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Theoretical Investigation of Nanofillers Effect on the Elastic Modulus and Relative Water Flux of Reverse Osmosis Membranes

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Abstract

This study theoretically investigates the effect of adding nanofillers on the mechanical behavior and relative water flux of reverse osmosis (RO) membranes used in seawater desalination. The Halpin–Tsai model was used to estimate the effective elastic modulus of nanofiller-reinforced membranes as a function of filler type, volume fraction, and shape factor. Three nanofillers were considered: graphene oxide (GO), silicon dioxide (SiO_2), and titanium dioxide (TiO_2). The calculated elastic modulus was then linked to membrane compressibility and relative water flux under different operating pressures. The results indicate that nanofiller incorporation improves membrane stiffness and reduces pressure-induced deformation. GO showed the highest predicted reinforcement effect, followed by TiO_2 and SiO_2.

Keywords: Nanofillers; Reverse osmosis; Halpin–Tsai model; Relative water flux; Membrane compaction; Desalination.

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دراسة نظرية لتأثير الحشوات النانوية على معامل المرونة والتدفق النسبي للماء في أغشية التناضح العكسي

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الملخص

تتناول هذه الدراسة نظريًا تأثير إضافة الحشوات النانوية في السلوك الميكانيكي والتدفق النسبي للماء لأغشية التناضح العكسي (RO) المستخدمة في تحلية مياه البحر. واستُخدم نموذج Halpin–Tsai لتقدير معامل المرونة الفعّال للأغشية المدعمة بالحشوات النانوية بدلالة نوع الحشو، وكسره الحجمي، ومعامل الشكل الهندسي للحشو. وشملت الدراسة ثلاثة أنواع من الحشوات النانوية، هي: أكسيد الجرافين (GO)، وثاني أكسيد السيليكون (SiO_2)، وثاني أكسيد التيتانيوم (TiO_2). وربط معامل المرونة المحسوب بعد ذلك بقابلية انضغاط الغشاء والتدفق النسبي للماء تحت ضغوط تشغيل مختلفة. وأظهرت النتائج أن دمج الحشوات النانوية يؤدي إلى زيادة صلابة الغشاء والحد من التشوه الناجم عن الضغط. وقد أظهر أكسيد الجرافين (GO) أعلى تأثير تدعيمي متوقَّع، يليه TiO_2، SiO_2.

الكلمات المفتاحية: الحشوات النانوية؛ التناضح العكسي؛ نموذج Halpin–Tsai؛ التدفق النسبي للماء؛ انضغاط الغشاء؛ تحلية المياه.

1. Introduction

Reverse osmosis (RO) is one of the most widely used membrane-based technologies for seawater desalination and freshwater production [1]. It depends on the selective passage of water molecules through a semi-permeable membrane while rejecting dissolved salts, ions, and other contaminants [2]. In natural osmosis, water moves from the dilute solution to the concentrated solution due to osmotic pressure. In reverse osmosis, however, an external hydraulic pressure greater than the osmotic pressure is applied to the saline feed solution, forcing water to move in the opposite direction through the membrane [3].

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The basic operating condition of reverse osmosis can be expressed as [1]: $\mathbf{P > \pi}$

where **P** is the applied hydraulic pressure and $\boldsymbol{\pi}$ is the osmotic pressure of the saline solution. When the applied pressure exceeds the osmotic pressure, water transport across the membrane becomes possible, while most dissolved salts remain on the feed side. This mechanism makes RO an effective separation process because it does not require phase change and consumes less energy than many thermal desalination methods [3].

Despite its efficiency, the performance of RO membranes can decline under high operating pressure. Thin polymeric membranes may undergo mechanical compaction, which reduces the effective free volume and narrows the water transport pathways. As a result, water permeability and flux may decrease during operation, affecting membrane stability and lifetime [4].

To reduce this limitation, nanofillers can be incorporated into the polymeric membrane matrix. Materials such as graphene oxide (GO), titanium dioxide (TiO_2), and silicon dioxide (SiO_2) may improve membrane stiffness, structural stability, and resistance to pressure-induced deformation. The effectiveness of this improvement depends on filler type, filler shape, volume fraction, dispersion quality, and bonding with the polymer matrix [5].

The Halpin–Tsai model is commonly used to estimate the effective elastic modulus of composite Materials [6]. In this study, it is applied to predict the mechanical reinforcement of RO membranes modified with different nanofillers. The calculated modulus is then used to interpret the expected change in membrane compressibility and relative water flux under different operating pressures [7].

Despite the widespread use of RO membranes in desalination systems, their hydraulic performance may deteriorate under high operating pressure because membrane compaction reduces the effective free volume and restricts water-transport pathways [8]. Nanofiller incorporation offers a promising means of increasing membrane stiffness; however, the extent of reinforcement depends on the nanofiller type, volume fraction, and shape factor [9].

Although nanofiller-modified reverse osmosis (RO) membranes have advanced considerably and have shown improved mechanical

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stability and resistance to pressure-driven compaction, a unified quantitative description is still lacking. In particular, the combined effects of nanofiller geometry, expressed through shape factor and volume fraction, on the effective elastic modulus, membrane compaction, and relative water flux have not yet been fully integrated within a single mathematical framework. Accordingly, this study formulates a Halpin–Tsai-based model to estimate the effective elastic modulus of RO membranes containing graphene oxide (GO), titanium dioxide (TiO_2), or silicon dioxide (SiO_2). The framework examines how filler loading and geometric shape factor govern membrane reinforcement, and then relates the predicted increase in stiffness to compaction under the applied operating pressure and the resulting relative water flux. The three nanofillers are subsequently compared to determine the material that provides the strongest reinforcement under the investigated operating conditions.

2. Methodology and Mathematical Model

This study follows a theoretical analytical methodology based on mathematical modeling. The approach uses established mathematical relationships to theoretically evaluate the effects of applied pressure and nanofiller reinforcement on membrane mechanical behavior and relative water flux.

The membrane is treated as a polymeric composite consisting of a pure polymer matrix reinforced with a certain volume fraction of nanofillers. Three types of nanofillers were considered: graphene oxide (GO), silicon dioxide (SiO_2), and titanium dioxide (TiO_2). The analysis assumes homogeneous filler dispersion, good interfacial bonding between the filler and polymer matrix, and elastic membrane behavior under the selected pressure range.

The modeling procedure was carried out in three main steps. First, the effective elastic modulus of the nanofiller-reinforced membrane was calculated using the Halpin–Tsai model. Second, the pressure-induced volumetric strain of the membrane was estimated using the calculated modulus. Third, the relative water flux was obtained by comparing the flux of the reinforced membrane with that of the pristine membrane under the same operating pressure.

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The effective elastic modulus of the reinforced membrane is expressed by the Halpin–Tsai equation [7]:

$$E_{eff} = E_m \left(\frac{1+\xi\eta V_f}{1-\eta V_f} \right) \quad (1)$$

Where E_{eff} is the effective elastic modulus of the nanocomposite membrane, E_m is the elastic
modulus of the pure polymer membrane, V_f is the filler volume fraction, ξ is the filler shape factor, and η is an intermediate parameter given by:

$$\eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_m}+1} \quad (2)$$

Where E_f is the elastic modulus of the nanofiller. This equation shows that the effective modulus depends mainly on filler stiffness, filler loading ratio, and filler geometry.

When hydraulic pressure is applied to the RO membrane, the membrane may undergo compression. The volumetric strain can be approximated as:

$$\varepsilon_V = \frac{P}{E_{eff}} \quad (3)$$

where ε_V is the volumetric strain and P is the applied operating pressure. For the pristine membrane, the corresponding strain is:

$$\varepsilon_{V_0} = \frac{P}{E_m} \quad (4)$$

Since nanofiller addition increases E_{eff} [6], the reinforced membrane is expected to have lower strain than the pristine membrane, which means lower pressure-induced compaction [8].
Water flux through the membrane can be represented using a modified Darcy-type expression [10]:

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$$J_C = L_P\,(\Delta P - \Delta\pi)e^{-\alpha\varepsilon_V} \qquad (5)$$

where J_C is the water flux of the reinforced membrane, L_P is the initial membrane permeability, ΔP is the hydraulic pressure difference, $\Delta\pi$ is the osmotic pressure difference, and $\boldsymbol{\alpha}$ is the sensitivity parameter representing the effect of membrane compaction on flux decline. For the pristine membrane:

$$J_0 = L_P\,(\Delta P - \Delta\pi)e^{-\alpha\varepsilon_{V_0}} \qquad (6)$$

The relative water flux is then defined as:

$$J_{rel} = \frac{J_C}{J_0} \qquad (7)$$

By substituting the two flux expressions, the common terms cancel out, giving:

$$J_{rel} = e^{[\alpha(\varepsilon_{V_0} - \varepsilon_V)]} \qquad (8)$$

Substituting Eqs. (3) and (4) in to Eq, (8), gives the final form:

$$J_{rel} = e^{[\alpha P(\frac{1}{E_m} - \frac{1}{E_{eff}})]} \qquad (9)$$

This equation represents the theoretical link between mechanical reinforcement and relative water flux. It indicates that increasing the effective elastic modulus reduces membrane compression and increases the relative flux compared with the pristine membrane.
To clarify the magnitude of improvement, the relative flux values were also expressed as percentage improvement:

$$Flux\ improvement\ (\%) = (J_{rel} - 1) \times 100 \qquad (10)$$

This calculation is important because several relative flux values are close to unity, and presenting them as percentages helps determine whether the improvement is physically meaningful or limited.
MATLAB was used to perform all numerical computations, implement the mathematical model, and generate the result plots.

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Throughout the analysis, the numerical procedure was checked for dimensional and mathematical consistency in order to support the accuracy and reliability of the predicted results.

3. Input Data

The theoretical model was applied to three nanofillers: graphene oxide (GO), silicon dioxide (SiO_2), and titanium dioxide (TiO_2). The elastic modulus of the pure polymer membrane (***E*m**) was set at 2 Gpa [11]. The elastic moduli assigned to the nanofillers (***E****f*) were 1000 GPa for GO [12], 70 Gpa for SiO_2 [13], and 200 GPa for TiO_2 [14]. Their corresponding geometric shape factors (ξ) were 50, 1.5, and 3, respectively. These valuse were adopted as representative shape parameters for the theoretical analysis [15]. The filler volume fraction (V_f) ranged from 1% to 5% [16], while the applied operating pressure varied between 30 and 70 bar [17]. A seawater osmotic pressure of 25 bar was used in the relative water-flux calculations [18]. The material parameter values were selected based on values reported or used in the published literature, while the filler volume fraction and applied pressure ranges were selected to evaluate the theoretical response under practically relevant RO conditions. The parameters were substituted into Eqs. (1) and (2) to determine the effective elastic modulus; the resulting values were then used in Eqs. (9) and (10) to estimate the relative water flux and the corresponding percentage improvement under the investigated operating conditions.

4. Results and Discussion

The effective elastic modulus values calculated using the Halpin–Tsai model are shown in Table 1.

Table 1. Effective elastic modulus of nanofiller-reinforced membranes.

Filler volume fraction %	GO (GPa)	SiO_2 (GPa)	TiO_2 (GPa)
1	2.9338	2.0470	2.0776
2	3.8850	2.0949	2.1568
3	4.8539	2.1437	2.2375
4	5.8410	2.1935	2.3198
5	6.8469	2.2442	2.4038

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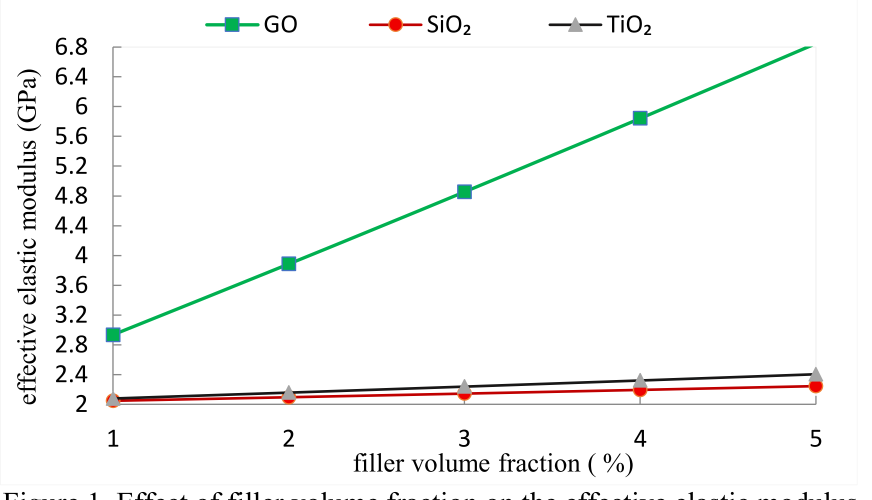

Figure 1. Effect of filler volume fraction on the effective elastic modulus of the nanocomposite membranes.

The results show that the effective elastic modulus increases as the filler volume fraction increases (figure 1). However, the degree of improvement differs clearly among the fillers. GO produces the highest increase in membrane stiffness, reaching 6.8469 GPa at 5% filler loading. This represents an increase of about 242.35% compared with the pristine polymer membrane. TiO_2 increases the modulus to 2.4038 GPa at 5% loading, while SiO_2 increases it to 2.2442 GPa. Therefore, the predicted reinforcement order is:

$$GO > TiO_2 > SiO_2$$

This result can be explained by the geometry and aspect ratio of the fillers. GO has a plate-like structure and high aspect ratio, which provides a larger effective interfacial area and facilitates stress transfer within the polymer matrix [19]. In contrast, SiO_2 and TiO_2 have more compact, spherical or quasi-spherical particle geometries and lower aspect ratios than the platelet-like GO structure [20]. Therefore, under the assumptions of the present Halpin–Tsai model, their load-transfer efficiency and predicted reinforcing effect are more limited than that of GO.

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The relative water flux results show a consistent increase with applied operating pressure for all three nanofillers, with GO exhibiting the largest increase. The calculated values are summarized in Table 2, and their pressure dependence is presented graphically in Figure 2.

Table 2: Relative water flux of GO, SiO_2, and TiO_2 Nanocomposite Membranes at 5% filler volume fractions as a function of applied operating pressure.

P(bar)	GO (5%)	SiO_2(5%)	TiO_2(5%)
30	1.016	1.002	1.004
40	1.021	1.003	1.005
50	1.027	1.004	1.006
60	1.032	1.005	1.008
70	1.038	1.006	1.009

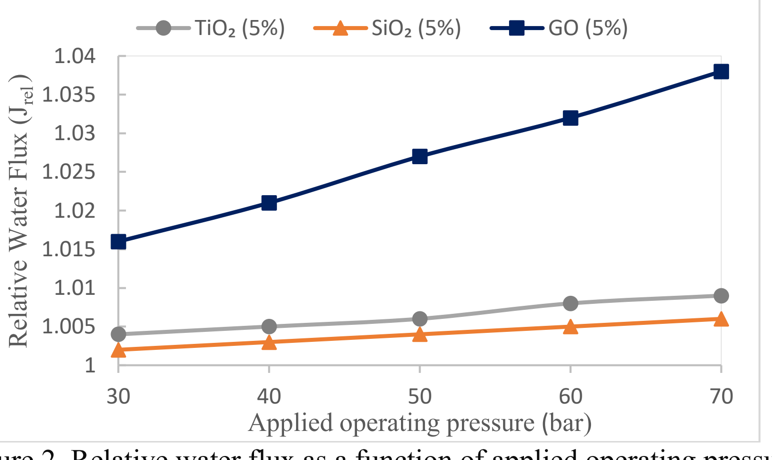

Figure 2. Relative water flux as a function of applied operating pressure for GO, SiO_2, and TiO_2 nanocomposite membranes at 5% filler volume fraction.

GO-reinforced membranes show the highest predicted improvement in relative flux, especially at higher pressure at higher filler loading. At the maximum tested condition, the relative flux of GO reaches approximately 1.038, corresponding to an improvement of about 3.8% compared with the pristine membrane.

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For TiO_2, the maximum relative flux is approximately 1.009, corresponding to an improvement of about 0.9%. In contrast, SiO_2 shows a very limited improvement, with a maximum relative flux of 1.006, equivalent to an approximate performance improvement of 0.6%. These results are summarized in Table 3.
Given the small numerical differences among the relative-flux coefficients of the investigated fillers, the results are discussed using flux-improvement percentages in addition to the relative-flux values, rather than relying on relative-flux values alone.

Table 3. Maximum predicted relative flux improvement.

Filler	Maximum J_{rel}	improvement (%)	Interpretation
GO	1.038	3.8%	Greatest predicted gain from the high-aspect-ratio, plate-like geometry
TiO_2	1.009	0.9%	Moderate predicted gain linked to near-spherical particle geometry
SiO_2	1.006	0.6%	Minor predicted gain under the examined conditions

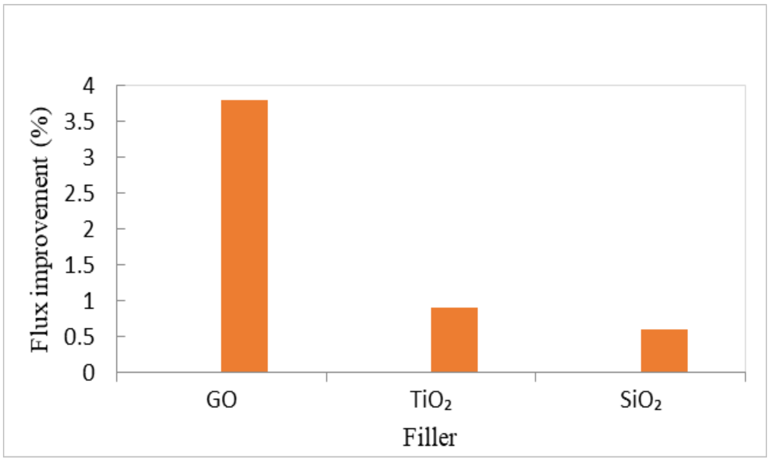

Figure 3. Maximum predicted relative water-flux improvement for the investigated nanofillers.

The results indicate that nanofiller incorporation can improve membrane resistance to pressure-induced compaction. However, the

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improvement is not equally strong for all fillers. GO gives the most meaningful improvement because it produces the largest increase in effective elastic modulus. TiO_2 and SiO_2 show smaller improvements, which explains the small differences between several calculated values, as illustrated in figure 3.

The sensitivity parameter also affects the predicted relative water flux. Higher sensitivity values produce clearer differences between reinforced and pristine membranes. Therefore, using only close sensitivity values may not be sufficient to show the effect clearly. A wider sensitivity range, such as $\alpha = 5$, 15, and 30, is recommended for future analysis to make the effect of membrane compaction more visible.

5. Comparison Of the present Results with Previous Studies

The theoretical results of the present study are consistent with trends reported in previous published experimental studies in the scientific literature on nanocomposite reverse osmosis membranes. The variation in elastic modulus with filler content agrees with the findings of Idarraga-Mora et al. [21], who reported that increasing nanofiller loading can increase the elastic modulus of the support layer in thin-film membranes. The general trend of relative flux with filler content and filler type is also consistent with the findings of Ahmad et al. [22], who reported that nanofillers can improve membrane mechanical stability and affect water transport and operational performance depending on the filler type and its interaction with the polymer matrix. These results are also in agreement with the findings of Bhoje et al. [23], who reported higher water flux for graphene oxide-reinforced membranes compared with unreinforced polymer membranes. The higher performance predicted for graphene oxide in the present study is further consistent with the findings of Feng et al. [24], who reported that graphene oxide sheets with a higher aspect ratio provide a greater reinforcing effect on the elastic modulus. Because the present study is theoretical and does not include experimental validation, the comparison was based on the general trend rather than direct numerical verification. This limitation opens the way for future experimental studies to quantify prediction accuracy and confirm the expected performance ranking.

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6. Conclusions

This study used the Halpin–Tsai model to theoretically investigate the effect of GO, SiO_2, and TiO_2 nanofillers on the effective elastic modulus and relative water flux of RO membranes. The main conclusions are:

1. Nanofiller incorporation increases the effective elastic modulus of the polymeric membrane and reduces its pressure-induced compressibility.
2. The effective elastic modulus increases with increasing filler volume fraction for all studied nanofillers.
3. GO shows the highest reinforcement effect, followed by TiO_2 Then SiO_2.
4. The superior effect of GO is related to its plate-like geometry and high aspect ratio, which improve stress transfer within the polymer matrix.
5. The maximum predicted relative flux improvement reaches about 3.8% for GO, while TiO_2 and SiO_2 show limited improvements of about 0.9% and 0.6%, respectively.
6. The theoretical results agree with the general direction of previous studies, but experimental validation is still required.

7. Recommendations

Based on the results of this study, the following recommendations are proposed:

1. Experimental studies should be conducted to validate the theoretical model and compare measured flux values with predicted results.
2. Future work should include salt rejection, membrane fouling, and long-term compaction behavior, because these factors strongly affect real RO membrane performance.
3. A wider range of sensitivity parameter values should be tested to clarify the effect of membrane compaction on relative flux.
4. The results should always be presented using relative flux, percentage improvement, and absolute differences to avoid overestimating small numerical changes.
5. The effect of higher filler loading ratios may be studied theoretically, but practical application should consider possible agglomeration and membrane defects.

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6. Future models should include temperature and feed salinity effects to better represent real desalination operating conditions.

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