A preliminary study on cellulose acetate composite membranes: effect of nanoparticles types in their preparation and application

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Abstract

This work reported a new perspective on improving the incorporation of nanoparticles (NPs) into membranes for several applications. Composite membranes were produced via the phase inversion method using cellulose acetate (CA) as the polymer, mixed with four different NPs: ZnO and Fe3O4 NPs were prepared by the co-precipitation method, while SiO2 and TiO2 NPs were commercial NPs. The impact of NPs on the membrane morphology was investigated by SEM and AFM. The composite CA membranes have been characterized by their contact angle, porosity, and water content. Membrane performance has been investigated in terms of water permeability and salt retention such as NaCl and Na2SO4. The produced CA composite membrane could be successfully applied for salt removal, particularly the CA-Fe3O4 composite membrane, which shows good water permeability (15.41 m2 h bar−1) and higher salt rejection (93%). Consequently, the use of low-density hydrophilic NPs in the polymeric dope solution produces membranes with higher hydrophilicity and the ability to reduce the membrane fouling.

1. Introduction

Membrane technology can be successfully applied in several manufacturing industry fields as a suitable separation technique for water treatment and purification (e.g., wastewater treatment and desalination). Furthermore, membrane technology has several advantages over other separation technologies due to its easy scale-up, low energy consumption, low operating pressures, and high fluxes. Furthermore, it plays a significant role in water purification due to its low environmental impacts [1, 2]. Among the different membrane processes, nanofiltration (NF) represents a well-established technology for applications involving aqueous streams. NF performance can be considered among ultrafiltration (UF) and reverse osmosis (RO), with a molecular weight cut-off (MWCO) comprised of from 200 to 1000 Da, depending on their surface charges (ion-selective membrane). Moreover, the NF process is one of the most widely used for salt retention, dyes, and textiles wastewater, due to its superior rejection of multivalent ions [3]. Several types of polymers are commonly used for the production of NF membranes, such as polyimide (PI), polyamide (PA), polydimethylsiloxane (PDMS), polyacrylonitrile (PAN), polysulfone (PS), and cellulose acetate (CA) [1]. In this context, CA polymer is known for its environmentally-friendly properties, low cost, and good resistance to solvents and chlorine [5]. In addition, due to its hydroxyl groups, CA has a high affinity for water [6], but one of the disadvantages of the CA membrane might be its sensitivity to fouling [7–9]. Several approaches have been developed by many researchers to solve this problem and improve the performance of CA membranes. Shen et al [7] prepared antifouling CA
membranes using a novel hydrophilic and oleophobic additive. Lavanya et al [5] prepared CA and poly (methyl vinyl ether) maleic acid (PMVEMA) blend membranes for removal of heavy metal ions. Similarly, Saljoughi et al [10] reported the use of polyvinylpyrrolidone (PVP), for CA blend membrane preparation. In addition, other ways to improve membrane performance is the use of nanoparticles (NPs). In fact, as widely reported in the literature, NP incorporation in membranes leads to a range of advantages: (i) improvement of hydrophilicity (ii) reduction of the fouling phenomena, (iii) improvement of rejection, and (iv) physical efficiency (mechanical and thermal stability) [8, 11]. In this context, NPs can be employed to produce tailored CA membranes. Abedini et al [12] produced CA/TiO2 composite membranes with higher pore size and water permeability, up to 47.42 l m⁻² h⁻¹ bar⁻¹. Arthanareeswaran et al [13] investigated whether SiO2 NPs affected the UF-CA membranes. Similar work reported as SiO2/CA nanocomposite membrane has been successfully used to treat triazines (98%) from water [14]. To improve the performance of the CA forward osmosis (FO) membrane in terms of water flux (26.57 l m⁻² h⁻¹), and salt rejection (99.5% of Na⁺, 100% of Cl⁻, and 99.6% of Mg²⁺) [15]. Recently, many works have reported the preparation of blended membranes using other inorganic materials such as titania, silica etc Das et al reported that increasing the content of TiO2 NPs on the CA membranes, leads to largely interconnected fiber networks: the roughness was enhanced and the membranes degradation decreased [16].

Gebru et al prepared CA-PVP-TiO2 (CATP) membranes via a phase inversion (PI) process for the removal of bovine serum albumin (BSA) [17]. The authors reported that the addition of PVP and TiO2 to the dope solution reduces the formations of finger-like structures and macrovoids, while improving porosity, average pore size, and hydrophilic contact angle of the CA membranes. Also, Gebru et al also reported the preparation of blended from CA/polyethylene glycol (PEG) membranes, using a modified amine-TiO2 NPs by PI technique [18]. They pointed out that incorporation of modified amine-TiO2 improves the membrane fouling and the efficiency of the membranes during the test of chromium removal via UF.

On the basis of literature review, the aim of this work is to improve the performance of CA membranes by adding NPs such as TiO2, SiO2, ZnO, and Fe3O4 in the polymeric dope solution. Therefore, the effects of SiO2, TiO2, ZnO, and Fe3O4 NPs on the structure of the CA NF composite membrane were studied and evaluated. Membrane performance was valued in terms of PWF and salt retention. CA composite and CA control membranes have been fully featured based on morphology (SEM and AFM), contact angle, porosity, and equilibrium water content. As a novelty of this work, a comparison of four NPs for the preparation of CA NF membranes was developed for the first time.

2. Materials and methods

2.1. Materials

Cellulose acetate (CA, Mw = 30.000 g.mol⁻¹), formamide, acetone, iron(III) chloride hexahydrate 97% (FeCl3·6H2O), iron(II) chloride tetrahydrate 99% (FeCl2·4H2O), ammonium hydroxide 28% NH3 (NH4OH), zinc acetate dehydrates (Zn(CH3COO)2·2H2O, 99%), ethanol, 2-propanol, fumed silica powders (SiO2; 20 nm), titania NPs (TiO2; 95nm particle size), and sodium salts (NaCl, and Na2SO4) were purchased from Sigma Aldrich.

2.2. Synthesis of ZnO and Fe3O4 nanoparticles

The ZnO and Fe3O4 NPs were prepared according to the chemical co-precipitation method, as reported in the literature [19–21].

2.2.1. ZnO synthesis

Initially, 50 ml of the solution of Zn (CH3COO)2·2H2O (0.2M) was added as a precursor, followed by 50 ml of NH3·H2O (2M) solution in drops. During the addition, the zinc acetate dehydrates storage solution was kept under non-stop stirring for 3 h. After this time, the precipitate was recovered and placed in a muffle furnace at 300 °C. The ZnO NP size was 47 ± 2.1 nm [19].

2.2.2. Fe3O4 synthesis

Magnetite oxide (Fe3O4) NPs (~20–40 nm) were synthesized using iron (III) chloride hexahydrate 97% (FeCl3·6H2O) and iron (III) chloride tetrahydrate 99% (FeCl2·4H2O), as a source of Fe²⁺ and Fe³⁺ ions, respectively. In particular, 4.6 g of FeCl3·6H2O, and 1.5 g of FeCl2·4H2O, were mixed into 50 ml of distillate water under an N2 atmosphere. The solution was stirred for 20 min at 400 rpm. Then, 10 ml of NH3·H2O was added to the solution, to obtain a black precipitate. The liquid solution was further agitated for 2 h. Finally, the obtained black precipitate, consisting of Fe3O4 NPs, was recovered using a magnet, cleaned using water and alcohol (ethanol), and dried in a vacuum at 65 °C overnight [20, 21].
2.3. Polymeric dope solution
Polymeric dope solution was prepared by mixing 22 wt% CA polymers with 1.5 g of the sampled NPs with SiO₂, TiO₂, ZnO, and Fe₃O₄ in a binary diluent system of acetone and formamide (2:1) at 25 °C. The liquid underwent 24 h of agitation until it obtained a homogeneous casting solution with optimal dispersion of the NPS. Before casting, the liquid solution was degassed for 6 h.

2.4. CA composite membrane preparation
CA composite membranes were produced by casting the dope solution onto glass support using a doctor’s blade (gap size of 200 μm). According to the PI technique, CA polymer is transformed in a controlled manner from a liquid (dope solution) to a solid state (nascent membrane). Before the immersion in the water coagulation bath (4 °C for 1 h), the nascent membranes were exposed to air for 2 min, to promote solvent evaporation [22]. Finally, the produced membranes were washed for 10 min in a water bath at a temperature of 60 °C. A blank control membrane was prepared without NPs in the dope solution. All produced membranes are summarized in Table 1.

3. Membrane characterization

3.1. SEM (Scanning Electron Microscope)
Morphology (cross section, top and bottom side) of the CA composite membranes was studied by scanning electron microscopy (Zeiss EVO MA100, Assing, Italy). Before the analysis, the membranes were sputter-coated with gold (Quorum Q150R S).

3.2. AFM (Atomic force microscopy)
Topography of the CA composite membranes was measured by atomic force microscopy (NanoScope III, Digital Instruments, VEECO Metrology Group). The images, with a scan size of 5 μm × 5 μm, were acquired in tapping mode using silicon probes (200–300 kHz). Roughness was assessed by the root mean square difference, RMS (Rq), and the mean absolute value difference (Ra). The reported roughness data values are the average, and the relative standard deviation, of 50 measurements on a 1 μm² area.

3.3. Contact Angle WCA
The hydrophobicity and hydrophilicity characteristics of CA composite membranes were investigated by WCA. The measures were performed using the Attention Theta T200 blood pressure monitor (Biolin Scientific, Sweden) instrument, using ultrapure water drop of 5 μl. For all membranes, four measurements were taken; both the mean and the standard deviation are reported.

3.4. Equilibrium Water Content EWC
EWC of the CA composite membranes was determined according to the equation (1):

\[ \text{EWC} = \frac{m_w - m_d}{m_w} \times 100 \]  

A membrane sample was initially dipped in distillate water for 24 h and then weighed (m_w). Finally, the membrane specimen was dried in an oven at 75 °C for 24 h, and the weight (m_d) was evaluated again. For each sample, five measurements were taken, with a calculated mean and corresponding standard deviation.

3.5. Porosity (ε)
Porosity was evaluated by measuring the weight of the membrane sample before (W_w) and after (W_d) the immersion in 2-propanol for 24 h, as reported in the literature [22, 23]. Membrane porosity (ε) represents the ratio between the total volume of the membrane and the volume of its voids, according to the applied equation (2):

Table 1. CA composite membranes.

| Membrane name | NPs type | NPs (wt %) |
|---------------|----------|------------|
| CA-control   | —        | —          |
| CA-SiO₂      | SiO₂     | 1.5        |
| CA-TiO₂      | TiO₂     | —          |
| CA-ZnO       | ZnO      | —          |
| CA-Fe₃O₄     | Fe₃O₄    | —          |

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\[ \varepsilon(\%) = \frac{W_w - W_D/\rho_K}{(W_w - W_D/\rho_K) + (W_D/\rho_P))} \times 100 \]  

(2)

Where \( \rho_K \) and \( \rho_P \) are the densities of 2-propanol (0.78 g ml\(^{-1}\)) and CA polymer (1.28 g ml\(^{-1}\)), respectively. For all membranes, three measurements were performed, and then the mean values and corresponding standard deviation were plotted.

### 3.6. Water flux and salts rejections experiments

Water flux (Jw) experiments were performed using a dead-end stainless-steel cell (Millipore) with a total volume of 500 ml, 5.96 cm of diameter, and an effective membrane area of 38.54 cm\(^2\). The experiments, which conducted at room temperature, were carried out by applying different N\(_2\) gas pressures (trans-membrane pressure (TMP)) from 2 to 14 bar. Before the Jw tests, for 2 h, the membrane was conditioned at a TMP of 16 bar. Jw was estimated according to this equation (3):

\[ J_w = \frac{Q}{A \cdot t} \]  

(3)

Where ‘Q’ is the volume of permeate (L), ‘A’ is the area of the membrane (m\(^2\)), and ‘t’ is the time (hours). Permeability experiments were also conducted using a sodium salt solution (1 g l\(^{-1}\)). Feed and permeate salt solution concentration (NaCl and Na\(_2\)SO\(_4\)) was determined by measuring the electrical conductivity with the use of a calibrated conductivity meter (Consort NV, model C832, Turnhout, Belgium). Retention (R\%) was then calculated according to the following equation (4):

\[ R(\%) = \left( \frac{C_f - C_p}{C_f} \right) \times 100 \]  

(4)

Where \( C_f \) and \( C_p \), represent the feed and permeate concentrations (expressed in mS cm\(^{-1}\)), respectively.

### 4. Results and discussion

#### 4.1. Characterization membranes

##### 4.1.1. SEM, AFM, and WCA analyses

SEM images of the produced CA composite membranes were reported in figure 1. The top surface of the CA control membrane has smaller pore sizes with a roughened surface. When NPs are added, the surface of the composite membranes becomes smoother. However, the NPs appear uniformly distributed on the membrane surface, with no apparent aggregation. Typically, during the preparation of the CA membrane, the rate of solvent/non-solvent exchange is delayed, and polymer precipitation is slow. This effect depends on the nature of the solvent, as reported in the literature [22]. Therefore, the consequence of this L/L phase separation (PS) is the emerging of an asymmetric membrane with a thin dense layer over a porous sublayer, therefore the membrane consists of two layers: a top layer and a sublayer [24]. The presence of the NPs in the dope solution influences the velocity of the membrane formation during the PS, obtaining membranes with different morphology. For the control membrane, CA-SiO\(_2\), CA-TiO\(_2\) and CA-FeO\(_3\) membranes is visible the formation of the top layer. The thickness of this layer, which acts as selective layer, increases in relation to the velocity of the solvent diffusion through the sublayer. In this case, the demixing happens quickly with the formation of membranes they present a thin top layer and a sublayer with a lot of macropores. In particular, CA-control and CA-SiO\(_2\) membranes, presented a finger like structure due to the fast solvent and non-solvent diffusion. The thickness of the selective layer increases (∼3 \( \mu \)m) when the composite membrane was prepared using SiO\(_2\) NPs, where similar results were reported by Arthanareeswaran et al [13]. While, using TiO\(_2\) NPs, the macropore occurrence decreased, probably because the NPs influences the phase transition, delaying it and the resulting CA-TiO\(_2\) membrane was characterized by a sponge structure. Only the CA-ZnO membrane seems thick. The addition of ZnO NPs in the dope solution further delays demixing during the membrane formation process, creating over densification with suppression of macropores and formation of a denser structure. In fact, according to literature in the case of ZnO membrane, the top layer limits the non-solvent diffusion during the L/L PS with formation of dense structure [25].

An AFM analysis was performed in order to visualize the surface roughness of the prepared membranes. Also, the morphology and the topography affect the resulting membrane and their investigation gives us the possibility to predict the effect on performance. Moreover, AFM gives not only qualitative information but also quantitative, such roughness. Figure 2 reports the AFM images of the produced CA membranes (CA-control, CA-SiO\(_2\), CA-TiO\(_2\), CA-ZnO, CA-FeO\(_3\)). The analysis of AFM micrographs (figure 2) shows that the surface of the compositemembranes was uniform, and the addition of NPs results in a smoother texture, as can be seen by comparing the CA-control membrane image with the other ones. In fact, when the NPs were added to the dope
solution, the demixing rate during membrane formation was changed. The lower rate results in a smoother surface in comparison with the native membrane (without NPs). In fact, the addition of low amounts of the NPs, reduced the membrane roughness, as expected [26, 27].

In table 2, the roughness values in terms of Ra and RMS are reported. Both the values are the result of 50 measurement media on 1 μm² areas and are expressed in nm. Furthermore, the 3D images describe the tiny nodules’ structure on membrane surface.

Water contact angle (WCA) measurements are in agreement with AFM images based on the Wenzel equation [28]:

$$\cos \theta_{\#} = \cos \theta \times r$$  \hspace{1cm} (5)

Where $\theta$ is Young’s angle and $r$ is the surface area of the solid.

The NPs addition reduces the roughness and enhances the hydrophilicity of the membranes [8, 27, 29]. In fact, as mentioned in figure 3, WCA decreases from 67° to 60° when the NPs are added to the membranes.

4.1.2. Equilibrium water content (EWC) and porosity

The EWC of the membrane is not only directly related to the hydrophilicity [30] but also to the membrane porosity. As expected, a jump in water content is due to the increase in membrane hydrophilicity and we can explain this to a high level of hydrophilicity promotes the diffusion of a water molecule into the membrane. In this paper, a gravimetric method reported in sections 3.4 and 3.5, was used to determine the EWC, and porosity and the results were summarized in figure 4.
In all cases, both porosity and EWC are enhanced when the NPs are added to the membrane. Notably, the porosity increases from 72 to 75%, while the EWC jumps from 66 to 73%. According to the literature, the presence of NPs not only raises the hydrophilicity, but affects the rate and speed of the exchange solvent/solvent, during the membrane formation and therefore influences the final structure of the membranes \[31\].

The highest values were obtained for the CA-ZnO composite membrane (75% porosity and 73% EWC). This result is in accordance with the contact angle, with a lower data of 58° for the CA-ZnO composite membrane. In comparison with the other NPs, ZnO oxide showed an improvement in EWC and higher membrane porosity, making the membrane surface more hydrophilic.

### 4.2. Membranes’ performances

#### 4.2.1. Pure water flux (PWF) and salt retention

The CA and CA-composite membranes’ performance was evaluated in terms of water permeability and salt retention. In figure 5, it is possible to evaluate the trend of the flux in relation to the applied pressure. As
expected, the flux increases linearly with the pressure, and the CA-composite membranes exhibited a higher flow than the pure membrane (CA-control). This phenomenon is due to the enhanced hydrophilicity porosity of the membrane. The water permeability ranged from 9.93 l m\(^{-2}\) h bar\(^{-1}\) for the CA-SiO\(_2\) membrane to...
15.4 l m² h⁻¹ bar⁻¹ obtained for CA-Fe₃O₄ membrane. The CA-control membrane possesses a permeability of 8.07 l m² h⁻¹ bar⁻¹. These results reflect the SEM images and characterization tests. The CA-Fe₃O₄ composite membrane, which presented a higher permeability value (15.4 l m² h⁻¹ bar⁻¹), is strongly related to its structure, having a thin selective layer and macrovoids [32]. On the contrary, the CA-SiO₂ composite membrane presented the lowest permeability value due to its thicker elective layer (9.94 l m² h⁻¹ bar⁻¹). The total thickness of the membranes is shown in Table 3.

Figure 6 (a) and (b) reports the NaCl and Na₂SO₄ rejection, of the produced CA and CA composite membranes (salts concentration 1000 mg l⁻¹; ΔP = 14).

As expected, for each CA composite membrane, the retention sequence was R(Na₂SO₄) > R(NaCl), as expected. This effect is due to two contributions: i) by the steric hindrance mechanism and ii) by the dehydration phenomenon. As reported in the existing literature [23, 33], the divalent ions are sterically retained due to their larger hydrated size. The HE of SO₂⁻ was 1047 kJ mol⁻¹, whereas it was 325 kJ mol⁻¹ in the case of Cl⁻ (Table 4). In addition, the divalent ions exhibited a higher hydrated radius than the monovalent ions (0.379 and 0.332 nm for SO₂⁻ and Cl⁻, respectively). The obtained retention results are comparable with those reported in the literature for membranes prepared with NPs (Table 5).

Furthermore, in all cases, the retention results of the CA composite membranes were higher than those of the CA control membrane, indicating how the NPs addition enhances the performance of the membrane. In particular, the CA-Fe₃O₄ membrane possesses the higher values, both in terms of flow and retention,

| Membrane name | Thickness (µm) |
|---------------|----------------|
| CA-control    | 180 ± 0.05     |
| CA-SiO₂       | 180 ± 0.7      |
| CA-TiO₂       | 94 ± 0.4       |
| CA-ZnO        | 60 ± 1.1       |
| CA-Fe₃O₄      | 163 ± 0.8      |

| Ions  | Hydration energies (HE) (kJ mol⁻¹) | Hydrated radius (nm) | Diffusion coefficients (D) (10⁹ m²s⁻¹) |
|-------|-----------------------------------|----------------------|----------------------------------------|
| Na⁺   | 454                               | 0.358                | 1.333                                  |
| Cl⁻   | 325                               | 0.332                | 0.379                                  |
| SO₂⁻  | 1047                              | 0.379                | 1.065                                  |
accordance with its low roughness value (table 2). The addition of Fe$_3$O$_4$NPs leads to a significant improvement in the membrane performance, resulting in an important increase in terms of NaCl and Na$_2$SO$_4$ retention (90.3% and 93%, respectively). This meaningful result suggests that the addition of the Fe$_3$O$_4$ NPs could be attributed to their highly hydrophilic properties and chemical stability due to hydroxyl groups on their surface. Consequently, a lower roughness corresponds to a lower tendency to fouling. Concerning water flux, during the experiments with salty solutions, the water flux was around 40% for the investigated membranes, while they maintained a higher rejection value (up to 93% in the case of Na$_2$SO$_4$ (figure 7)).

### 5. Conclusion

In this work, CA composite NF membranes were prepared via PI using four types of NPs: TiO$_2$, SiO$_2$, ZnO, and Fe$_3$O$_4$. In particular, this work showed an easy and direct method to prepare polymeric nano-enhanced membrane using NPs. The study highlighted that the NPs addition in the polymeric dope solution strongly affects the properties of the membrane. Most of the produced membranes showed a selective top-layer with a porous sub-layer, and AFM data reveals significant changes in surface roughness compared with the CA-control membrane. Contact angle analysis confirmed that the NPs enhanced the membrane hydrophilicity, with the lowest value of 58°. Similar results were obtained for EWC and porosity. Performance results were in accordance with characterization tests: in all cases, the water flux of the CA-composite membranes was higher than the CA-control membrane. Finally, NPs improved the salt retention of the membranes with $R$(Na$_2$SO$_4$) > $R$(NaCl). We have obtained the best result in the case of the CA-Fe$_3$O$_4$ membrane with a water flux of 15.4 l m$^{-2}$ h$^{-1}$ and a retention of 93%. Therefore, there are good prospects for CA-Fe$_3$O$_4$ composite membrane. This membrane, in particular, could be used for heavy metal removal [39, 40] and/or in all wastewater treatment to reduce fouling activity [8–38] due to its competitive properties. Consequently, the presented results herein may be extended to commercial, biotechnological, and industrial applications.
Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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