Applications of Synthesized Nanocomposite Membranes for Water Purification in Iraqi Brackish Water

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Abstract
The objective of this research is to study the properties of salt water in Wassit Province (Iraq), represented by water of general downstream river(TDS 4054 mg/L), that established to be channel tanker salt water to the Gulf and means to revive more than 6 million acres of farmland in order to increase the yield produced by this land. Trying purified, using nanoscale membranes containing MWCNTs and MCM-41 nanomaterial. Poly sulfone support layers were containing (0.0, and 0.4w. %) MWCNTs are used as ultrafiltration membranes and two types of synthesis membranes, TFC (thin film composite membrane) and 0.05TFN0.4 (nanocomposite membrane containing 0.4w. %MWCNTs in support layer and 0.05w. % MCM-41 in thin layer) were used in this study. All types of membranes were synthesized in laboratory of Building and Construction Engineering Department – University of Technology- Baghdad using chemical ACS reagents grade. The application of the synthesized nanocoposite membrane shows good capability of producing purified water from general downstream salt water (TDS 256 mg/L). As a result (0.05TFN0.4) membrane show it is more stable and less losses in pure water flux than (TFC) membrane. These properties explained due to antifouling properties of MWCNTs and its formation of macro voids in support layer in addition the pore structure of MCM-41 in the thin film. It was expected that collection of detailed information about the characteristic of downstream raw water with pilot study of the raw water pretreatment with perfect choice of TFN materials make possible to produce a good quality of water with economic price.

Keywords: application, nanocomposite, water, brackish, Iraq

1-1 Introduction

Water shortage is among the highest difficulties to be challenged by many societies and the World in the current time. Water consumption has been rising at more than double the rate of population growth in the last century. United Nations (UN) report indicated by 2025, 1800 million people will be living in states or counties with complete water shortage, and two-thirds of the world population could be under pressure conditions [1].

Water scarcity requests for supported global assistance in the fields of technologies for improved water yield. Recent years have seen remarkable innovations toward application of nanostructured materials like, carbon nanotubes (CNTs), metal/metal-oxide nanoparticles, zeolites, in the field of water purification. The objective of this research is to study the properties of salt water in Wassit province (Iraq), which currently do not use for the purposes of municipal drinking water (unsuitable, containing high concentrations of dissolved salts), represented by water of general downstream river(Al-Msab-Alam river). Trying purified using nanoscale membranes containing MWCNTs and MCM-41 nanomaterial, then evaluate the results occurring with Iraqi standard values for water purification, and the extent of benefit from this waters in the future using membranes nanotechnology.

2- Experimental Work

2-1 Materials

Poly sulfone support layers were containing (0.0, and 0.4w. %) MWCNTs. Two types of synthesis membranes, TFC (thin film composite membrane) and 0.05TFN0.4 (nanocomposite membrane containing 0.4w. %MWCNTs in support layer and 0.05w. % MCM-41 in thin layer. All types of membranes were synthesized in laboratory of building and construction engineering department – University of technology Baghdad. Using chemical ACS reagents grade which include polysulfone (PSU, Sigma-Aldrich) pellets, density 1.24 g/mL at 25 °C, average Mw ~35,000 purchased from sigma –Aldrich USA. Used as polymer and N, N- dimethyl form amide, Colorless liquid, Odor fishy, ammoniac, Molar mass 73.09 g/ mol (DMF, 99.8%, Aldrich) were used as solvent for the casting solution to make the support layer. Poly (vinyl pyrolidone) (PVP, 25kDa) used as additive was purchased from local market. Carbon nanotube, multi-walled(Sigma-Aldrich, Appearance form: solid, , multi-walled≥98% carbon basis, O.D. × I.D. × L 10 nm ± 1 nm × 4.5 nm ± 0.5 nm × 3-~6 μm). Cetyltrimethyl ammonium bromide (CTAB, 95%, Aldrich) was used as surfactant and tetraethyl orthosilicates (TEOS, 98%, Sigma-Aldrich) was used as silica source for the synthesis of MCM- 41, in addition to Sodium Hydroxide (NaOH, Molar mass 39.9971 g mol^{-1}). M-phenyl diamine (MPD, 99%, Aldrich) and trimesoylchloride (TMC, 98.5%, Aldrich) were monomers used in the IP process for synthesis of nanocomposite membranes. Method of membranes synthesis are not shown here.

3-0 Result and Discussion

3-1 General Downstream River

General downstream river is 528 km long which stretch of the north and west of Baghdad and hurt in the Khor Al-Zubair in the Gulf Arab.

3-2 Sampling Method

Raw Water samples were collected from the site on 15 October and 22 December 2014. Water samples from the site were collected in sample bottles supplied by the laboratory of Wassit water directorate, the samples on each date were placed into coolers, packed and placed on ice until the water in the bottles was completely chilled, and the samples were shipped to the laboratory in Kut. The samples were received by the laboratory the morning after sampling, the samples logged in, and sample processing and analyses initiated.

3-3 Analysis of Raw Water Results.

The results from the laboratory analyses of the raw water sampled are presented in the table 1, which summarizes the results of the laboratory analyses. It includes a list of parameters analyzed, the analytical methods used, reporting units and national drinking water standards.

Table 1. Summary of laboratory analytical results for raw water samples collected 15 October and 22 December 2014from the general downstream river.

Parameter Name	Analytical method(index)	Reporting unit	Iraqi standard	General down stream	
				15October 2014	22December 2014
Water Temperature	thermometer	Degrees C	-	30	23
Alkalinity, Total (as $CaCO_3$	2320 B	mg/L $CaCO_3$	125	105	108
Chloride	4500	mg/L	250	420	643
pH	4500 B	pH units	6.5-8.5	7.7	7.6
Specific Conductance	2540 E	µ s/cm	-	5128	5610
Sulfate	4500	mg/L	250	1265	1288
Total Dissolved Solids	2540 C	mg/l	500	3690	4054
T.S.S	2540 D	mg/L	50	825	1125
Turbidity	2130 D	NTU	5	12	32
Hardness (as $CaCO_3$	2340 C	mg/L	500	1350	1462
Ca^{+2}	3500	mg/L	100	310	345
Mg^{+2}	3500	mg/L	100	198	123
Na^{+1}	3500	mg/L	100	315	332

The high concentrations of total dissolve solids, hardness, chloride, sulfate, Ca^{+2}, $Mg^{+2,}$ Na^{+1} and total suspended solids are so clear in table 1. The traditional water treatment plant cannot treat this type of water. The comparison between the laboratory results of raw water tests of October and December 2014 shows an increase of most of parameters. The concentration of total dissolved solids and total hardness as well as salts have been increased in raw water in December due to rainfall water which enter into the river after washing the saline soil in the region process.

3-4 Pretreatment of Raw Water

The primary goal of pretreatment is to make the feed water compatible with membrane. Pretreatment is required to increase the efficiency and life expectancy of the membrane elements by reducing fouling, scaling and degradation of the membrane [2]. The raw water samples of downstream river were pretreated by coagulation, flocculation, and sedimentation using alum sulfate (Al_2 $(SO_4)_3.14H_2O$) as coagulant to remove the suspended solid and color. Then the water filtered by using two types of membranes (polysulfone ultrafiltration membrane and polysulfone ultrafiltration membrane containing 0.4w%MWCNTs). The filtrations were conducted at room temperature (23 C^0 ±1 C^0) using high pressure cross flow system with pressure 4 bars and flow 40 L/h. The water flux and recycling properties of polysulfone support layer with and without MWCNTs which are used as ultrafiltration membranes are shown in table 2.

Table 2. Water flux and recycling properties of polysulfone membrane with and without MWCNTs.

Time (min)	Flux L/m^2*h (PSU)	Flux L/m^2*h (PSU+ 0.4MWCNTs)
30	290	450
60	265	430
90	255	405
120	210	369
Washing for 15min. with distilled water		
150	240	390
180	225	375
210	205	355
240	195	335

The following data were obtained from the table 2:

1-The pure water flux for PSU support layer at first 30 min of filtration of settled water of downstream river (290 L/m^2.h), this represents (91.1%) of its flux using DI water. Data are not shown here.

2-The pure water flux for PSU support layer containing 0.4w% MWCNTs (using settled downstream river water) after 30 minute (450 L/m^2.h), this represents (92.4%) of its flux using DI water. Data are not shown here.

3-The addition of modified MWCNTs to PSU increases the pure water flux about (450/290) 55%.

4-The pure water flux for PSU support layer after 120 min. of filtration of settled water of downstream river (210 L/m^2.h), this mean losses of flux about (27.5%) due to clogging of PSU membrane (organic fouling)

5-The pure water flux for PSU support layer containing 0.4w%MWCNTs after 120 min. of filtration of settled water of downstream river (369L/m^2.h), this mean losses of flux about (18%) due to clogging of PSU membrane (organic fouling).

6- After 120 min. The PSU membrane with and without MWCNTs was washed by distilled water for 15 min. and reused it in filtration.

7-The recovery flux of PSU membrane after 30 min. filtration (240L/m^2.h), this means that the membrane recovered about (82.7%) of its original flux before clogging.

8-The recovery flux of PSU membrane containing 0.4w% MWCNTs after 30 min. filtration (390L/m^2.h), this means that the membrane recovered about (86.7%) of its original flux before clogging.

9-After 4 hr. of filtration the flux of PSU membrane was (195 L/m^{2}h), this represents (67.2%) of original flux. While the flux of PSU+ 0.4wMWCNTs (335L/m^{2}h), this represents (74.4%).

The values of water flux showed in table above represent the average values of three coupons of each type of membrane.

From the above data it was clear that the addition of MWCNTs to polysulfone support layer increased the pure water flux of membrane in addition increasing the recovery properties, this is because of macro void which produced in polysulfone structure during the phase inversion process and antifouling properties of MWCNTs.

The pretreatment systems can be chemical, mechanical or combination. Table 3. Show the guidelines for acceptable RO/NF feed water. Inadequate pretreatment often required frequent cleaning to restore product flux and salt rejection. This will result in excessive chemical cleaning cost, increases system downtime, and in severe cases will result in permanent loss of performance, membrane degradation and therefore shorter membrane life.

Table 3. Guidelines for acceptable RO/NF feed water.

parameter	Recommended maxim value
Turbidity	0.5 NTU
TOC	2mg/l
Iron[1]	0.1 mg/l
Manganese	0.05 mg/l
Oil & grease	0.1 mg/l
SDI 15	3

1-If absolutely no chance of air entry / oxidation and pH ≤7, values as high as 1-2mg/L. may be acceptable.

3-5 Evaluation of the pretreated water adequacy for final membrane filtration.

The pretreated water samples of downstream river were tested to qualify its adequacy to be filtered by synthesized nanocomposite membrane. **SDI_{15}** test is used to examine the pretreated water. The silt density index

(SDI) is one of the most standard methods used to measure the fouling potential. It is used as a predictive tool for assessing the adequacy of pretreatment water. Compared to others parameters like turbidity or suspended solids, it is more sensitive.

SDI analytical protocol is standardized in the ASTM D 4189-95, re- approved 2002, and it evaluates the amount of 0.45µm filter plugging caused by passing a sample of water through the filter for 15 minutes.

The test is carried out at pressure 2.05 bars through a membrane with a cut-off threshold of 0.45µm. The measurement is made over a period of 15 minute (SDI_{15}) on the pretreated water [2].

When the water has very high fouling properties, it may be made over a period of 10, 5, 3 minutes. SDI is calculated according to the following formula:-

$$SDI = \frac{100}{Td} * \left[1 - \frac{Ti}{Tf}\right] \quad (1)$$

Where

Td is the overall filtration time (3, 5, 10, 15) minute.

Ti is the initial time (in second) to filter 500ml of water on a 0.45µm membrane at 2.05 bars.

Tf is the final time (in second) to filter 500ml after 15 minute.

The SDI must be as low as possible to limit the fouling of the filtration membranes. The results of SDI_{15} tests of downstream pretreated water were tabulated in table 4.

Table 4. SDI_{15} of pretreated water of downstream river.

Type of pretreatment	Temperature	pH	SDI_{15}
Coagulation, flocculation, and sedimentation.	25	7.5	5.2
Coagulation, flocculation, sedimentation and filtration on polysulfone ultrafiltration membrane	24	7.8	2.9

From the Table 4, the SDI_{15} of downstream water samples pretreated by coagulation, flocculation and sedimentation was 5.2. This type of pretreatment was not removed all suspended solid in raw water, especially colloidal materials and the pretreated water is required further pretreatment to be suitable for filtration on nanocomposite membrane. After filtration of pretreated water samples on the polysulfone ultra membrane, the SDI_{15} of pretreated water became 2.9, which is slightly less than the standard limitation of acceptable water for RO/NF. It was expected to obtain SDI_{15} of pretreated water less than 2.9, by choosing the proper coagulant and controlling the coagulant dosage with filtration on polysulfone ultra filtration.

3-6 Final treatment of downstream water and nanocomposite membrane evaluation.

The raw water samples of downstream river after flocculation, coagulation, sedimentation and filtration on polysulfone support layer containing MWCNTs was filtered on two types of syntheses membranes (TFC and 0.05TFN0.4). The tests were conducted at room temperature and at pressure 20 bars using high pressure cross flow filtration system with flow (160L/h). The results of tests are presented in figure (3-1)

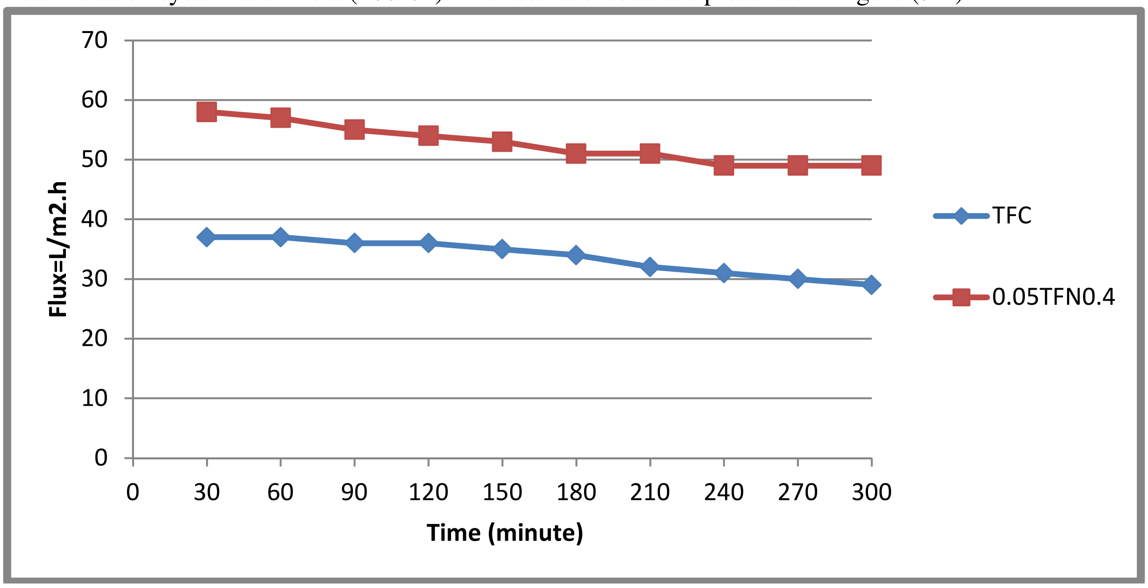

Figure 1. Pure water flux of (pretreated downstream water river), pressure 20 bars, flow 160L/h, temperature 25 ^{0}C.

The following results are obtained from the figure 1.

1-The average pure water flux of (TFC) membrane was (33.7 L/m^2.h), after 5h of filtration of pretreated downstream water. While the pure water flux of (0.05TFN0.4) was (52.2 L/m^2.h), this means the flux of (0.05TFN0.4) is more than (TFC) about (54.85%).

2- The pure water flux of (TFC) was decreased from (37L/m^2.h) to (29 L/m^2.h) after 5 h of filtration, which means a losses of flux about (21.6%).while the flux of (0.05TFN0.4) was decreased from (58L/m^2.h) to (49L/m^2.h), which means a losses of flux about (15.5%).

3- As a result (0.05TFN0.4) membrane is more stable and less losses in pure water flux than (TFC) membrane. These properties can explained due to antifouling properties of MWCNTs in support layer and its formation of macro voids in addition the pore structure of MCM-41 in the thin film.

The total dissolved solids removed during filtration of downstream pretreated water were presented in figure 2. The two types of syntheses membrane (TFC and 0.05TFN0.4) exhibits as follow in salt removal.

At start of filtration and after 30 minute, the TFC membrane removed (97%) of total dissolved solids, while the (0.05TFN0.4) membrane removed (96%). After 3.5 hours of filtration the total dissolved solids removal was sustained at (92%) for (0.05NTF0.4) membrane, while the TFC membrane performance became less than (92%). As average both types have similar salt rejection about (93.7%).

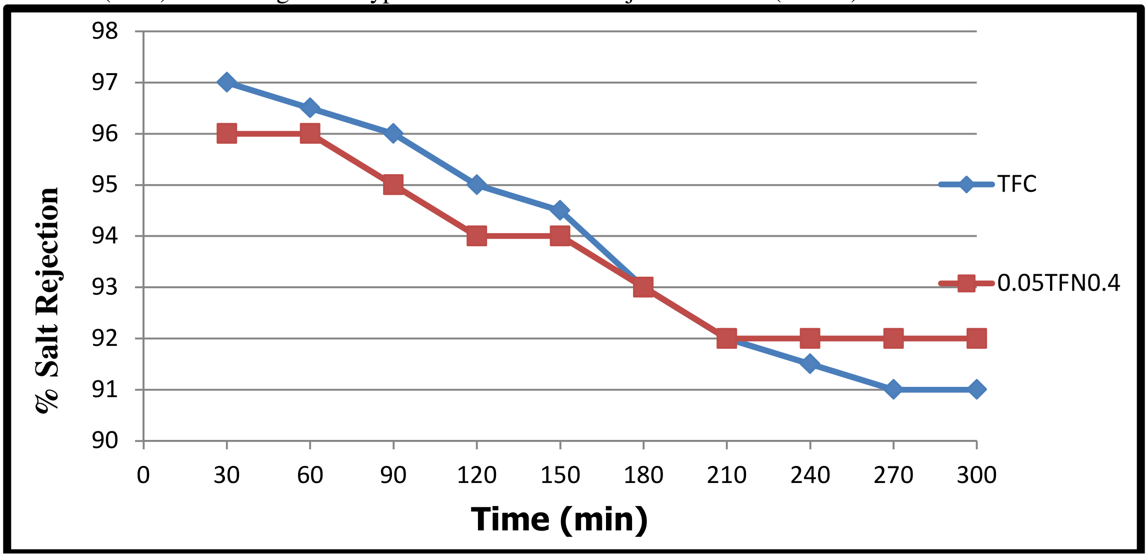

Figure 2. % Salt rejection performance of downstream water, pressure 20 bars, flow 160L/h, and temperature 25 ^{0}C.

After finishing the pure water flux and total dissolve solids removed tests. Two samples of final filtered water were tested for all parameters to explain its satisfaction to drinking water quality. The analytical results of raw water, final filtered water and percentage of removal of samples of downstream rivers are tabulated in table 5.

Table 5. Summary of laboratory analytical results for raw and filtered water samples from general downstream river.

Parameter Name	Reporting unit	Iraqi standard	Raw water	Filtered water	% removal
Water Temperature	Degrees C	--	23	19.6	---
Alkalinity, Total (as $CaCO_3$	mg/l $CaCO_3$	125	108	76	29.6
Chloride	mg/l	250	643	60.9	90.5
pH	pH units	6.5-8.5	7.6	7.2	--
Specific Conductance	µ s/cm	------	5610	450	91.97
Sulfate	mg/l	250	1288	82.7	93.5
T.D.S	mg/l	500	4054	256	93.7
Turbidity	NTU	5	32	0.3	99
T.S.S	mg/l	50	1125	5	99.5
Hardness (as $CaCO_3$	mg/l	500	1462	124.9	91.4
Ca^{+2}	mg/l	100	345	28.7	91.7
Mg^{+2}	mg/l	100	123	10.6	91.4
Na^{+1}	mg/l	100	332	29.2	91.2

From the table 5 it was shown that all final treated water parameters are within Iraqi standard quality. The percentage removal of total dissolved solid (93.7 %) and the percentage removal of other parameters are ranged between (90.5% for chloride) to (93.5% for sulfate). To obtain a better quality of water, the characteristics of downstream river must be study during a long period, the parameters such as total dissolved solids, total suspended solids, total organic carbon, pH and temperature must be recorded as highest, minimum and average values to choice the perfect pretreated requirement for raw water. Also the factors that affected the composition and quality variability by seasonal factors, climate conditions and/or activates on the surface water must study sufficiently. It was expected that collection of detailed information about the characteristic of downstream raw water with pilot study of the raw water pretreatment with choice of perfect NF materials make possible to produce a good quality of water with economic price.

3-7 Evaluation of syntheses nanocomposite membrane exposure to chlorine.

Syntheses nanocomposte membrane exposure to chlorine was evaluated by comparing the permeate flux and NaCl rejection of membranes before and after exposure to aqueous chlorine solution in a manner similar to that of other literatures [3, 4].

16 ml of aqueous sodium hypo chlorite solution (10- 15% available chlorine, local market) was added to a volumetric flask and diluted to obtain 1 liter of 2000ppm aqueous sodium hypochlorite solution with DI water. The solution pH was then adjusted to 11 using NaOH.

Membrane samples were immersed for 8 hour in aqueous sodium hypo chlorite solution of approximately 2000ppm. The membrane samples total chlorine exposure was 16000ppm-h. Following chlorine exposure, membrane samples were rinsed with DI water for 3 minutes before characterization. Table 6 shows the comparison of permeate flux and salt rejection of membranes before and after exposure to chlorine.

Table 6. Effect of chlorine exposure on synthesized nanocoposite membrane in real field conditions.

Membrane	Before chlorine exposure		After chlorine exposure	
	Flux ($L/m^2.h$)	Salt Rejection (%)	Flux ($L/m^2.h$)	Salt Rejection (%)
TFC	33.7	93.7	39.2	91
0.05TFN0.4	52.2	93.7	65.8	91.5

The selectivity of both types of membrane was decreased when exposure to chlorine. This represented by decreasing the salt rejection of TFC membrane from 93.7% to 91% and 0.05TFN0.4 membrane from 93.7% to 91.5%. From table 5, it was so clear increases of pure water flux of both types of membrane due to reduction of selectivity, which mean affecting both types of membrane to chlorine exposure.

3-8 Conclusions

The application of the synthesized nanocoposite membrane shows good capability of producing purified water from general downstream salt water. As a result (0.05TFN0.4) membrane is more stable and less losses in pure water flux than (TFC) membrane. These properties explained due to antifouling properties of MWCNTs and its formation of macro voids in support layer in addition the pore structure of MCM-41 in the thin film

It was expected that collection of detailed information about the characteristic of downstream raw water with pilot study of the raw water pretreatment with choice of perfect NF materials make possible to produce a good quality of water with economic price.

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