The Effect of Functionalized SiO₂ Nanoparticles on the Morphology and Triazines Separation Properties of Cellulose Acetate Membranes

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Abstract

This study investigates the removal of triazines from an aqueous solution using a novel SiO₂/CA nanocomposite membrane. The membranes were fabricated with phase inversion by dispersing SiO₂ nanoparticles in the CA casting solutions in the range of 0.01-0.1wt %. ATR-IR, FESEM, AFM, and contact angle analyses were employed to characterize the prepared membranes. The effect of silica nanoparticles on the performance of membranes was studied through the pure water flux and MgSO₄ rejection obtained at an applied pressure of 10 bars. Nanocomposite CA membranes generally showed higher salt rejection and experienced less flux than neat CA membranes, due to morphology changes. In addition, the observed salt rejection tended to enhance as silica loading increased up to a critical concentration. Three triazines (atrazine, propazine, and prometryn) were removed from water by the prepared membranes, and their rejections were compared. The results showed that the triazines rejection was increased by pressure and feed concentration. The effects of the molecules' properties, including molecular size, hydrophobicity and dipole moment, were studied. The results revealed that the rejection of prometryn with a larger molecular size was always higher than the other two triazines. It was observed that there was a direct relation between dipole moment and triazine rejection, while this relation was not observed in the case of hydrophobicity.

Keywords: *Functionalized SiO₂ nanoparticles, Triazine removal, asymmetric membrane, cellulose acetate, water treatment*

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1. Introduction

In recent years, herbicides have been extensively used as pesticides, mainly to control weed growth in agricultural fields[1]. Among herbicides, triazine compounds are considered to be significant environmental contaminants [2]. The presence of triazines in drinking water has a high potential for pollution and it may cause negative effects on human health [3]. Consequently, development and enhancement of conventional methods or presentation of a new technique for pesticide removal from water to protect both human health and the environment should be considered.

Numerous investigations have been conducted to develop effective treatment methods for removing various pesticides and other synthetic organic pollutants from contaminated water sources [4]. Pressure-driven membrane processes can be applied successfully as appropriate separation techniques for water treatment. Nanofiltration (NF) membranes have become increasingly preferred for removing pesticides and organic compounds from water [5-8]. Since the first asymmetric cellulose acetate membrane was made by Loeb and Sourirajan [9] in 1958, the technology on various types of membranes for water treatment has been extensively developed. Several commercially available NF/RO membranes, such as aromatic polyamide (PA), polyethylenimine (PEI) and CA membranes have been tested for the removal of various kinds of pesticides from water.

Cellulose acetate (CA) is an outstanding common membrane material for water treatment because of its low cost, good resistance to chlorine and solvents [10] and less fouling due to its high hydrophilicity potential [11]. The CA membranes can be prepared by the phase inversion technique and consist of a thin selective layer on a spongy support layer [12].

Nanocomposite membranes are advanced membranes with nanoparticles dispersed in their polymer matrix. Fabrication of conventional asymmetric nanocomposite membranes is mostly based on the phase inversion (PI) method in which nanofillers are dispersed in polymer solution prior to the casting process, and can be prepared in a flat sheet [13]. Various additives are used to improve the performance of CA membranes such as PVP [14], PEG [15], SDS [10], TiSiO₄ [16]. The main objective of mentioned studies was the preparation of CA membranes with higher performance. Nevertheless, several studies still need to be conducted to optimize the design of the nanocomposite membranes for industrial applications on a large scale and it is important to

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4 ensure the consistency of nanofillers with polymers. The consistency will determine both the
5 optimum membrane performance and the stability of the nanofillers in the polymeric phase.

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7 To improve the surface attachment of inorganic nanoparticles onto the polymer chains and
8 improve the dispersion stability of the particles inside the polymer phase, the surface of the
9 nanoparticles is typically modified by using various agents [17-22]. It has been reported that
10 silica (SiO₂) nanoparticles modification by oleic acid (OA), have improved their dispersive
11 capacity in the organic phase significantly [23]. In our previous work [24], adding OA modified
12 SiO₂ to polyamide membrane reduced the pore size and increased rejection of pesticides
13 significantly. Ghaemi et al. [10] investigated the effect of addition of sodium dodecyl sulfate
14 (SDS) anionic surfactant on the performance of cellulose acetate (CA) nanofiltration membrane.
15 They claimed that modified membrane showed superior rejection, and flux in comparison to CA
16 membrane. In another study, surface-modified membrane with tailor-made charged surface
17 modifying macromolecules (CSMMs) additives resulted in significantly lower MWCO than
18 unmodified membrane [25]. Also, there are many reports where it has been shown that
19 membrane modified by hydrophobic additive favors less fouling [26-27].

20
21 Several research groups have systematically studied the role of one or more of the pesticide
22 parameters on membrane rejection [28-29]. All of these studies were based on the use of
23 commercial membranes. However, to the best of our knowledge, the application of
24 nanocomposite CA membranes for triazines removal from aqueous media has not been studied
25 previously. Therefore, in this study a novel oleic acid-modified SiO₂/CA nanocomposite
26 membrane was fabricated via the phase inversion method and used for the removal of pesticides
27 from water. The morphology, structure, hydrophilicity and surface roughness of as-prepared
28 nanocomposite membranes were studied. Furthermore, the performance of the prepared
29 membrane was evaluated by measurement of pure water flux (PWF) and MgSO₄ rejection. The
30 removal of three triazines including atrazine, propazine and prometryn were investigated by the
31 prepared membranes. Finally, the influences of pesticide molecule properties such as molecular
32 weight, hydrophobicity and dipole moment as well as the effect of operating conditions on
33 rejection were studied.

2. Experimental

2.1. Materials

CA with an average molecular weight of 50,000 g/mol, and 39.7 wt.% acetyl content (Sigma Aldrich) was used as the polymer. Acetone (Sigma Aldrich, purity $\geq 99.8\%$) and deionized water were used as solvent and non-solvent, respectively. A commercial form of fumed SiO_2 with a nominal diameter of 15 nm (PlasmaChem, Germany) was used as nanofiller after surface modification with oleic acid. The three important herbicides that were used for this experiment are: atrazine, propazine, and prometryn (purity $> 98\%$, Riedel-de Haen, Germany). The structure and physicochemical characteristics of the triazines are shown in Table 1.

2.2. Modification of SiO_2 nanoparticles by oleic acid (OA)

Oleic acid was used to functionalize silica nanoparticles according to a previously reported procedure [24]. Hexane (100 ml) and OA (1 g) were mixed under stirring, and then 1g of SiO_2 nanoparticle was added to the solution. The mixture was heated to 60°C under vigorous stirring for 4h. Then the solution was filtered and the precipitate was thoroughly rinsed with 2-propanol alcohol and deionized water. The precipitate was kept in an oven for 24 hours at 100°C . A white powder of OA-modified SiO_2 nanoparticles was obtained.

2.3. Membrane preparation

OA modified SiO_2 /CA flat sheet membranes were prepared by the phase inversion method. Solutions were made by slowly adding cellulose acetate (20 wt.%) to acetone (45 wt%) and formamide (35 wt%) with stirring. SiO_2 was dissolved in the acetone prior to the addition of cellulose acetate and formamide, stirred for 4 hours and sonicated for 30 minutes to ensure homogeneous spread of the nanoparticles. Then the CA was added to the initial mixture with vigorous stirring. Different loading contents of the nanoparticles were used in order to obtain the mixtures of 0.01, 0.05, and 0.1 wt.% SiO_2 in polymer solutions. Table 2 shows the composition for each solution.

The casting solution was kept for 24 hours in order to remove air bubbles. The CA membranes (with and without the nanofiller additive) were prepared by casting solutions onto a non-woven

polyester substrate taped to a glass plate using a film applicator with 250 μm film thickness. Then it was directly immersed in a deionized water bath and kept at room temperature for phase inversion by solvent/non-solvent demixing. The membrane was stored in water until it was used for separation.

2.4. Characterization of the OA modified SiO_2 nanoparticles

The successful modification of nanoparticles was confirmed using IR analysis of SiO_2 nanoparticles, oleic acid and OA-modified SiO_2 nanoparticles. The analysis was carried out using a Thermo Nicolet Avatar 370 FT-IR spectrometer. The result has been thoroughly explained in our previous study [24].

2.5. Membrane characterization

2.5.1. Fourier transform infrared analysis (FTIR)

The presence of functional groups on the surface of the membrane was detected by Fourier transform infrared (FTIR) spectroscopy (Nicolet 8700, ThermoScientific, USA) with an attenuated total reflection (ATR) unit (ZnSe crystal, 45°). The IR spectra of the membranes were recorded in transmittance mode over a wave number range of 4000 to 650 cm^{-1} at 25 $^\circ\text{C}$.

2.5.2. Field emission scanning electron microscopy (FESEM)

The membrane surface and the cross-section morphologies of the CA and the SiO_2/CA membranes were investigated by FESEM analysis using SIGMA/VP (ZEISS, Germany). The membrane samples were cryogenically fractured in liquid nitrogen to examine the cross sectional morphology of the membranes. The surface and the cross section of the membranes were coated with gold for FESEM observations.

2.5.3. Atomic force microscopy (AFM)

The surface roughness of the membranes was characterized by Easyscan 2 Flex AFM (Nanosurf, Switzerland). The samples were cut into pieces of 1 cm by 1 cm, and the surface areas equal to 10 $\mu\text{m} \times 10 \mu\text{m}$ of each sample were scanned using tapping mode AFM. The

surface roughness parameters of the membranes which are expressed in terms of the mean roughness (S_a), the root mean square of the Z data (S_q) and the mean difference between the five highest peaks and lowest valleys (S_z) were calculated from the AFM images.

2.5.4. Contact angle

The hydrophilicity of the membranes was obtained by contact angle measured using the sessile drop method (OCA15 plus Goniometer, Dataphysics, CA). The water contact angle is measured for the small water droplet on the surface of the membranes. This angle is measured immediately after the release of the drops. The average of at least 5 measurements was reported.

2.5.5. Performance of the membrane

All permeation experiments were performed in a high pressure permeation set-up (Fig. 1) in a total recycle mode. The performance was evaluated in terms of flux and solute rejection. The measurements were conducted at 10 bars and at room temperature with the effective membrane area of 0.002 m². The temperature of the feed solution was fixed at 23°C.

The performance of the prepared membranes was first evaluated using a feed solution of MgSO₄ with 2000 ppm concentration. Then, the feed solutions of the three selected triazines were prepared by using deionized water at neutral pH with different concentrations of 0.1-10 mg/L.

The filtration protocol involves the following three steps: (1) membrane preconditioning with water under pressure of 10 bar for 1 h and after ensuring about stability of water flux, PWF was measured. (2) The feed solution was passed through the cell for 30 min without pressure. In this way, the membrane surface was assumed to saturate with herbicide adsorption (3) after applying the pressure, 30 ml of permeate was collected for 3 times continuously, to reach stable flux. For each experiment a new membrane was used in order to prevent adsorption effects from previously treated solutes. The permeate flux and rejection was evaluated based on the stable permeates by the following equations:

$$J = V/A.t \quad (1)$$

where V is the permeate volume (L), A the membrane area (m²) and t is the permeation time (h).

$$R = 1 - C_p/C_f \quad (2)$$

where C_f is the concentration of the feed solution and C_p is the concentration of the permeate. A gas chromatography, employing a single quadrupole mass spectrometer (QP 2010 plus, Shimadzu, Japan) was used to determine the concentration of the feed and permeate samples. The GC-mass was equipped with a Rpx 5MS, 0.25mm i.d. $\times$ 30m long RESTEK column and the mobile phase was 5% diphenyl / 95% dimethylpolysiloxane.

The **nominal** pore size of the membranes was estimated using the exclusion model from the Eq(3) [30]:

$$R = [\lambda (2 - \lambda)]^2, \quad \lambda = \frac{r_s}{r_p} \quad (3)$$

where r_p is pore radius and r_s is solute radius assumed for $MgSO_4$ ($r_s = 0.341$ nm for Mg^{2+} [31]).

3. Results and discussion

3.1. Membrane characterization

3.1.1. ATR-IR analyses of SiO_2/CA membranes

ATR-IR analysis was employed to study the chemical characterization of the prepared membranes. ATR-IR spectrums of the neat CA and the modified SiO_2/CA membranes are given in Fig. 2. The spectrum of the neat CA membrane revealed a band at 2890 cm^{-1} and 2920 cm^{-1} for stretching vibration of asymmetric and symmetric C–H band [32], the strong peak at 1740 cm^{-1} illustrated the C = O stretching vibration, followed by peaks at 1370 cm^{-1} , 1220 cm^{-1} and 1060 cm^{-1} which described C–O stretching of ester, C–O stretching of carboxylic acid, and C–O stretching of ether, respectively [33-34]. The new broad band around $3200\text{--}3600\text{ cm}^{-1}$ in the spectra of CA-1 to CA-3 membranes could be attributed to OH bonds in the entrapped CA membranes of the SiO_2 nanoparticles. The strengthening of OH bonds conforms to the presence of SiO_2 nanoparticles on the membrane surface structure [35].

3.1.2. Contact angle

The water contact angle measurement is the main method **for investigating** the effect of SiO_2 nanoparticles on the hydrophilicity of the membranes. In this method, the angle between a small droplet of water and the flat horizontal surface of the membrane is measured. The higher hydrophilic surface shows a lower contact angle and vice versa. Water contact angle of the neat

CA and the modified SiO₂/CA membranes are shown in Table 3. It is evident from Table 3 that there is a decrease in the contact angle by increasing nanoparticle concentration in such a way this parameter dropped from 65.9° for CA-0 to 54.6° for CA-3. These results demonstrate that silica particles can improve the hydrophilicity of the membrane.

3.1.3. Membrane morphologies

Figs. 3–5 present FESEM images and show the morphologies of the 0.0, 0.01, 0.05 and 0.1 wt% SiO₂/CA membranes. To understand the influence of SiO₂ loading on the membrane structure, the cross-section of the prepared membranes is shown in Fig. 3. As depicted in this figure, all the membranes exhibit an asymmetric structure, consisting of a skin layer as a selective barrier and a much thicker finger-like support layer with microvoids. Generally, this structure is obtained when the casting solution is immersed in the non-solvent bath and the solvent is replaced with the non-solvent during phase separation [36]. This image shows that the increase of SiO₂ concentration leads to a membrane containing a less porous sub-layer with smaller finger-like macrovoids [37]. The effect of the SiO₂ concentration on the thicknesses of the top and the support layer of the prepared membranes has been reported in Table 4. It can be seen that the thickness of the skin layer from the top surface of the membrane increases with the increasing of SiO₂ nanoparticles, which may enhance the resistance of the membrane against permeate flow. The thickness of the skin layer of the neat CA membrane was about 983 nm, while the thickness of this layer increased to 1.99 µm for CA-2 membrane. Also the spongy layer of the membranes increased from 41.2 µm to 85.7 µm by increasing the nanoparticles loading. The surface FESEM images of the neat CA and the SiO₂/CA membranes are shown in Fig. 4. As this Figure indicates, the surface of the neat CA membrane exhibits a porous structure with relatively moderate pores, while it becomes dense and smooth by depositing SiO₂ nanoparticles due to the delayed demixing during the phase inversion process. During the phase inversion process, the more rapid solvent and the non-solvent replacing caused the formation of a more porous membrane with a higher pore size, especially at the top surface. Consequently, a reduction in replacing velocity during phase inversion has suppressed the growth of the macrovoids and the morphology of the top layer has changed from a porous morphology to a dense one [37]. Fig. 5 represents the cross-section of the membranes with different silica loadings with a higher degree of magnification.

The white circle region is clearly detected nanoparticles. At higher concentrations of SiO₂, the aggregation of nanoparticles is visible in the CA-3 membrane.

3.1.4. AFM images and surface roughness of the membranes

Fig. 6 indicates AFM images of the neat CA and the SiO₂/CA membranes surfaces prepared at a scan size of 10 μm $\times$ 10 μm . The surface morphologies of the membranes were strongly influenced by the concentration of SiO₂ nanoparticles. This shows that the surface roughness of the membranes with SiO₂ nanoparticles is lower than the neat CA membrane. The surface roughness parameters of the membranes, which are expressed in terms of the mean roughness (S_a), the root mean square of the Z data (S_q) and the mean difference between the highest peaks and lowest valleys (S_z) were reported in Table 3. The roughness parameters for the membranes drop from CA-0 to CA-1, but with increased SiO₂ nanoparticles loading up to 0.1%, the roughness is increased again for CA0-3 due to agglomeration of nanoparticles as revealed by the FESEM image of CA-3 sample given in Fig. 5.

3.2. Performance of prepared membranes

3.2.1. Pure water flux and MgSO₄ rejection

The pure water flux (PWF) and salt rejection of neat and nanocomposite membranes are depicted in Fig.7. The PWF and rejection data of all membranes were calculated at a pressure of 10 bars. The CA-0 membrane showed a maximum flux while it exhibited a minimum salt rejection capacity. The PWF of the nanocomposite membranes dropped from 21.6 to 15.1 L/ m² h with the addition of 0.1 wt.% SiO₂ in the casting solution of the CA-3. The CA-2 membrane had the maximum salt rejection but its flux was lower than CA-0 sample. Experimental data were analyzed by using Eq. (3) to obtain the pore radius of the prepared membranes. Table 3 shows the pore radius of the prepared membrane. The value of pore size decreased slightly from CA-0 to CA-2 membrane. Then it increased again with the addition of extra SiO₂ due to the agglomeration of nanoparticles. Pore size data validated the results of FESEM analysis that the addition of SiO₂ causes a structural compactness of the composite membranes because of the strong interaction between SiO₂ and the CA matrix. The porous surface changes to a smooth top

surface with smaller pores due to formation a new network structure [38-39]. This network structure increases by increasing the amount of SiO₂ in the membrane [40-41]. Therefore, decreasing the water flux and increasing the rejection with nanoparticles loading was expected, considering the effect of molecular sieve on membrane separation. At high SiO₂ loading (CA-3 sample), the agglomeration of nanoparticles in the CA matrix causes the formation of new voids inside the polymer matrix of the top layer, which leads to a lower rejection. A similar result has been reported by Rahimpour et al. [42] for PVDF/SPES membranes. Their results showed that by adding TiO₂ nanoparticles to the blend membrane, the flux rapidly declined but the BSA rejection of the modified membranes improved. They mentioned that this behavior may be due to decreasing the pore size by incorporation of TiO₂ nanoparticles into the polymer matrix.

3.2.2. Triazines retention

The performance of the membranes, in terms of triazine retention, is illustrated in Figs. 8-12. The performance of the membranes regarding rejection of the three triazines follows the order CA-2 > CA-1 > CA-3 > CA-0, which confirms the results of the MgSO₄ rejection. As seen in Figs. 8 and 9, when the SiO₂ concentration increases up to 0.05 wt%, the permeate flux slightly decreases and the triazines rejection increases. Above 0.05wt%, the rejection is decreased for the CA-3 sample containing the highest silica loading (0.1 wt.%). However, the rejection of the CA-3 sample is higher than that of the neat CA membrane. The rejection is enhanced with an increase in the silica content of the nanocomposite. As mentioned above, the addition of nanoparticles causes a structural compactness of the composite membranes. This is mainly due to the interaction of modified SiO₂ with polymer matrix suggesting a network structure. This compactness increases with increasing the amount of SiO₂ in the composite. Thus, the lower permeability and higher salt rejection may be attributed to this network structure [40-41]. But, by increasing extra amount of nanoparticles, they may agglomerate and produce some voids between polymer chains. This means that the silica loading up to a critical concentration significantly modifies the CA matrix structure as well as its rejection properties. When the PWF is compared with the permeate flux, the adsorption of pesticides on the surface or inside pores causes a reduction in the permeate flux through the membranes.

Comparison of the experimental results at different operating pressures in the case of the CA-2 (Fig.10), shows a slight enhancement of triazine rejection by increasing the pressure. Atrazine rejection was increased from 96% to 98.3% when the transmembrane pressure was increased from 10 to 20 bars. The effect of the applied pressure on the propazine and prometryn rejection is similar. The enhancement in the membrane rejection with pressure can be explained by the solution-diffusion model [43]. In this model, both the flux and the solute rejection are dependent on the applied pressure and predict these parameters increase with an increase in pressure. In similar studies, Riungu et al. [44] and Ahmad et al. [45] have also reported that the rejection of pesticides in different nanofiltration membranes has increased with an increase in transmembrane pressure from 6 to 12 bars.

Fig. 11 illustrates the effect of feed concentration on the triazines rejection of the CA-2 membrane sample at a constant pressure of 10 bars and a feed concentration range of 0.1–10 mg/L. An increase in rejection is observed with an increase of feed concentration for all of the triazines. However, the most pronounced increase occurred for the propazine with higher dipole moments while the rejection of atrazine exhibited little change. The rejection of triazines was enhanced from 0.1 mg/L to 10 mg/L of feed concentration. This behavior may be described by the pesticide adsorption on the membrane surface [3]. When pesticide solutions come in contact with membrane filaments, they may adsorb on the surface of membrane in adsorption sites which is directly related to membrane surface properties [46]. When the concentration of pesticide increases, the value of adsorption sites is not changed and therefore sorption of molecules on the surface of membrane is controlled by feed concentration. Therefore, by increasing feed concentration, the amount of permeated molecules is not affected and rejection should be enhanced according to Eq (2).

Rejection of organic compounds has been discussed along with a number of physicochemical properties such as molecular size, solubility, dissociation, polarity and hydrophobicity. The molecular size is the most important parameter, and may be represented by molecular weight, or more accurately by a molecular stoke diameter.

Fig. 12 shows the plots of the rejection vs. molecular weight (M_w) and stoke radius (r_s) of triazines. The most easily accessible parameter that indicates the size of a molecule is molecular weight. The Stokes diameter is also an indirect parameter to describe molecular size.

Among the three tested molecules, prometryn (the triazine with the largest molecular weight and size) displays the highest rejection, followed by atrazine and propazine for the all prepared membranes. Although the propazine molecule is larger than that of atrazine, its measured rejection is lower for all membranes. This trend is attributed to the higher polarity and the solute-membrane affinity on rejection of propazine, which results in an easier transmission through the membrane [46]. A similar effect due to solute polarity was observed by Hofman et al. [28] in nanofiltration where diuron with greater molecular weight values than those of the present pesticides showed lower retention. Pesticides can be rejected by either size exclusion or diffusion-controlled mechanisms. In cases where the molecule is in the range of a membrane pore size, the interaction between the membrane surface and the molecule will play a more effective role in rejection [29]. So, the rejection of propazine was lower than atrazine. When a molecule is larger than the membrane pore size, its passing through the membrane is affected strongly by molecular sieve mechanism. Prometryn is larger and heavier than two other triazines due to the branched functional groups. Therefore, the rejection increased again for prometryn compared to propazine.

Several reported studies [2-7, 47] showed that almost all pesticides were adsorbed on several types of NF membranes, and the adsorption property was correlated with hydrophobicity of the solute. Hydrophobic property of a pesticide is defined as the logarithm of the n-octanol / water partition coefficient ($\log P$) [47].

The effect of the hydrophobicity of the solutes on rejection is presented in Fig. 12-c. This graph shows that the hydrophobicity was not capable of describing solute rejection in nanofiltration. Although, atrazine has a lower hydrophobic property than propazine, the rejection of atrazine is greater than that of propazine. Propazine showed the lowest rejection of about 74 - 82% among all the membrane samples despite its greater $\log P$ compared with that of atrazine. In a similar finding by Jung et al. [48], no significant relation between $\log P$ and rejection has been observed and in some cases, more hydrophobic organic solutes have shown a lower rejection. This behavior can be justified by considering the dipole moments of the solutes.

The effects of dipole moments as well as size and other molecular properties have also been investigated and found to have an important parameter to describe the membrane rejection [49-53]. Fig. 12-d shows that the dipole moment can be used to describe the rejection of triazines with a low dipole moment (<4 Debye). For all membrane samples, the rejection of propazine

with a higher dipole moment is substantially lower than that exhibited by prometryn and atrazine. This indicates that dipole moment is a parameter that influences the rejection in nanofiltration. Experimental results obtained by Van der Bruggen et al. [5] illustrated that the rejection could be dependent on the dipole moment of the solutes. They suggested that when a solute molecule come near to the membrane surface, the electrostatic attraction between the solute molecule and the membrane cause the molecule to rotate as the opposite charge side nears the membrane surface. Hence, the molecule enters easily into the pore in liner vector and decreases the effect of molecular sieve so the rejection is decreased.

Some of the commercially available membranes with their rejection results for atrazine are compared to this study in Table 5. The wide range of rejection reported in the literatures could be related to different operating conditions and the chemical properties of the membranes. According to Table 5, atrazine rejection for the prepared membranes determined in this work could be comparable to that of commercially available membranes. The value of atrazine rejection for CA-2 sample membrane at a feed concentration of 1 mg/L is better than the rejection of reported commercial membranes.

4. Conclusion

The present study focuses on preparation of OA modified SiO₂/CA nanocomposite membranes by dispersing the nanoparticles in the casting solution with different loadings. The ATR-IR, FESEM, AFM and contact angle analyzes indicated that addition of the SiO₂ nanoparticles has affected the various properties of the membrane.

The performance of the prepared membranes was investigated in terms of the pure water flux, MgSO₄ rejection and solutions containing three triazines (atrazine, propazine and prometryn) under different operating pressures and feed concentrations. Adding modified nanoparticles resulted in the membranes with significantly Salt and triazines rejection. The membranes rejection were raised up to a critical amount of additives (0.05 wt.%). It is also noted that the pore size of the nanocomposite membranes are lower than those of neat CA membrane.

The effects of various physicochemical factors such as weight, size, hydrophobicity, and dipole moment of triazines molecules on membranes rejection were studied. It was shown that

electrostatic attraction between the pesticide molecule and the membrane was the main effective factor. Therefore, the lowest rejection obtained for propazine due to its higher dipole moment and prometryn, with the largest molecule, showed the highest rejection.

The prepared nanocomposite membranes were compared with NF membranes which used in other studies. Results showed that the rejection of CA-2 sample has the best rejection than other commercial NF membrane and nearly the same as nanocomposite PA membrane which prepared in our previous work.

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References

- [1] Y. Wanga, L. Shu, V. Jegatheesan, B. Gaoa, Separation and Purification Technology 74 (2010) 236–241.
- [2] K.V. Plakas, A.J. Karabelas, J. Membr. Sci. 336 (2009) 86–100.
- [3] Y. Zhang, B. Van der Bruggen, G.X. Chena, L. Braeken, C. Vandecasteele, Separation and Purification Tech. 38 (2004) 163–172.
- [4] K. V. Plakas, A. J. Karabelas, Desalination 287 (2012) 255–265.
- [5] B. Van der Bruggen, J. Schaep, W. Maes, D. Wilms, C. Vandecasteele, Desalination 117 (1998) 139-147.
- [6] P. A. C. Bonne , E.F. Beerendonk, J.P. van der Hoek, J. A. M. H. Hofman, Desalination 132 (2000) 189-193.
- [7] R. Boussahel, S. Boulard, K.M. Moussaoui, A. Montiel, Desalination 132 (2000) 205-209.
- [8] Y. Kiso, A. Mizuno, R. A. Adawiah binti Othman, Y-J. Jung, A. Kumano, A. Arijji, Desalination 143 (2002) 147-157.
- [9] S. Loeb, S., Souiirajan, UCLA Dept. of Chem. Eng. Report No. 60-60, 1961.
- [10] N. Ghaemi, S. S. Madaeni, A. Alizadeh, P. Daraei, V. Vatanpour, M. Falsafi, Desalination 290 (2012) 99–106.
- [11] L. A. Nezam El-Dein, A. El-Gendi, N. Ismail, K.A. Abed, A. I. Ahmed, J. Industrial and Engineering Chemistry, 2014

- [12] J. Su, S. Zhang, H. Chen, H. Chenc, Y.C. Jean, T-S. Chung, J. Membr. Sci. 364 (2010) 344–353.
- [13] B. S. Lalia, V. Kochkodan, R. Hashaikh, N. Hilal, Desalination 326 (2013) 77–95.
- [14] M. Sivakumar, D.R. Mohan, R. Rangarajan, J. Membr. Sci. 268 (2006) 208–219.
- [15] G. Arthanareeswaran, P. Thanikaivelan, K. Srinivasn, D. Mohan, M. Rajendran, Eur. Polym. J. 40 (2004) 2153–2159.
- [16] R. Abedini, S. M. Mousavi, R. Aminzadeh, Desalination 277 (2011) 40–45.
- [17] J. Zhao, M. Milanova, M.M.C.G. Warmoeskerken, V. Dutschk, Colloids and Surfaces A: Physicochemical and Engineering Aspects 413 (2012) 273–279.
- [18] A. Martín, J.M. Arsuaga, N. Roldán, J. de Abajo, A. Martínez, A. Sotto, Desalination 357 (2015) 16–25.
- [19] X.Q. Xie, S.V. Ranade, A.T. Dibenedetto, Polymer 40 (1999) 6297–6306.
- [20] H. Shirono, Y. Amano, M. Kawaguchi, T. Kato, J. Colloid Interface Sci. 239 (2001) 555–562.
- [21] A. Dehghani Kiadehi, M. Jahanshahi, A. Rahimpour, S. A. A. Ghoreysh, Chemical Engineering and Processing: Process Intensification 90 (2015) 41–48.
- [22] J. T. Park, J. A. Seo, Sung Hoon Ahn, Jong Hak Kim, Sang Wook Kang, J. Industrial and Engineering Chemistry 16 (2010) 517–522.
- [23] Z. Li, Y. Zhu, Applied Surface Science 211 (2003) 315–320.
- [22] Y. Kiso, Y. Nishimura, T. Kitao, K. Nishimura, J. Membr. Sci. 171 (2000) 229–237.
- [23] K.V. Plakas, A.J. Karabelas, Journal of Membrane Science 320 (2008) 325–334.
- [24] N. Rakhshsan, M. Pakizeh, Separa. & Purifica. Tech. 147 (2015) 245–256.
- [25] D. Rana, R. M. Narbaitz, A.M. Garand-Sheridan, A. Westgate, T. Matsuura, S. Tabe, S. Y. Jasim, J Mater Chem A 2 (2014) 10059–10072.
- [26] D. Rana, T. Matsuura, Chem. Rev. 110 (2010) 2448–2471.
- [27] L. Zhang, G. Chowdhury; C. Feng, T. Matsuura, R. Narbaitz, J. Appl. Polym. Sci. 2003, 88, 3132.
- [28] J. A. M. H. Hofman, E. F. Beerendonk, H. C. Folmer, J. C. Kruithof, Desalination 113 (1997) 209–214.

- [29] S. Chen, J. S. Taylor, L. A. Mulford, C. D. Norris, *Desalination* 160 (2004) 103-111.
- [30] A. K. Ghosh, E. M. V. Hoek, *J. Membr. Sci.* 336 (2009) 140-148.
- [31] A. A. Hussain, M. E. E. Abashar, I. S. Al-Mutaz, *Desalination* 214 (2007) 150-166.
- [32] C. Liu, R. Bai, *J. Membr. Sci.* 267 (2005) 68-77.
- [33] S. Waheed, A. Ahmad, S.M. Khan, S. Gul, T. Jamil, A. Islam, T. Jamil, Hussain, *Desalination* 351 (2014) 59-69.
- [34] P. Innocenzi, *J. Non-Cryst. Solids* 316 (2003) 309-319.
- [35] p. Van de Witte, P.J. Dijkstra, J.W.A. Van den Berg, J. Feijen, *J. Membr Sci* 117 (1996) 1-31.
- [36] A. Rahimpour, M. Jahanshahi, B. Rajaeian, M. Rahimnejad, *Desalination* 278 (2011) 343-353.
- [37] A. V. D. Boomgaard, University of Twente, Enschede, 1998.
- [38] W. Li, X. Chen, C. Chen, L. Xu, Z. Yang, Y. Wang, *Polym. Compos.* 29 (9) (2008) 972-977.
- [39] R. Song, D. Yang, L. He, *J. Mater. Sci.* 43 (2008) 1205-1213.
- [40] S. Y. Lee, H. J. Kim, R. Patel, S. J. Im, J. H. Kim, B. R. Min, *Polym. Adv. Technol.* 18 (2007) 562-568.
- [41] C. K. Kim, J. H. Kim, I. J. Roh, J. J. Kim, *J. Membr. Sci.* 165 (2000) 189-199.
- [42] A. Rahimpour, M. Jahanshahi, A. Mollahosseini, B. Rajaeian, *Desalination* 285 (2012) 31-38.
- [43] K. V. Plakas, A. J. Karabelas, *Desalination* 287 (2012) 255-265.
- [44] N. J. Riungu, M. Hesampour, A. Pihlajamaki, M. Manttari, P. G. Home, G. M. Ndegwa, *J. Engineering, Computers & Applied Sciences (JEC&AS)* 1 (2012) 50-60.
- [45] A. L. Ahmad, L. S. Tan, S. R. A. Shukor, *Journal of Hazardous Materials* 151 (2008) 71-77.
- [46] B. Van der Bruggen, K. Everaert, D. Wilms, C. Vandecasteele, *J. Membr. Sci.* 193 (2001) 239-248.
- [47] A. Noble, *J. Chromatography*, 642 (1993) 3-14.

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3
4
5
6 [48] Y. Jung, Y. Kiso, R. A. Adawih binti Othman, A. Ikeda, K. Nishimura, K. Min, A. Kumano,
7 A. Arijji, Desalination 180 (2005) 63-71.
8
9 [49] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, J. Membr. Sci. 156 (1999) 29-
10 41.
11
12 [50] I. Musbah, D. Ciceron, A. Saboni, S. Alexandrova, Desalination 313 (2013) 51–56.
13
14 [51] I. Vergili, J. Environ.Manag. 127 (2013) 177–187.
15
16 [52] J. Shirley, S. Mandale, V. Kochkodan, Desalination 344 (2014) 116–122.
17
18 [53] K. Kosutic, L. Furac, L. Sipos, B. Kunst, Separ. Purifi. Tech. 42 (2005) 137–144.
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Graphical abstract

The effect of SiO₂ on the morphology, permeate flux and triazines rejection of CA membrane.

Fig.1. The schematic diagram of separation system: (1) feed tank (2) cooling system (3) valve (4) pump (5) barometer (6) filtration cell (7) permeate flow (8) retentate flow (9) bypass.

Fig.2. ATR-IR spectra of membranes.

Fig.3. FESEM cross-section images of membranes

Fig. 4. FESEM pictures of different CA membrane surfaces

Fig. 5. FESEM cross-section images of membranes with higher magnification.

Fig. 6. Three-dimensional AFM surface images of membranes.

Fig.7. Pure water flux and MgSO_4 rejection of membranes.

Fig.8. Triazine rejections of membranes ($P = 10$ bar and $C_f = 100$ ppb).

Fig.9. Permeate flux of membranes ($P = 10$ bar and $C_f = 100$ ppb).

Fig.10. Rejection of the triazines vs. pressure for CA-2 membrane sample ($C_f = 100$ ppb).

Fig.11. Rejection of the triazines vs. different feed concentration for CA-2 membrane sample
(p = 10 bar).

Fig.12. Rejection vs. a) molecular weight, b) molecular size, c) log P and d) dipole moment of the triazines ($P = 10$ bar and $C_f = 100$ ppb).

Table 1
Properties of the pesticides used in this study.

	Chemical structure	Formula	Molecular weight (g/mol)	LogP	Dipole moment (Debye)
Atrazine		C ₈ H ₁₄ ClN ₅	215.7	2.40	3.32
Propazine		C ₉ H ₁₆ ClN ₅	229.7	2.91	3.50
Prometryn		C ₁₀ H ₁₉ N ₅ S	241.4	3.34	2.26

Table 2
Composition of prepared nanocomposite membranes.

Membrane	Polymer (Wt%) CA	Modified SiO ₂ (Wt%)	Mixture of solvent (Wt%)
CA-0	20	0	80
CA-1	20	0.01	79.99
CA-2	20	0.05	79.95
CA-3	20	0.1	79.90

Table 3

Nominal pore size, water contact angle and surface roughness parameters of the membranes.

Membrane	Nominal pore size (nm)	Contact angle (degree)	Surface roughness		
			S_a (nm)	S_q (nm)	S_z (nm)
CA-0	0.458	65.9±1.2	2.877	3.619	12.853
CA-1	0.425	60.3±0.6	0.543	1.303	7.376
CA-2	0.413	58.8±2.1	1.671	2.768	27.591
CA-3	0.448	54.6±1.8	2.768	3.198	22.574

Table 4

Effect of different concentration of SiO_2 on membranes top and sub layer thickness.

Membrane	Membrane thickness (μm)	Top layer thickness (μm)	Spongy layer thickness (μm)
CA-0	87.1	0.983	41.2
CA-1	88.2	1.27	47.1
CA-2	70.6	1.99	49.4
CA-3	87.2	1.43	85.7

Table 5

Comparison of atrazine removal by commercial membranes with prepared membrane in this study.

membrane	operating pressure (bar)	C _F (mg/L)	R (%)	Ref.
UTC20 (polyamide)	8	0.1	~72	[3]
UTC20 (polyamide)	8	5	~93	[3]
NF270 (polyamide)	5	~0.8	80	[23]
NF-70 (polyamide)	-	0.010	94.7	[25]
NF-70 (polyamide)	15	0.3	96.8	[4]
NTR-729HF (polyamide)	10	0.5-1.5	97.5	[22]
CPA2 (polyamide)	10	2-4	95.9	[50]
NF PES 10	20	0.74	20	[51]
NF (polyamide)	10	0.1	94.2	[26]
NF (OA modified silica/polyamide)	10	0.1	98.2	[26]
CA-0	10	0.1	82.7	This study
CA-2	10	0.1	96	This study
CA-2	10	1	98	This study