentially improve not only photocatalytic activity but filtration parameters as well. In addition, silver possesses disinfectant properties [35,36], which can be a further advantage, by preventing the formation of biofilms on membrane surfaces.

To investigate the potential advantages of TiO₂–Ag-coated membranes used in the field of crude-oil-contaminated wastewater purification (emulsion separation), we synthesized
TiO$_2$-Ag composites, prepared TiO$_2$- and TiO$_2$-Ag-coated polyvinylidene fluoride (PVDF) membranes and analyzed their photocatalytic activity and filtration properties. We described the photocatalytic activity not just by the degradation of widely used methyl orange (MO) but also via the photocatalytic treatment of an oil-in-water emulsion. Furthermore, to describe the cause-and-effect relationships, we carried out diffuse reflectance and photoluminescence spectroscopy measurements, including a detailed surface characterization via contact angle, zeta potential, scanning electron microscopy (SEM), and atomic force microscopy (AFM) measurements.

2. Materials and Methods
2.1. Synthesis and Characterization of the Nanoparticles

To modify the membranes, we used pure commercial Aeroxide P25 TiO$_2$ (Degussa-Evonik, Essen, Germany) and a silver-deposited Aeroxide P25 TiO$_2$ composite. The silver deposition was carried out according to the following procedure: 10 g of P25 TiO$_2$ was dispersed in 200 mL of MilliQ water, and 60 mL of 7.76 mM AgNO$_3$ (VWR, >99.8%) solution was added during continuous stirring. The pH was then adjusted to 7.2 using a 0.1 M NaOH solution (Sigma-Aldrich, >98%, St. Louis, MO, USA), and 80 mL of 0.242 M NaBH$_4$ (Thermo Scientific, >98%, Kandel, Germany) solution was added dropwise during continuous stirring. The beaker was covered and stirred continuously overnight to ensure the deposition of Ag nanoparticles onto the titania nanoparticles. Finally, the resulting TiO$_2$-Ag photocatalyst was washed via centrifugation (three times at 14,500 rpm for 3 min) using MilliQ water and dried at 70°C. The silver content was determined to be 0.21 wt.% (Figure S1) with a HITACHI S-4700 Type II scanning electron microscope operated using its Röntec QX2 EDS detector.

The optical properties of the photocatalysts were determined via diffuse reflectance spectroscopy (DRS) between 200 and 800 nm using a CHEM 2000 UV–vis spectrometer (Ocean Optics Inc., Orlando, FL, USA). The band gap was determined by identifying the maximum of the first-order derivative of the spectrum [37]. The photoluminescence (PL) of the nanoparticles was measured with a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer (Horiba Ltd., Kyoto, Japan) with an excitation wavelength of 350 nm. A band-pass filter (350 nm) was used downstream of the light source monochromator, and a high-pass filter (370 nm) was used upstream of the detector monochromator.

2.2. Modification of the Membranes with TiO$_2$ and TiO$_2$-Ag Nanomaterials

To produce the TiO$_2$ and TiO$_2$-Ag membranes, we coated commercial PVDF microfilter membranes (New Logic Research Inc., Minden, NV, USA; 0.2 µm pore diameter; ~0.0036 m$^2$ surface area) with physical immobilization [38]. First, 40 mg of the nanomaterial (TiO$_2$ or TiO$_2$-Ag) was suspended in 100 mL of isopropanol (c = 0.4 g·L$^{-1}$), followed by ultrasonication for 1 min. Then, the homogenized suspension was immediately poured into a dead-end membrane reactor (Millipore XFUF07601, Burlington, MA, USA) and filtered through the membrane at a pressure of 0.3 MPa. The as-prepared membranes were left to dry at room temperature for two days before application.

2.3. Production of Oil Emulsions and Filtration Experiments

To produce the oil emulsions used for the filtration experiments, first, we thoroughly blended 1 wt.% crude oil (provided by MOL Zrt, Algyő, Hungary) with ultrapure water at 35,000 rpm for 1 min using a mixer (Einhell TC-MG 135 E, Landau an der Isar, Germany). Then, 20 mL of the as-prepared oil dispersion was added into 480 mL of ultrapure water and homogenized for 10 min with an immersion-type ultrasonicator (Hielscher UP200S, Teltow, Germany) to create stable oil-in-water emulsions. The main parameters of the prepared oil emulsions are given in Table 1.
Table 1. Main parameters of the oil emulsion used for filtration experiments.

<table>
<thead>
<tr>
<th>COD (mg L⁻¹)</th>
<th>Turbidity (NTU)</th>
<th>TOG/TPH (mg L⁻¹)</th>
<th>pH</th>
<th>Zeta Potential (mV)</th>
<th>Average Oil Droplet Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>549 ± 12</td>
<td>280 ± 9</td>
<td>108 ± 2.5</td>
<td>6.2 ± 0.1</td>
<td>−43.3 ± 7.1</td>
<td>587</td>
</tr>
</tbody>
</table>

To filter the crude oil emulsions (V = 250 mL), we placed the membranes (active filtration area = 36.2 cm²) in the same membrane reactor (Millipore XFUF07601, Burlington, MA, USA), and the process was carried out at a transmembrane pressure of 0.1 MPa up to a volume reduction ratio (VRR) of five (until producing 200 mL of permeate) at a constant stirring rate of 350 rpm.

We evaluated the purification efficiency of the membranes via turbidity and chemical oxygen demand (COD) measurements. For this purpose, we used the standard potassium dichromate oxidation method. The experiments were preceded by digestion at 150 °C for 120 min; then, standard test tubes were used (Hanna Instruments, Woonsocket, RI, USA). We measured the turbidity values with a nephelometric turbidity meter (Hach 2100 N, Loveland, CO, USA). The values are expressed as “NTU” (nephelometric turbidity units). We calculated the purification efficiencies (R) based on Equation (1):

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

During the measurements, we recorded the flux (J) continuously by following the permeate weight and using Equation (2):

$$J = \frac{dV}{A_m \times dt} \left(\frac{L}{m^2 \times h}\right) \quad (2)$$

where dt is the time (h) at which the permeate weight was measured, $A_m$ is the active filtration area of the membrane we applied (m²), J is the flux, and dV is the permeate volume (L).

We investigated the fouling properties of the membranes via the resistance-in-series model [39,40]. The own resistance of the membranes ($R_m$) and the irreversible ($R_{irrev}$), re-versible ($R_{rev}$), and total ($R_{total}$) filtration resistances were calculated using the following equations:

$$R_m = \frac{\Delta p}{J_w \times \eta_w} \quad (m^{-1}) \quad (3)$$

$$R_{irrev} = \frac{\Delta p}{J_{ww} \times \eta_w} - R_m \quad (m^{-1}) \quad (4)$$

$$R_{rev} = \frac{\Delta p}{J_c \times \eta_{ww}} - R_{irrev} - R_m \quad (m^{-1}) \quad (5)$$

$$R_{total} = R_m + R_{rev} + R_{irrev} \quad (m^{-1}) \quad (6)$$

where $\Delta p$ is the transmembrane pressure we applied (0.1 MPa), $J_w$ is the flux of the water defined by the clean membrane, $\eta_w$ is the water viscosity at 25 °C (Pa·s), $J_{ww}$ is the flux of the water measured following the filtration of oil and the purification of the membranes we used (by rinsing vigorously with ultrapure water), $J_c$ is the steady-state flux measured at the end of the filtrations experiments (VRR = 5), and $\eta_{ww}$ is the viscosity of the wastewater (that is, the used oil-in-water emulsion).

As the next step, we calculated the flux recovery ratio (FRR). FRR shows the degree of the initial water flux that can be recovered by rinsing the membrane after its application (that is, after filtering oil emulsions). FRR can be determined based on Equation (7):

$$FRR = \frac{J_{wA}}{J_w} \times 100 \quad (\%) \quad (7)$$
where $J_w$ is the pure water flux of the membrane measured prior to its utilization for filtering oil emulsions, and $J_{wA}$ is the pure water flux after filtering and cleaning the surface of the membrane surface.

By comparing the flux value measured at the end of filtration experiments ($J_c$) to the clean water flux measured with ultrapure water before filtering oil emulsions ($J_w$), we can obtain the flux decay ratio (FDR) as follows:

$$FDR = \frac{J_w - J_c}{J_w} \times 100 \% \ (8)$$

2.4. Characterization of the Membrane Surface

The morphology of the membrane surfaces was investigated by SEM (Hitachi S-4700 Type II) using an acceleration voltage of 10 kV.

AFM was used to characterize the surface roughness of the coated membranes using a PSIA XE-100 type device (South Korea; NC-AFM head mode).

Membrane surfaces were also characterized by zeta potential measurements. For this purpose, we employed a streaming potential technique and an Anton Paar SurPASS 3 instrument (AntonPaar GmbH, Graz, Austria). The measurement was carried out using an adjustable gap cell and two membrane pieces (10 mm × 20 mm) fixed via double-sided adhesive tapes. The pH range we used was ~2–8 ($c_{KCl} = 0.001 \text{ mol} \cdot \text{L}^{-1}$), which was set by KOH and HCl solutions. The pH values were continuously recorded with a pH electrode.

Wetting properties of both modified and unmodified membranes were investigated by contact angle measurements with a Dataphysics Contact Angle System OCA15Pro (Filderstadt, Germany) device. For this purpose, a Hamilton pipette was used to precisely dispense 10 μL of ultrapure water onto the membrane surfaces. Then, the contact angles were recorded within 1 s between the water droplets and the membrane. The measurements were repeated three times, and the average values were considered.

2.5. Photocatalytic Experiments

The photocatalytic activities of the modified membranes were measured via the photocatalytic oxidation of 300 mL of a methyl orange solution ($c = 10^{-5} \text{ M}$) or an oil-in-water emulsion ($c = 50 \text{ mg} \cdot \text{L}^{-1}$) in a double-walled glass photoreactor (Figure 1) at 20 ºC.

![Figure 1. Schematic figure (a) and photograph of the photocatalytic reactor (b) used for measuring the photocatalytic activities of the membranes.](image-url)
Hungary) immersed into the reactor, while two membranes were fixed on the inner wall of the photoreactor. The methyl orange decompositions were carried out for 4 h, preceded by 1 h of adsorption. Samples were taken every 20 min, and changes in absorbance values were monitored with a UV–vis spectrophotometer (Biowave WPA II) at 466 nm. The photocatalytic degradation of oil emulsions was conducted for 8 h, samples were taken every 2 h, and finally, the COD values were measured (Hanna Instruments, Woonsocket, RI, USA).

3. Results

3.1. Photocatalytic Activity of the Modified Membranes

To the best of our knowledge, the photocatalytic activity of silver-deposited titanium dioxide-coated membranes has not been demonstrated for oil emulsions before. Therefore, in this work, the photocatalytic degradations of methyl orange solutions and oil emulsions were examined (Figure 2).

![Figure 2](image-url) Photocatalytic degradation of (a) the methyl orange solution (c = 10⁻⁵ M) and (b) the oil emulsion (c = 50 mg L⁻¹).

No photocatalytic degradation was measured for the neat PVDF membrane, as expected. However, the modified membranes proved to be photocatalytically active, as both the dye concentration and the COD of the oil emulsion decreased significantly. Regarding the methyl orange solution (Figure 2a), the presence of silver on the TiO₂ nanoparticles outstandingly improved the photocatalytic activity, reaching a decomposition of 87%. In comparison, the TiO₂-modified membrane demonstrated only 46% decomposition after 240 min of irradiation. The increased photocatalytic activity of the silver-deposited TiO₂ was also proved for oil emulsion decomposition. The COD reduction was ~1.5 times higher compared to that of the pure TiO₂-coated membrane: the COD of the initial oil emulsion was reduced by ~30% with the TiO₂-Ag-coated membranes during the 8 h of photodegradation, while the reduction was ~20% when the pure TiO₂-coated membrane was applied. To give some explanation for the significant difference in the photocatalytic activities of TiO₂ and TiO₂-Ag photocatalysts, we performed DRS and PL measurements.

The light absorption properties of the samples were measured by DRS (Figure 3a), and the first-order derivatives of the reflectance values as a function of wavelength are shown in Figure 3b. Figure 3a shows that the silver-deposited titania absorbs a significant number of photons in the visible light range, especially around 550 nm, in accordance with the slightly purplish color of this composite. However, this does not necessarily mean that it can be excited by those absorbed photons. Based on the first-order derive DR spectra in Figure 3b, which provide reliable information about the excitability of photocatalysts [37], there is no significant difference in the band gap values of these titania, so the deposited silver did not extend the excitability range of the TiO₂.
The PL spectra of the samples provide important information about the recombination of photogenerated charge carriers. The variation in the emission intensity (Figure 4) shows the extent of recombination by photon emission relative to each other [41]. The emission intensity of the TiO₂-Ag sample is reduced compared to that of TiO₂, which means that recombination by photon emission is lower in TiO₂-Ag than in TiO₂. Since fewer excitons (electron/hole pairs) recombine, the electrons are involved in useful processes such as the direct oxidation of contaminants and/or the production of oxidative free radicals. These findings are supported by the literature, according to which the silver deposited on the surface of TiO₂ serves as a location where electrons accumulate [42].

Figure 3. (a) Diffuse reflectance spectra of the nanomaterials and (b) their first-order derivatives.

Figure 4. Photoluminescence spectra of the nanomaterials.

3.2. Filtration of the Oil-in-Water Emulsions with the Different Membranes

The filtration parameters and key characteristics of the commercial (unmodified) PVDF membranes and the TiO₂- and TiO₂-Ag-coated membranes are summarized in Table 2. Additionally, the calculated filtration resistance values are illustrated in Figure 5.

Table 2. Membrane filtration parameters and the main surface properties of the membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Contact Angles (°)</th>
<th>( J_{\text{filtrate}} ) (L m(^{-2}) h(^{-1}))</th>
<th>( J_{\text{effluent}} ) (L m(^{-2}) h(^{-1}))</th>
<th>( J_{\text{filtrate}} ) (L m(^{-2}) h(^{-1}))</th>
<th>FRR (%)</th>
<th>FDR (%)</th>
<th>Turbidity Reduction (%)</th>
<th>COD Reduction (%)</th>
<th>Zeta Potential at pH-6 (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF neat</td>
<td>46.6 ± 0.9</td>
<td>5638</td>
<td>24</td>
<td>2567</td>
<td>45.5</td>
<td>99.6</td>
<td>97.3</td>
<td>94.4</td>
<td>−11 ± 0.7</td>
</tr>
<tr>
<td>PVDF TiO₂</td>
<td>0 ± 0.3</td>
<td>3608</td>
<td>37</td>
<td>2572</td>
<td>71.3</td>
<td>99</td>
<td>99</td>
<td>96.4</td>
<td>−25 ± 3.4</td>
</tr>
<tr>
<td>PVDF TiO₂-Ag</td>
<td>13.5 ± 0.7</td>
<td>2285</td>
<td>83</td>
<td>2112</td>
<td>92.4</td>
<td>96.4</td>
<td>99.9</td>
<td>98.5</td>
<td>−37.6 ± 1.6</td>
</tr>
</tbody>
</table>
3.2. Filtration of the Oil-in-Water Emulsions with the Different Membranes

Membrane hydrophilicity is a crucial parameter in oil/water separation that affects the filtration parameters significantly, as higher hydrophilicity (lower water contact angle) reduces the adhesion ability of the hydrophobic oil droplets. As expected, both surface modifications effectively reduced the water contact angles on the membranes compared to the uncoated (PVDF-Neat) membrane (contact angle: 46.6 ± 0.9°). Coating with TiO₂ nanoparticles resulted in a superhydrophilic surface (contact angle: 0 ± 0.3°), while after coating with the TiO₂-Ag composite, a slightly higher value was obtained (contact angle: 13.5 ± 0.7°). This can be attributed to the hydrophobic nature of AgO [43–45], which can form on the surface of the deposited silver. Table 2 demonstrates that the pure water fluxes of the modified membranes are significantly lower compared to those of the neat membrane (5638, 3608, and 2285 L m⁻² h⁻¹ for the neat, TiO₂-coated, and TiO₂-Ag-coated membranes, respectively). This is a natural consequence of the additional nanoparticle layer on the surface. The water flux of the TiO₂-Ag-coated membrane is ~37% lower than that of the TiO₂-coated membrane, even though its hydrophilicity is only slightly lower (Table 2). This means that the pure TiO₂ layer allows easier water penetration compared to the TiO₂-Ag layer. This statement is in good accordance with the higher hydrophilicity of the pure TiO₂ coating, but the significant difference suggests further affecting factors that will be discussed later. Based on the flux values measured at the end of the filtration experiments (at VRR = 5), it can be inferred that the surface modification with TiO₂ resulted in a flux improvement of ~54%, while the modification with the TiO₂-Ag composite provided a much more significant improvement of ~246%. Additionally, the FRRs also showed significant improvement, as the 45.5% value of the neat membrane increased to 71.3% and 92.4% in the case of the TiO₂-coated and the TiO₂-Ag-coated membranes, respectively.

For a more detailed discussion, the filtration resistances were also calculated and are demonstrated in Figure 5.

In accordance with the flux enhancements, Figure 5a demonstrates a significant reduction in the total and reversible filtration resistances achieved by the TiO₂ and TiO₂-Ag surface modifications. Even though the resistance of the neat PVDF membrane was increased by the coating layers, the irreversible filtration resistance was significantly reduced (Figure 5b). Irreversible resistance is the resistance that is caused by contaminants that cannot be removed by simple water flushing, which also provides information about the fouling of the membrane. The reduction in this resistance can lead to the improved lifetime and cleanability of the membranes, especially in the case of the TiO₂-Ag composite coating.

The TiO₂-Ag coating was also the most advantageous regarding the purification efficiencies of the filtration experiments (the calculated values are given in Table 2). Even the unmodified membrane ensured good purification efficiency with 94% and 97% COD and turbidity reductions, respectively. For the TiO₂-Ag-coated membrane, these values were 98.5% and 99.9%, respectively, which are even higher than the values obtained for the pure TiO₂-coated membrane.
The advantageous effects conveyed by the TiO$_2$-Ag coating (higher flux of the oil emulsion, lower total and irreversible filtration resistances, and higher purification efficiency) are in good accordance with its sufficiently high hydrophilicity and the relatively higher zeta potential (compared to the TiO$_2$ coating; Table 2). However, the relatively high membrane resistance and the relatively low water flux of the TiO$_2$-Ag-modified membrane suggest some significant morphological differences between the pure TiO$_2$- and the TiO$_2$-Ag-composite-coated membranes. According to the DVLO theory, the uniformity of particles (titania particles in our case) in suspensions is affected by the balance between the attractive and repulsive forces that exist between them. The zeta potential of the particles functions as a repulsive force, resulting in electrostatic stabilization [46,47]. Therefore, the differences in the zeta potential of the two titania (Table 2) could alter the morphology of the nanolayers of the membranes. This hypothesis is supported by the SEM images of the membrane surfaces presented in Figure 6 and by the AFM images in Figure 7 as well.

![Figure 6. SEM micrographs of the (a) TiO$_2$- and (b) TiO$_2$-Ag-coated membranes. The red arrows indicate the difference in the continuity/homogeneity of membrane coatings.](image)

The nanoparticle layer on the TiO$_2$-modified membranes consists of large aggregates and does not form a continuous, homogeneous layer (Figure 6a). In contrast, when the surface was modified with TiO$_2$-Ag, a less significant aggregation of the nanoparticles was observed (Figure 6b). AFM images (Figure 7) also show big aggregates and a rougher surface for the TiO$_2$-coated membrane compared to the much smoother surface of the TiO$_2$-Ag-coated membrane. These results are in good accordance with the zeta potential values (Table 2) of the TiO$_2$ and TiO$_2$-Ag-coated membrane surfaces, as the latter was ~50% more negative (−37.6 ± 1.6 mV) than the former (−25 ± 3.4 mV). Moreover, based on the literature, the nanoparticles can form stable and homogeneous suspensions when the surface charge is above +30 mV or below −30 mV [46,47]. This can explain the significant differences in the homogeneity of the nanolayers, as their zeta potentials are above (for TiO$_2$) and below (for TiO$_2$-Ag) this crucial −30 mV value. The resulting more homogeneous and compact TiO$_2$-Ag composite layer explains the significantly lower pure water flux and higher membrane resistance of the TiO$_2$-Ag-coated membrane compared to the TiO$_2$-coated membrane. These properties, together with the reduced surface roughness, could also contribute to the significantly higher emulsion fluxes and purification efficiencies. Moreover, the negative zeta potential of the TiO$_2$-Ag-coated membrane was beneficial concerning the electrostatic repulsive forces between the membrane and the negatively charged oil droplets. Thus, their ability to attach to the surface was reduced, contributing to the measured higher flux and flux recovery ratio and the reduced irreversible resistance.
Figure 6. SEM micrographs of the (a) TiO$_2$- and (b) TiO$_2$-Ag-coated membranes. The red arrows indicate the difference in the continuity/homogeneity of membrane coatings.

Figure 7. AFM images of the (a,b) TiO$_2$- and (c,d) TiO$_2$-Ag-coated membranes.

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3.3. Comparison of the Main Separation Results with Other Relevant Studies

For comparison, Table 3 demonstrates a comprehensive summary of the main parameters of other studies, which also used TiO$_2$-Ag- (or Ag-) modified membranes for the separation of different kinds of oil emulsions. It should be noted that the membrane modification techniques and the types/concentrations of oil emulsions used in these studies differ from those used in our study. Despite this, in general, the results of these studies also indicate that the utilization of Ag nanoparticles for membrane modification usually significantly improved the filtration properties, reduced the fouling rate, and yielded retention values similar to the results presented in our work (>98.5%). For instance, R. Torres Mendiate et al. [48] modified PVDF membranes with silver nanoparticles and achieved a fourfold increase in the flux value (12 and 45 L m$^{-2}$ h$^{-1}$ were measured for the unmodified and modified membranes, respectively) in the case of a vegetable oil-containing emulsion. This result is consistent with our flux increase (24 and 83 L m$^{-2}$ h$^{-1}$ for the unmodified and modified membranes, respectively).
Table 3. Comparison of the main parameters and results with other relevant studies, applying TiO$_2$-Ag- or Ag- modified membranes for the separation of oil emulsions.

<table>
<thead>
<tr>
<th>Membrane or Underlayer</th>
<th>Modifier Nanomaterial</th>
<th>Type of Oil (Concentration)</th>
<th>Pressure</th>
<th>Surfactants (Concentration)</th>
<th>Water Flux (L m$^{-2}$ h$^{-1}$)</th>
<th>Effluent Flux (L m$^{-2}$ h$^{-1}$)</th>
<th>Rejection (%)</th>
<th>Fouling Indicators</th>
</tr>
</thead>
</table>
| [48] PVDF              | Ag                    | vegetable oil ($w/w = 1/1$ o:w) | 0.002 MPa | Triton X100                 | unmodified: -                    | unmodified: -12                 | ~96           | unmodified: 22.4 (FRR)
|                        |                       |                            |          |                             | modified: ~45                   | modified:                  |               | modified: 38.1 (FRR)—after ten runs |
| [49] CA                | RGO-Ag-TiO$_2$        | n.a. ($v/v = 1/100$ o:w)   | 0.09 MPa (vacuum) | SDS (0.4 g·L$^{-1}$) | unmodified: 20,472               | ~30               | >97           | no obvious decline after six cycled experiments |
| [50] Copper mesh       | TiO$_2$-SGO-Ag        | gasoline, n-heptane ($v/v = 1/10$ o:w) | gravity | CTAB (0.5 g·L$^{-1}$) | unmodified: ~50                 | ~50               | >99           | no obvious decline after ten cycled experiments |
| [51] Ceramic (TiO$_2$/ZrO$_2$) | Ag-CuO               | gasoline (1000 ppm)         | 0.1 MPa (vacuum) | Tween-20 (0.5 g·L$^{-1}$) | unmodified: ~230                 | unmodified: ~130      | >97           | unmodified: 77.19 (FRR)
|                        |                       |                            |          |                             | modified: ~300                  | modified: ~220       |               | modified: 90.62 (FRR) |
| Current study          | PVDF                  | crude oil (400 ppm)         | 0.1 MP   | -                           | unmodified: 5638                | unmodified: 24         | >98.5         | unmodified: 45.5 (FRR)
|                        | TiO$_2$-Ag            |                            |          |                             | modified: 2285                 | modified: 83          |               | modified: 92.4 (FRR) |
4. Conclusions

To the best of our knowledge, this study describes first in detail the reasons behind the beneficial properties of silver-containing titanium dioxide as a membrane surface modifier for both the photocatalytic degradation and membrane separation of crude oil-contaminated wastewater (emulsion).

Applying TiO$_2$-Ag nanocomposite on the membrane surface significantly improved the photocatalytic decomposition of the oil emulsion, as the COD reduction was ~1.5 times higher compared to the pure TiO$_2$-coated membrane. The first-order derivatives of the DR spectra did not demonstrate significant differences in the bandgap values of the two titania. However, the PL spectra indicated that recombination by photon emission was suppressed in the TiO$_2$-Ag composite (compared to pure TiO$_2$), which explained the enhanced photocatalytic activity.

Surface modification with the TiO$_2$ resulted in a flux improvement of ~54%, while modification with the TiO$_2$-Ag composite provided a much higher enhancement of ~246%. The FRRs also showed a significant improvement, as the 45.5% value of the neat membrane increased to 71.3% and 92.4% for the TiO$_2$-coated and the TiO$_2$-Ag-coated membranes, respectively. In accordance with the flux enhancements, a significant reduction in both the total and reversible filtration resistances was achieved by TiO$_2$ and TiO$_2$-Ag surface modifications. Moreover, the irreversible filtration resistance was also reduced, especially for the TiO$_2$-Ag composite coating, improving the lifetime and cleanability of the membranes. Coating with TiO$_2$-Ag was also the most advantageous regarding the purification efficiencies of the emulsion filtrations.

All these advantageous effects of TiO$_2$-Ag coating directly originate from its sufficiently high hydrophilicity and relatively high zeta potential. The latter also resulted in a smoother, more continuous, and homogeneous coating compared to the one obtained for the pure TiO$_2$-coated membranes, which also contributed to the beneficial filtration properties.

Based on the presented results, TiO$_2$-Ag nanocomposites are promising for modifying membranes used for the filtration of oily wastewater. Therefore, this composite is worth investigating further in future studies aiming to develop nanocomposite membranes produced by either grafting and/or blending methods, which are durable enough for long-term (practical) utilization as well.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations11040112/s1, Figure S1: Elemental analysis of the TiO$_2$-Ag-coated PVDF membrane.

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