BRACKISH GROUNDWATER DESALINATION USING THE SYNTHETIC PA-g-AAC/TIO₂ MEMBRANE

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Abstract

The possibility of producing drinking water from brackish groundwater using synthetic polyamide grafted acrylic acid/ titanium oxide (PA-g-AAc/TiO_2) membrane was studied. The optimum conditions for preparation of the synthetic membrane were PA concentration (7 % w/v of solvent), LiCl concentration (40 % w/w of PA), AAc concentration (20 % w/w of PA), TiO_2 concentration (3 % w/w of PA), evaporation time (24 hr.) and temperature (70 °C). Brackish groundwater sample was taken from El-Maghara area, Mid. Sinai, Egypt and analyzed by the standard methods. The obtained results showed that the total dissolved solids (TDS) and ionic composition of permeate water decrease as the operation time increases. The cations and anions rejection (R %) showed that the divalent cations and anions are more rejected than the monovalent ones, where the order of cations rejection was R Mg^{2+} > R Ca^{2+} > R Na^+, while the anions rejection was in the order R SO_4^{2-} >R HCO_3^- > R Cl^-. After the desalination process, the hypothetical salts of such sample do not change; but the change was only in its concentration expressed as TDS. The sequence of salts rejection (R_s %) related to initial concentration of each salt arranged was R_s $MgSO_4$> R_s $MgCl_2$ > R_s $CaSO_4$ > R_s Ca $(HCO_3)_2$ >R_s NaCl. This can be explained according to Donnan theory.

The produced water permeate has a low value of TDS (933 ppm), where the salt rejection and water flux are 70 % and 10.28 x10^{-5} g/cm^2.sec., respectively. This produced water is accepted by international standards for drinking water.

Keywords: Polyamide; Acrylic acid; TiO_2; Membrane; Brackish groundwater; Desalination; Hypothetical salts

Introduction

It is well known that the water resources in Egypt are limited. Meanwhile, water demand is continually increasing due to population growth, agricultural, industrial and tourist development and the increase of living standards (Hafez, 2005). Because of population growth and the per capita share of water has dropped dramatically to less than 1000 m^3/capita according to international standards, this is considered the "water poverty limit". The value may even decrease to 500 m^3/capital in the year 2025. This urged the successive Egyptian government to draw various programs that depend totally or partially on local groundwater resources in desert areas and the development of non-conventional water resources such as water reuse and desalination of saline water.

Sinai represents 6 % of the total area of Egypt. El-Maghara area in Mid. Sinai is considered as an example of arid zone which suffers shortage of water resources except for high salinity groundwater. For this reason, many trials have been made to synthesize hybrid organic/inorganic membrane that can be used in desalination of brackish water. In this regard, membrane separation technology has been widely used for desalination of sea and brackish waters (Belfort, 1984, Sourirajan and Matsuura, 1985 and Košuti´c et al., 2000). The reverse osmosis (RO) process which uses polymeric membranes to achieve molecular separation excels all other methods of desalination and is considered the simplest and most efficient technique to desalt saline/seawater (Rao et al., 1997).

In recent years, inorganic nanoparticles have been introduced as filler to prepare composite membrane to improve the properties of polymeric membranes including, permeation, thermal stabilities, and mechanical properties (Yang et al., 2007 and Cao et al., 2006). Among many nanoparticles, TiO_2 nanopowder is investigated because it is non-toxic, chemically inert and low cost (Li et al., 2009). Three methods have been reported to prepare polymer-inorganic composite membranes: (1) Disperse the nanoparticles in the casting solution directly and prepare the composite membranes via phase inversion (Jian et al., 2006); (2) Add the prepared sol containing nanoparticles in the casting solution and prepare the composite membranes via phase inversion; (3) Dip the prepared membrane in the aqueous suspension containing nanoparticles and prepare the composite membranes via self-assembling (Bae et al., 2006).

Reverse osmosis performance parameters, salt rejection and permeate flux are known to be influenced by membrane characteristics, physicochemical properties of the system and operating variables such as solute concentration and operating pressure (Košuti´c et al., 2004). Two essential membrane parameters in the RO process are solubility and diffusivity of solutes and solvents to the active-layer polymers, which determine the membrane rejection and the flux (Matsuura, 1994 and Kwak, 1999).

The present work is devoted to the possible application of the synthetic PA-g-AAc/TiO_2 membrane in desalination of brackish groundwater of El-Maghara area.

Materials and Methods
Materials

Aromatic polyamide, poly m-phenyleneisophthalamide (PMPIA) and solvents such as N, N-dimethyl acetamide (DMAc), N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP) and hexamethyl phosphoramide (HMPTA) were supplied by Aldrich. Acrylic acid (AAc), purity 99.9% was received and purchased from Merck, Germany. Titanium dioxide nanoparticles (TiO_2): a commercial form 80% anatase, 20% rutile, BET surface area 50m^2/g, P25 was obtained from Deggusa. The other chemicals such as the chemical initiator (benzoyl peroxide, BPO), additive inorganic salt as LiCl, sodium dodecyl sulphate (SDS) as surfactant and nitric acid were reagent grade and used without further purification.

Brackish groundwater sample collection and analysis

Brackish groundwater sample was collected from El-Maghara area, Mid. Sinai, Egypt and the position of such point (longitude 33^0 $17^/$ $34^{//}$ E & latitude 30^0 $42^/$ $33^{//}$ N) was determined using GPS model Magellan, Nava 5000 pro. Such water sample was collected in a clean, washed polyethylene bottle and subjected to the analysis of physical and chemical properties of water sample. The physical properties were detected by measuring the specific electrical conductance (EC) by EC meter Model LF 538, WTW, USA and expressed in micromhos per centimeter (µS/cm) at 25 °C, and pH value was measured by 3320 pH meter (Jenway, UK). The Chemical properties were determined by measuring total dissolved salts (TDS), Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{--}, HCO_3^-, SO_4^{--} and Cl^- ions concentration. All the analyses were carried out according to the methods adopted by **Rainwater and Thatcher, 1960, Fishman and Friedman, 1985** and, American Society for Testing and Materials **(ASTM 2002)**.The obtained chemical data are expressed in part per million (ppm), miliequivalent per liter (me/l) and percent (%).

Preparation of TiO_2 nanoparticle self-assembled aromatic polyamide membrane.

Asymmetric aromatic polyamide membrane was prepared by the dry casting method **(Altinkaya and Ozbas, 2004),** in which the dissolution of PA using DMAc as solvent and LiCl as an inorganic salt additive until the complete dissolution of PA and formation the casting solution was carried. The concentration of PA to DMAc solvent was 7 % w/v. A certain amount of inorganic salt LiCl (40 % w/w of PA) was added to PA/DMAc to complete the solubility process, then the casting solution of PA/LiCl/DMAc was gently heated with magnetic stirring until the dissolving process be completed. To prepare PA-g-AAc co-polymer membrane, BPO was added to such casting solution in concentration of 5 % w/w of AAc, where the concentration of AAc was 20 % w/w of PA. The reaction temperature and time were 85 °C and 2 hr., respectively.

TiO$_2$ nanoparticles were modified with sodium dodecyl sulphate (SDS) as a surfactant to prevent the aggregation of nanoparticles in the membrane matrix, where 1g of TiO$_2$ nanoparticles was added to 0.7 % SDS at adjustable pH 4 with nitric acid, and then stirring for 6 hr. The modified TiO$_2$ was obtained by centrifuge and then dried at 60 °C for 24 hr. TiO$_2$ concentration (3 % w/w of PA) was added to PA-g-AAc co-polymer solution to form the nanocomposite of PA-g-AAc/TiO$_2$

Finally, the casting solution (PA-g-AAc/TiO$_2$) was put within the glass plate and dried at evaporation time and temperature 24 hr. and 70 ˚C, respectively, to obtain the flat sheet of the membrane. After this process, the membrane was immersed in de-ionized water for about 12 hr. at 25 °C to the complete removal of excess solvent and LiCl salt and then dried completely at room temperature. The nanocomposite membrane (PA-g-AAc/TiO$_2$) that used in desalination of brackish groundwater was prepared under these optimum conditions.

RO performance

Reverse osmosis properties, salt rejection (R$_s$ %) and water flux (J$_w$) of the prepared membranes were measured by laboratory DDS reverse osmosis system, model LAB-M20, manufactured by Alfa Laval Comp., Denmark which consists of stainless steel cylindrical vessel, 20 cm diameter and 70 cm height, with control panel. The effective membrane areas range from 0.036 to 0.72 m^2 (0.018 m^2 per membrane). The salt rejection percent (R$_s$ %) was calculated as:

$$R_s \ (\%) = (C_f - C_p/C_f) \ x \ 100$$

Where C$_f$ and C$_p$ are the concentrations of feed and permeate water (product), respectively.

The water flux through a semi-permeable membrane was expressed in weight of the product per unit membrane area during operation time in seconds (J$_w$ x 10^{-5} g/cm^2.sec).
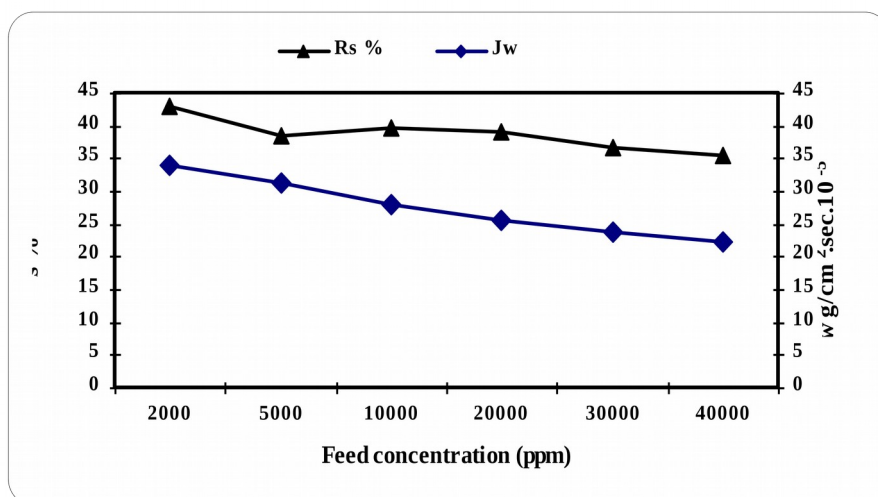
Results and Discussions
Membrane performance

Reverse osmosis properties (salt rejection and water flux) for the synthetic PA-g-AAc/TiO$_2$ membranes were studied at different concentrations of NaCl (2000 to 40000 ppm) of feed solution with applied pressure 30 bar, flow rate 5 l/min for 8 hr. as operation time at 25 °C. The results are shown in Fig. (1), it is obvious that both water flux and salt rejection decrease with increasing feed concentrations of NaCl solution, where the PA-g-AAc/TiO$_2$ nanocomposite membrane possess the highest water flux (J$_w$= 34 g/cm^2.sec×10^{-5}) with acceptable salt rejection (R$_s$= 42 %) at NaCl

of 2000 ppm for one run operation process. Therefore, this membrane can be used effectively in desalination process of the selected brackish groundwater sample of the area under investigation.

The decrease of water flux (water permeate, J_w) with increasing the feed concentration can be explained on the basis that the water flux through the membrane is proportional to the effective pressure (P_{eff}), which is defined as (J_w α P_{eff}) and (P_{eff} α P-Δπ) where; P_{eff} and P are the effective and applied pressures and Δπ is the osmotic pressure. The presence of sodium chloride in the feed solution leads to the reduction in permeates flux. The transmembrane salt concentration gives rise to transmembrane osmotic pressure (Δπ) leading to a lowery of the driving pressure. By taking into account the net pressure in the flux calculation, it can be shown that Δπ is mainly responsible for the flux decline (**Jiraratanon et al., 2000).** However, the presence of TiO_2 on such membrane, where the TiO_2 nanoparticles act as a lacy structure with higher porosity formed on the top surface of membrane; this leads to enhancement of the flux through the skin layer that became a little denser. At the same time, the improved hydrophilicity of the membrane due to presence of hydroxyl groups on TiO_2 surface can attract water molecules inside the membrane matrix and promote them to pass through the membrane and consequently enhance the membrane permeability **[Li et al., 2009]**.

Fig. (1) Effect of feed concentration (NaCl) on reverse osmosis performance of aromatic PA-g-AAc/ TiO₂ nanocomposite membrane.

On the other hand, the decrease of the salt rejection with increasing feed concentration is due to the effect of Donnan exclusion which reduces with increasing feed electrolyte concentration. In case of a higher ionic strength, the membrane charge will be shielded, to a large extent, resulting in a lower effective charge and consequently a lower rejection is obtained. This type of NaCl salt retention was observed by several authors as well and attributed this effect to the negative charge of the PA-g-AAc/TiO$_2$ nanocomposite membrane used (**Bhattacharyya et al., 1974, Simpson et al., 1987, Ikeda et al., 1988 and Peeters et al., 1998**).

Brackish groundwater desalination

The brackish groundwater sample of Bir El-Maghara 5, wadi El-Khariq is tapping the limestone aquifer, where both water salinity and pH are 3333 ppm and 7.8, respectively. Such water was pumped into a closed vessel through the Lab RO unit at a flow rate of 5 l/min and the applied pressure of 30 bar against the selected membrane. This pressure is needed to enable the fresh water to pass through the membrane leaving an amount of rejected salts; some amounts of salts pass through the membrane and remained in the water product. The obtained results showed that the values of electrical conductivity (EC, µmhos/cm) and total dissolved solids (TDS, ppm) of such groundwater sample decrease gradually as the operation time increases. The EC and TDS of post treated water became (2800 µmhos, 1620 ppm), (2200 µmhos, 1301 ppm) and (1680 µmhos, 933 ppm) at the operating times 8, 16 and 24 hr., respectively, table (1). Also, the ionic composition of permeate water decreases as operation time increases, Fig. (2).

Legend: EC/100, SO4--, Cl-, HCO3-, Ca++, Mg++, Na+

...rackish groundwater as a ...mposite membrane

Table (1): Chemical analysis data of pre-treated and post-treated brackish groundwater sample (Bir El- Maghara 5, limestone aquifer) using PA-g-AAc/TiO2 nanocomposite membrane after each operating time through desalination process.

Operation time	TDS (ppm)	unit	Ca++	Mg++	Na+	K+	Total cations	CO3-	HCO3-	SO4-	Cl-	Total anions	Hypothetical salts (%)				
													Na Cl	Mg Cl	Mg SO4	Ca SO4	Ca (HCO3)2
pre-treatment (Raw water)	3333	ppm	334.8	180.8	614	5.09	58.41	0	244	900	1176	55.89	46	18	7	22	7
		meq/l	16.71	14.87	26.70	0.13		0	3.989	18.73	33.16						
		%	28.6	25.46	45.72	0.22		0	7.14	33.53	59.33						
Produced water after 8 hr.	1620	ppm	167.4	79.1	316.6	1.82	28.67	0	122	370	624	27.29	48	17	6	22	7
		meq/l	8.353	6.505	13.77	0.04		0	1.99	7.7	17.59						
		%	29.13	22.68	48.03	0.16		0	7.42	28.22	64.27						
Produced water after 16 hr.	1301	Ppm	130.2	56.5	252	1.36	22.14	0	106.8	280	528	22.46	50	15	6	21	8
		meq/l	6.497	4.65	10.96	0.034		0	1.74	5.82	14.88						
		%	29.33	21	49.51	0.16		0	7.77	25.39	64.84						
Produced water after 24hr.	933	ppm	93	33.9	209	1.36	16.53	0	76.25	150	408	15.87	55	14	3	20	8
		meq/l	4.641	2.79	9.07	0.034		0	1.24	3.123	11.50						
		%	28.07	16.86	54.86	0.21		0	7.85	18.79	69.21						

Hypothetical salts rejection

Hypothetically, the ions of strong acids (Cl^- and SO_4^{2-}) form chemical combination with alkalis (Na^+ and K^+) and the rest the acid radicals combine with the alkaline earths (Ca^{2+} and Mg^{2+}). If the cations of alkalis and alkaline earths are surplus in water, they will combine with the weak acid radicals (CO_3^{2-} and HCO_3^-). To clarify such combinations, the relations between cations and anions in the investigated waters, are illustrated in the form of bar graphs as outlined by **Collin's (1923)**.

Figures (3 and 4) show the rejection (%) of the hypothetical salts present in brackish groundwater sample the equilibrium conditions as a function of the operation time. Noteworthy to mention that the different salts permeated are in equilibrium condition after each desalination process. From such figures, it is obvious that the sequence of salts rejection related to initial concentration of each salt can be arranged as follows:

R_s $MgSO_4$ > R_s $MgCl_2$ > R_s $CaSO_4$ > R_s $Ca (HCO_3)_2$ > R_s $NaCl$

The membrane shows high rejection for magnesium salts, moderate rejection for calcium salts and low rejection for NaCl salt. This rejection behaviour can be illustrated on the idea that the membrane appeared to be positively charged in presence of $MgSO_4$, $MgCl_2$, $CaSO_4$ and $Ca (HCO_3)_2$ salts and negatively charged in the presence of NaCl **(Schaep et al., 2001).** These results suggest that each ion could have its individual contribution to the membrane charge by means of adsorption; this phenomenon is attributed to ionic adsorption at the membrane/solution interface. In case of $MgSO_4$, $MgCl_2$, $CaSO_4$ and $Ca (HCO_3)_2$ salts, there is a strong adsorption of Mg^{2+} and Ca^{2+} ions leading to reverse in the sign of the membrane charge so that the membrane becomes positively charged. This could explain the fact that these salts are better rejected than NaCl where Mg^{2+} and Ca^{2+} are the co-ions (ions with the same sign of charge as the membrane charge) and have a higher valency than chloride, which is the co-ion in case of NaCl. On the basis of Donnan exclusion theory, a high co-ion valence causes a higher salt rejection. Also, a strong affinity of chloride ions for the membrane material (as compared to sulfate and bicarbonate ions) has been found; this affinity causes a lower positive charge for $MgCl_2$ than that of $MgSO_4$.

Computation of the rejected ions as percent of TDS reveals that the salts of post treatment after 24 hr. does not change after the desalination process, but the changes are related to its rejection percent referred to as TDS of the pre- and post-treatments. Thus, the desalination process of pre-treatment does not change the salts

composition in both pre- and post- treated water which have the same types of salts NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$ and Ca $(HCO_3)_2$ but in low concentrations. It is evident that the appearance of $MgCl_2$ salt in the groundwater is mainly due to the formation of aquifer matrix under marine conditions, table (1).
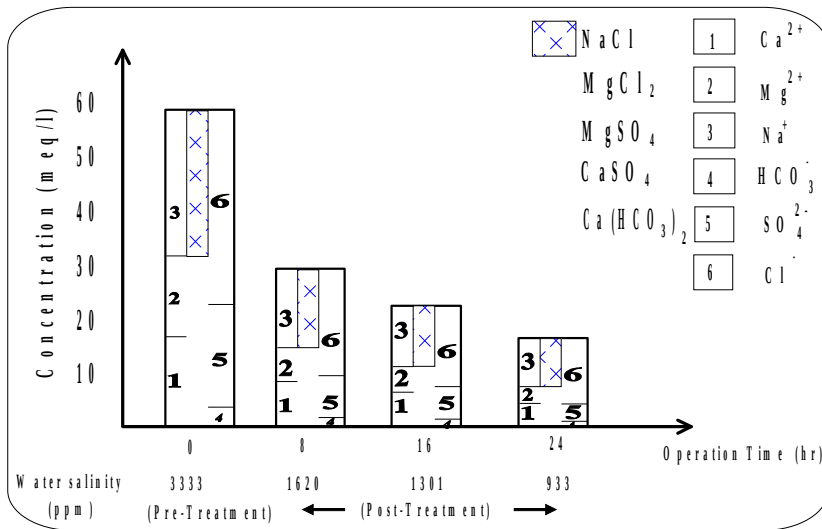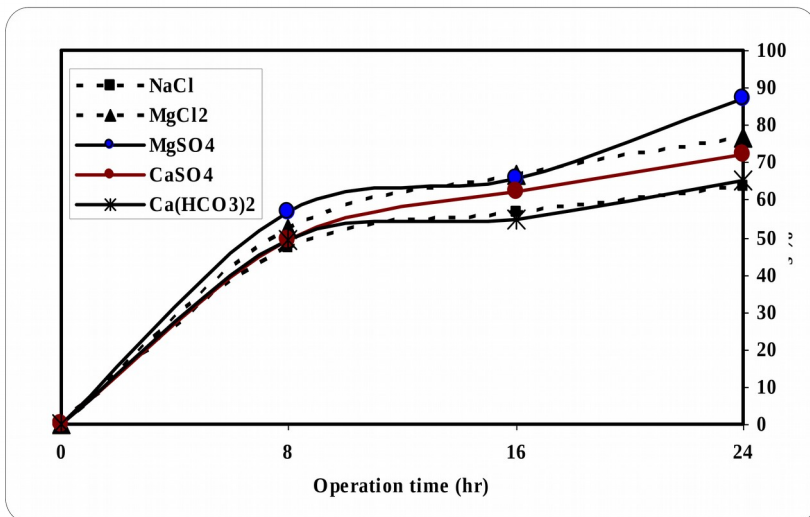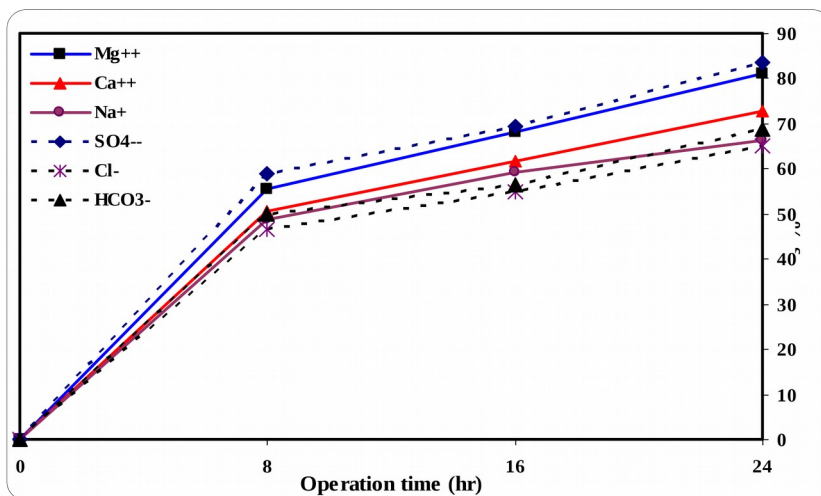

Fig.(3) Graphical representation of ions distribution of the pre-treatment and post-treatment for brackish water desalination process at different operation times using the selected RO membrane.

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Fig. (4) Rejection of the PA-g-AAc/TiO₂ nanocomposite membrane to the different salts present in the brackish groundwater sample (feed concentration 3333 ppm) as a function of operation time (hr).

Behavior of ions during desalination process.

The sequence of cations rejection (%) was R_s Mg^{2+} > R_s Ca^{2+} > R_s Na^+, while the sequence of anions rejection was R_s SO_4^{2-} > R_s HCO_3^- > R_s Cl^- , where the retention of the bivalent anions is lower than that of cations, also, the retention (%) of bivalent ions was higher than that of monovalent ones Fig. (5).

Fig. (5) Rejection of the PA-g-AAc/TiO₂ nanocomposite membrane to the different ions present in the brackish groundwater sample (feed concentration 3333 ppm) as a function of operation time (hr.).

This is due to one of the main four factors. The first is the ionic and hydrated ionic radii of divalent ions in solution which are larger than those of monovalent ions, table (2). The second is based on the different cationic valence rejection sequence which can be explained by the Donnan exclusion theory, which suggests that a higher valence co-ion causes a higher ion rejection, whereas a higher valence counter ion (neutral species) leads to a lower rejection of the salt. For the same valence ions, the rejection sequence could be affected by the difference in ion diffusivities, i.e., an ion is retained more if it has a smaller diffusivity, table (2) is inversely reflected in the rejection sequence **(Schaep et al., 2001).** The third is based on the interaction between the membrane surface and ions in solution, it is known that TiO₂ is an amphoteric oxide with an isoelectric point (IEP TiO₂ = 6). Therefore, when the solution pH is higher than IEP of TiO₂, its surface will be negatively charged (**Fu et al., 2005**). So the cations can be adsorbed on PA-g-AAc/TiO₂

surface. Also, these negative charges are repelled with the anion species in the electrolyte solution according to the Donnan exclusion mechanism (**Teixeira et al., 2005**). These factors can also explain the high rejection of Mg^{2+} and Ca^{2+} counter-ions more than Na^+. The fourth is based on the hydration energy, where the difference of retention can be attributed to the difference of hydration energy between the divalent and monovalent ions, i.e., the more hydrated divalent ions, the more difficult their transfer across the membrane, table (2), (**Antropov, 1975).** Consequently, SO_4^{2-} and HCO_3^- ions which are more strongly hydrated than Cl^- ions become difficult to permeate through the membrane. So, the rejection of ions is written in the order: $R_s\ SO_4^{2-} > R_s\ HCO_3^- > R_s\ Cl^-$ and $R_s\ Mg^{2+} > R_s\ Ca^{2+} > R_s\ Na^+$.

Table (2) Diffusivities, ionic radius and hydration energy for the studied ions
[After Schaep et al., 2001 and Antropov, 1975]

Ion	Diffusivity [D] $(10^9\ m^2.sec^{-1})$	Ionic radius [r] (nm)	Hydrated ionic radius [nm]	Hydration energy $[E_h]$ $(KJ.mol^{-1})$
Na^+	1.333	0.095	0.365	407
Mg^{2+}	0.706	0.074	0.429	1921
Ca^{2+}	0.92	0.099	0.349	1584
Cl^-	2.032	0.181	0.347	376
HCO_3^-	1.85	--	--	--
SO_4^{2-}	1.065	0.230	0.380	1138

From the data obtained, it is obvious that the salt rejection increases with increase of the operation time while water flux decreases, table (3). This is due to the fact that, as operation time increases the accumulation of salts in the pores of membrane is produced, reducing the water flux and increasing the salt rejection. It is evident that the salt rejection (%) is the absolute value of the difference between pre- and post- treated water.

Table (3): Revere osmosis parameter for the selected membrane in desalination of brackish groundwater sample

Time (hr)	Rs (%)	Salt passage (%)	J_w $(g/cm^2.s.10^{-5})$	Salinity of pre-treated water (Raw water) (ppm)	salts (%) of TDS of feed concentration				
					Na Cl	Mg Cl_2	Mg SO_4	Ca SO_4	Ca $(HCO_3)_2$
0	0	100	0	3333	46	18	7	22	7
				Salinity of post-treated water (ppm)	Salt rejection (%)				
					Na Cl	Mg Cl_2	Mg SO_4	Ca SO_4	Ca $(HCO_3)_2$
8	51	49	15.43	1619.9	22.67	9.74	4.08	11.31	3.60
16	61	39	14.20	1301.4	26.47	12.14	4.66	13.80	3.88

24	70	28	10.28	932.8	30.60	14.08	6.16	16.40	4.76

Electrolyte permeation mechanism through the synthetic membrane during desalination process:

To work out the mechanism of desalination process through the reverse osmosis membranes, an assumption based on the premise of active dissociation of hydrated ions into water molecules using high pressure and ions adsorption may roughly include four stages (Tsuru et al., 1991 and El-Sayed et al., 2001); these are:

1- The specific energy required for the pumping transport in a practical RO desalination, water transport across the membrane and dissociation of hydrated ions into water molecules and ions (present in groundwater solution), then water molecules pass through narrow passages (semi-permeable membranes) during the process.

2- Differences in diffusivity, where more diffusion of ions from the solution phase towards these passages and exchange surfaces.

3- Contact of ions with the exchange surfaces.

4- This sieving (depending on ionic radii of ions), and adsorption of ions on the exposed charge of the RO membranes through electrostatic interactions between the membrane and the ions or between the ions mutually.

Evaluation of the selected sample for drinking water

The desalination process of such sample shows that the obtained permeate water (TDS, 933 ppm) and ions concentration did not exceed the permissible international standards for drinking water quality**,** table (4); so, it is acceptable for drinking as potable water. Note to mention that these results of produced water were obtained for one run operation process through 24 hr.

Table (4): Physicochemical analysis of brackish groundwater sample compared with water quality guidelines for human drinking

Chemical constituent or Parameter	Pre-treatment (ppm)	Post-treatment (after 24 hr) (ppm)	Egyptian[1] maximum Permissible limit in ppm	World[2] Health Organization guidelines ppm	International[3] standards ppm
TDS	3333	933	1200	1000	500 – 1500
PH	7.9	7.9	--	6.5 – 9.2	--
Sodium	614	208	--	200	200
Sulfates	900	150	250 – 400	400	250
Calcium	334.8	93	200	--	75 - 200
Chloride	1176	408	500	250	--
Magnesium	180.8	33.9	150	--	<125

1- Egyptian standards for drinking and domestic uses (Higher committee for water, 1995)

2-Guidelines for drinking water quality,2nd ed. Vol.2 Health criteria and other supporting information, 1996 (pp.940-949) and Addendum to Vpl.2 1998 (pp.281-283) Geneva, World Health Organization.

3- World Health Organization, 1972.International standards for drinking water, 3rd ed., Geneva, WHO.

Conclusion

The aromatic polyamide grafted acrylic acid/ titanium dioxide (PA-g-AAc/TiO$_2$) membrane was prepared under optimum conditions, where PA concentration (7 % w/v of solvent), LiCl concentration (40 % w/w of PA), AAc concentration (20 % w/w of PA), TiO$_2$ concentration (3 % w/w of PA) and the evaporation time and temperature are 24 hr and 70 Č, respectively. By studying the RO performance (salt rejection and water flux) using different feed solutions of NaCl 2000 to 400000 ppm, it was found that nanocomposite membrane possess the highest water flux (J$_w$= 34 g/cm^2.sec×10^{-5}) with acceptable salt rejection (R$_s$= 42.9 %) at NaCl concentration of 2000 ppm for one run operation process. So, this membrane can be used effectively in desalination process of the selected brackish groundwater sample collected from El-Maghara area.

The hypothetical salts present in such sample were NaCl, MgCl$_2$, MgSO$_4$, CaSO$_4$ and Ca (HCO$_3$)$_2$. The sequence of these salts rejection related to initial concentration was R$_s$ MgSO$_4$> R$_s$ MgCl$_2$ > R$_s$ CaSO$_4$ > R$_s$ Ca (HCO$_3$)$_2$ >R$_s$ NaCl, where the membrane has shown high rejection for divalent cations (magnesium and calcium) salts and moderate rejection for monovalent cation (NaCl) salt.

The sequence of cations rejection during the desalination process was R$_s$ Mg^{2+} > R$_s$ Ca^{2+} > R$_s$ Na$^+$, while the anions rejection was R$_s$ SO$_4^{2-}$>R$_s$ HCO$_3^-$ > R$_s$ Cl$^-$, where the retention of bivalent ions was higher than that of monovalent ones. This is due to four factors; the first is the ionic radii and hydrated ionic radii, where the ionic and hydrated ionic radii of divalent ions in solution are larger than that of monovalent ions. The second is based on the different cationic valence rejection sequence which can be explained by the Donnan exclusion theory. The third is based on the interaction between the membrane surface and ions in solution. The fourth is based on the hydration energy, where the difference of retention can be attributed to the

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difference of hydration energy between the divalent and monovalent ions; the more hydrated the divalent ions, the more difficult their transfer across the membrane.

The obtained results show that the TDS of such groundwater sample (3333 ppm) decreases gradually as the operation time increases reaching 933 ppm after 24 hr., with salt rejection 70 % and water flux 10.28 x10^{-5}. g/cm^2. sec. Therefore, the obtained permeate is accepted by international standards because the salinity is not contradictory for human consumption of drinking water.

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تحلية المياه الجوفية متوسطة الملوحة باستخدام غشاء البولي أميد- حمض الأكريليك- ثاني أكسيد التيتانيوم المخلق

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يهدف هذا البحث الي تخليق غشاء البولي أميد- حمض الأكريليك - ثاني أكسيد التيتانيوم تحت ظروف قياسية (تركيز البولي أميد, 7 % (وزن/ حجم) من المذيب & تركيز كلوريد الليثيوم, 40 % (وزن/ وزن) من تركيز البولي آميد & تركيز حمض الأكريليك, 20 % (وزن/ وزن) من تركيز البولي آميد& تركيز ثاني أكسيد التيتانيوم 3 % وزن/ وزن من تركيز البولي آميد, حيث تم تجفيف الغشاء المحضر عند 70 °م ولمدة ساعتين) وذلك لانتاج مياه صالحة للشرب طبقا للمقايس العالمية من مياه متوسطة الملوحه (أسنة) التي جمعت من منطقة المغارة-وسط سيناء- مصر.ولتحقيق ذلك تم دراسة أداء الغشاء المخلق بأستخدام محاليل مختلفة الملوحة من كلوريد الصوديوم والتي تتراوح بين 2000إلي 40000 جزء في المليون حيث وجد أن الغشاء يعطي أعلي قيمة احتجاز أملاح (42.9 %) مع أعلي كمية مياه محلاة (34 جم/سم². ثانية× 10⁻⁵) عند تركيز 2000 جزء في المليون من محلول كلوريد الصوديوم عند استخدام الغشاء لدورة واحدة خلال 24 ساعة, لذلك يعتبر هذا الغشاء أكثر كفاءة عند استخدامه في تحلية المياة الجوفية متوسطة الملوحة. تم دراسة سلوك الأيونات الأساسية وهي, الكاتيونات (صوديوم, كالسيوم, ماغنيسيوم) والأيونات (الكلوريد, الكبريتات, البيكربونات), حيث وجد أن نسبة احتجاز الماغنيسيوم > الكالسيوم >الصوديوم بالنسبة للكاتيونات ونسبة احتجاز الكبريتات > البيكربونات >الكلوريد بالنسبة للأيونات ويرجع ذلك الي تأثير دونان, حيث ان نصف القطر الايوني للأيونات ثنائية التكافؤ اكبر من احادية التكافؤ. أيضا وجد أن نسبة احتجاز الكاتيونات والأيونات الثنائية أعلي من الكاتيونات والأيونات الأحادية. علي الجانب الأخر وجد أن تركيب الأملاح الإفتراضية الموجودة بالعينة (كبريتات ماغنيسيوم, كلوريد ماغنيسيوم, كبريتات كالسيوم, بيكربونات كالسيوم و كلوريد صوديوم) لم يتغير أثناء وبعد عملية التحلية. وجد أن نسبة احتجاز الأملاح كالأتي:

R_s MgSO₄> R_s MgCl₂ > R_s CaSO₄ > R_s Ca (HCO₃)₂ >R_s NaCl

أوضحت النتائج أن كمية الأملاح الكلية الذائبة والتي بلغت ملوحتها 3333 جزء في المليون تقل تدريجيا مع زيا دة وقت التشغيل حتي وصلت إلي 933 جزء في المليون

بعد دورة واحدة (نسبة احتجاز 70 %) وكمية المياه المحلاة 10,28جم/سم ^{2}. ثانية ×
10^{-5} عند 30 بار. وبتقييم العينة بعد تحليتها طبقا للمواصفات العالمية القياسية لمياه
الشرب وجد أنها صالحة لهذا الغرض.