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Rejuvenation of discarded RO membrane for new applications

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ABSTRACT

The sensitivity of thin film composite RO membrane (TFCs) with chlorine has been widely reported. In the present paper, attempt has been made to modify the chemical structure of thin film composite RO membrane by exposing the membrane to free chlorine in order to evaluate potential of utilizing the discarded membrane after its useful life. The different variants of thin film composite RO membrane in terms of flux and rejection could be prepared by altering the exposure time and concentration of sodium hypochlorite solution. Tailoring the membrane for solute rejection offers advantages over the conventional process for instance: (1) It avoids re-mineralization and directly produces the water of required quality; (2) It enhances flux of membrane and thereby improves the productivity of the membrane; (3) Improved recovery leads to lower capacity pre-treatment and thereby improves the operational efficiency; (4) Number of membrane required for the given capacity will be less and the associated unit cost, e.g. pumping cost will also decrease. Successful attempt has been made to enhance permeability seven times that of the terminally fouled membrane by sequential hypochlorite treatment in controlled fashion, i.e. fouled seawater RO membrane with flow 3.36 l/min and solute rejection of 97.21% has been converted to the membrane with flow 24 l/min and solute rejection 82.37%.Moreover, the thin film composite RO membrane has been degraded totally till its solute rejection efficiency falls to approximately zero in order to convert it to microfiltration/ultra-filtration membrane, i.e. the membrane with pure water permeability 257 gfd @50 psig pressure has been made by exposing 3286 mg/l free chlorine for 96 h to TFC RO membrane. The characterization of this membrane was performed by measuring molecular weight cut off of the membrane and pure water permeability of the membrane to evaluate its performance as an ultra-filtration membrane. These membranes were also tested for micro-organism removal and found that their performance resembles the new ultra-filtration membrane. The hypochlorite treated membranes were also evaluated for their permeability after bio-film formation with different micro-organisms where it manifested higher permeability as compared to untreated membrane.

Keywords: TFC RO membrane; Chlorine; Solute rejection; Flux; Ultrafiltration membrane; Biofilm

1. Introduction

Thin-film-composite membranes (TFCs) made from polysulfone–polyamide composite are widely commercialized for use in reverse osmosis (RO) separations due to their excellent perm-selective characteristics [1]. These TFCs can be fabricated with barrier layers that are sufficiently thin, of the order of 100–300 nm to allow high water flux at relatively low net trans-membrane pressures [2] as compared to the

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old generation cellulose acetate membrane. A much thicker porous supporting layer made of polysulfone membrane is used to provide the required mechanical support and stability.

The fine barrier layer of polyamide is formed by interfacial polymerization after absorbing a water/diamine solution onto the porous substrate followed by reaction with organic/acyl chloride. This provides a physical "anchoring" of the barrier layer to the support [3]. The TFC RO membrane has a major concern with its limitation in terms of susceptibility to oxidizing agents, such as aqueous chlorine, used in membrane cleaning and water disinfection [4].

In practice, two types of membranes are available in market, i.e. seawater and brackish water reverse osmosis membranes. Seawater reverse osmosis membranes are tuned for higher selectivity and relatively lower permeability as compared to brackish water RO membrane to make them fit for removal of total dissolved solids with greater efficiency. Brackish water reverse osmosis membrane on the hand requires higher permeability with lower selectivity.

The membranes available in market have typically more than 98% selectivity under standard test conditions, which is more than required for low salinity brackish water. Re-mineralization of product water is also practiced in case the water becomes more demineralized for drinking application.

Chlorine concentration exposure level can be measured in terms of PPM-Hr, which is multiplication of free chlorine concentration in ppm and exposure time in hour. After 500–2000 ppm h of exposure, the membrane salt rejection decreases and the water flux increases [4–7].

It has been reported that N–H group is converted to N–Cl group by N- halogenations in polyamide RO membrane. The resulting product undergoes intermolecular rearrangement to form various aromatic substitution products. Moreover, it induces a chain reaction to produce chloro-substituted benzene ring as the quinine derivatives or oxidation group [4,8]. This causes polyamide RO membrane resulting in decreased salt rejection and increased water flux [6,9,10].

The extensive research on possible chemical structure modification in polyamide by chlorine has provided insights into the mechanisms that cause polyamide barrier layer degradation [11–14], including chlorination of the amide N–H bond and the aromatic rings of the polymer backbone under ambient conditions.

It has also been reported that the commercial membranes may observe loss of the barrier layer at high chlorine exposures due to change in the mechanical properties of the barrier layer expressed primarily as a decrease in ductility. The loss of ductility may affect the physical anchoring of the polyamide layer to the polysulfone support. This response, in conjunction with the mechanical stresses and strains due to membrane operating conditions, may induce initially fractures and eventual losses in the barrier layer allowing increased salt passage and flux [15]. It is reported that the membrane performance declines because of free chlorine exposure of 1–5 mg/l for the period of 1–10 days [16].

The high reactivity of chlorine with polyamide can also be capitalized positively by tailoring the membrane for desired solute rejection and flux. The objective of the present paper is to make different grades of membrane by such modifications. The rejuvenation of discarded seawater RO membrane to form brackish water RO membrane has not been reported. There are niche applications of such membranes. And a systematic conversion of discarded SWRO to useful BWRO membrane may be of great value. An attempt has been made here to address this research gap.

2. Experimental

2.1. TFC RO membrane process

Interfacial polymerization is an instantaneous reaction which leads to coating of ultra-thin barrier layer over polysulfone membrane support [17]. Thin film composite membrane (TFC) is made by interfacial polymerization of metaphenylene diamine (MPD) and trimesoyl chloride (TMC) on polysulfone base membrane. The polysulfone base membrane and polyamide barrier layer were made in a pilot plant at CSIR – Central Salt & Marine Chemicals Research Institute.

Polysulfone membrane is passed in MPD bath where 2% MPD solution is poured over the PS membrane and then membrane subsequently passes through 0.1% TMC solution bath where the membrane is dipped in solution for 30 s. Interfacial polymerization form thin polyamide layer over polysulfone support layer, which subsequently stabilizes in curing zone where the membrane is passed through a hot chamber with temperature 70 °C for 1 min residence time. Curing zone facilitates the residual reaction to be completed and volatiles to be removed from the membrane surface. Post-treatment of TFC RO membrane includes hot water wash, citric acid wash, hot water wash again followed by passing the membrane through 1% sodium meta bisulfite, 10% glycerol aqueous solution to retain membrane morphology.

2.2. Sodium hypochlorite treatment

Thin film composite RO membrane was exposed to sodium hypochlorite solution at different concentration and pH to study modification in chemical structure of polyamide and as a result change in performance of the membrane.

The average temperature during experiment was 25 °C. It has been observed that the reaction with chlorine is dependent on concentration, time of exposure and pH. Moreover, free chlorine exposure at higher pH leads to improved flux and diminished solute rejection; hence the experiments were carried out at pH 12.0 in order to study the concentration and time dependence. The chlorine exposure level was measured in terms of ppm–h. The effect of chlorine exposure on membrane performance i.e. solute rejection and flux were evaluated.

The membrane flux and solute rejection were determined on the standard membrane testing kit by dead-end filtration method at 200 psi pressure and 25 °C temperature. The membrane samples were cut in 4.9 cm diameter circular shape and placed in the testing kit. The testing was done in standard testing kit and mode of filtration was dead-end filtration. The saline water solution was made with a concentration of 1500 mg/l NaCl. The pressure was kept at 200 psi for 20 min for bringing the membrane in its normal functioning and then pressure was kept at 200 psi and stabilized. Permeate was collected for 20 min. Conductivities of feed as well as permeates were measured. Four such samples were tested in a kit and the average of them was taken into consideration. The membrane flux was measured in terms of gallons per sq. ft. per day (gfd). The term solute rejection refers to salt (NaCl) rejection in this study.

The membranes with prolonged exposure of chlorine were tested for pure water permeability test @ 50 psi pressure to check its performance as an ultra-filtration membrane.

Sodium hypochlorite (4% active chlorine) is an efficient chlorinating agent used in the present study. In the present work, the hypochlorite solution has been subjected to TFC membrane to modify the performance.

The known quantity of sodium hypochlorite (LR grade) with 4% active chlorine was dissolved in pH buffer to make 4 l solution having known concentration of active chlorine in the solution.

pH buffer solution was prepared by taking 2 l 0.125 M NaOH and mixing it with 2 l of 0.1 M $NaHCO_3$ to make the solution of pH 12.0. pH was kept constant in all experiments. pH was measured by Hanna pH meter at the onset of exposure and at the end of exposure.

2.3. Evaluation of concentration

One gram of starch soluble (AR grade) was dissolved in distilled water to make 100 ml total solution and heated to 60 °C for 30 min and allowed to cool to ambient temperature to prepare the starch solution. Potassium iodide (15 g) (AR grade) was dissolved in distilled water to make 100 ml total solution of KI. Sodium thiosulfate ampule was diluted in distilled water to get 0.05 N sodium thiosulfate solution.

Concentration of free chlorine was determined by iodometric titration. 10 milliliter of prepared sample was taken in conical flask; 1 ml glacial acetic acid was added; 12 ml 15% potassium iodide solution was added and the sample was titrated against 0.05 N sodium thiosulfate solution. When the colour of sample turns light yellow, 1 ml of 1% starch solution was added and the colour change to violet was observed. Continuing titration, the end point was noted when the solution turned colourless.

The thin film composite membrane was cut in the size 10 cm width, 15 cm length and stuck on the glass plate. The membrane was washed with distilled water and dipped in the solution containing chlorine for the specified time i.e. 4, 8, 16, 24, 48,72, 96 and 144 h, so that reaction can be accomplished. The membrane was washed with distilled water soon after the treatment.

2.4. Molecular weight cut off determination

A typical membrane with prolonged chlorine exposure was tested for molecular weight cut off to test its ultra-filtration performance. The treated membrane were cut in circular shape of 74.72 mm diameter and placed in the test rig to subject it to aqueous polymer solution of definite molecular weight. The polymer samples of polyethylene glycol of molecular weight 15,000, 35,000 and 100,000 Dalton, respectively were dissolved in deionized water to make the solution concentration 500 mg/l each. These aqueous polymer solutions were passed through membrane for 45 min for flushing and subsequently the samples were collected and fluxes were taken. The system was under static pressure of 25 psig by compressed air.

The collected samples were tested for molecular weight determination by gel permeation chromatography. Gel permeation chromatography column was Ultrahydra gel 500 followed by Ultrahydra gel 120. Fifty microliters of solution was injected in the column. Depending on the molecular weight of polymer in the sample, the area under the curve for the specific peak varies. Hence, the area of feed sample subtracted by area of product sample divided by area of feed sample in % form gives % separation of the specific polymer from aqueous solution by membrane. Molecular weight cut off represents ≥90% separation of polymer from solution. In this way, molecular weight cut off of chlorine exposed membrane was derived.

2.5. Contact angle determination and scanning electron micrographs

TFC RO membrane made by the above-mentioned process was taken to determine contact angle and to take scanning electron micrographs. The TFC RO membrane was treated with 1000 mg/l free chlorine solution made in buffer of pH 12.0 for 1 h. The contact angles were measured at five different locations in the membrane sample of size 3 cm × 8 cm by Drop Shape Analyzer KRUSS/DSA100. The average contact angle for left and average contact angle for right has been worked out and reported.

The scanning electron micrographs were taken for TFC RO membrane and 1000 mg/l free chlorine treated membrane. SEM images were taken for membrane top surface. For top surface, the membrane was sticked over the stud and images are taken with the instrument from LEO electron microscopy limited-LEO 1430 VP.

2.6. Micro-organism removal by membrane

The membranes degraded by chlorine have been evaluated for bacterial separation. Ten litres of distilled water was taken and inoculated with *E. coli*. The membrane testing cell was made sterile by repeated passing of sterile distilled water and then the membrane coupons were taken for the study to compare the bacterial separation performance with MF/UF membrane.

Membranes with 2184 mg/l of chlorine exposure for 16 h, 2957 mg/l of chlorine exposure for 24 h and 2740 mg/l of chlorine exposure for 48 h have been tested for the microorganism separation performance and compared with fresh MF/UF membrane.

2.7. Biofilm formation over treated membrane

The treated TFC RO membranes have also been evaluated for bio-film formation. The membranes were subjected to the media as indicated in Table 1. The TFC RO membrane has been subjected to sodium hypochlorite solution with active chlorine concentration 1717 mg/l at pH 12.0 for 1, 2, 3 and 4 h, respectively, and thus treated membranes were dipped in culture media containing following bacteria for a period of 3 days. The membranes were taken out washed with distilled water and tested for solute rejection and flux with the procedure as mentioned above.

Table 1
Different micro-organisms subjected to TFC RO membrane

Sr. no.	Bacteria	Media	O.D.	pH
1	*Pseudomonas* sp.	King's B media	6.748	7.2
2	*Bacillus* sp.	Nutrient broth	3.983	7.4
3	*E. coli*	Luria Bertani broth	4.889	7.2

2.8. Fouled seawater RO membrane rejuvenation

Seawater reverse osmosis membrane (Hydranautics SWC4+) discarded after 4 years of continuous use in seawater reverse osmosis plant has been taken for study. Membrane module was torn off and unwound to take out the flat sheet membrane for hypochlorite treatment. Solution of 2000 mg/l active chlorine concentration was prepared by dissolving sodium hypochlorite in pH buffer. pH buffer of pH 12.0 was made by dissolving 96.18 g potassium chloride and 12.33 g sodium hydroxide in 8 l of distilled water.

Discarded seawater reverse osmosis membrane module (SWC4+) has been given successive sodium hypochlorite treatment. The sodium hypochlorite solution was prepared at pH 12 and passed through membrane module for the time as indicated in Table 5. And the performance of membrane module before and after treatment was monitored for feed water with 2000 mg/l NaCl solution passed at 225 psig pressure and 35 ^{o}C temperature. The temperature was kept higher for ease of operation especially because of the prevalent temperature in India in summer.

The ATR-FTIR study was done to evaluate modification in chemical structure by chlorination.

3. Results and discussion

The objective of this study was to enhance the performance of discarded RO membrane by controlled chlorine treatment. New TFC RO membrane has also been degraded to study the performance change with chlorine treatment and correlate the same for discarded RO membrane to check conformity (Table 2).

Chlorine exposure to membrane was done in buffer solution with pH 12; change in pH was negligible even after completion of experiment. Results showed that with increase in time of exposure of membrane to chlorine, RO-TFC membrane was deteriorated, with increase in its flux and decrease in its salt rejection rate. These results indicate improvement in permeability with decline in selectivity by chlorine treatment.

Fig. 1a and 1b indicate the effect of chlorine exposure level on flux and solute rejection of TFC RO membrane. It is observed that there is nearly linear rise in flux with chlorine exposure level whereas the fall in solute rejection is logarithmic. The maximum possibility of change in solute rejection is limited by –100%, hence the plot for % change in solute rejection versus free chlorine exposure

Table 2
Free chlorine exposure to TFC RO membrane for systematic degradation

Sr. no.	Time of exposure (h)	Concn. of free chlorine (mg/l)	Exposure level (ppm h)	Initial flux (gfd)	Final flux (gfd)	Initial solute rejection (%)	Final solute rejection (%)
1	4	1750	7000	18.33	42.50	91.97	85.43
2	8	1750	14,000	18.33	69.60	91.97	38.20
4	16	2184	34,944	13.16	71.50	88.76	65.04
5	16	1639	26,233	13.82	62.37	90.28	50.10
6	16	1550	24,808	12.25	92.25	91.08	29.63
7	24	2957	70,968	18.87	106	90.75	6.50
8	48	2740	131,520	18.87	177	90.75	2.20
9	24	1000	24,000	18.82	35.63	91.18	61.77
10	48	1000	48,000	18.82	100.44	91.18	5.15

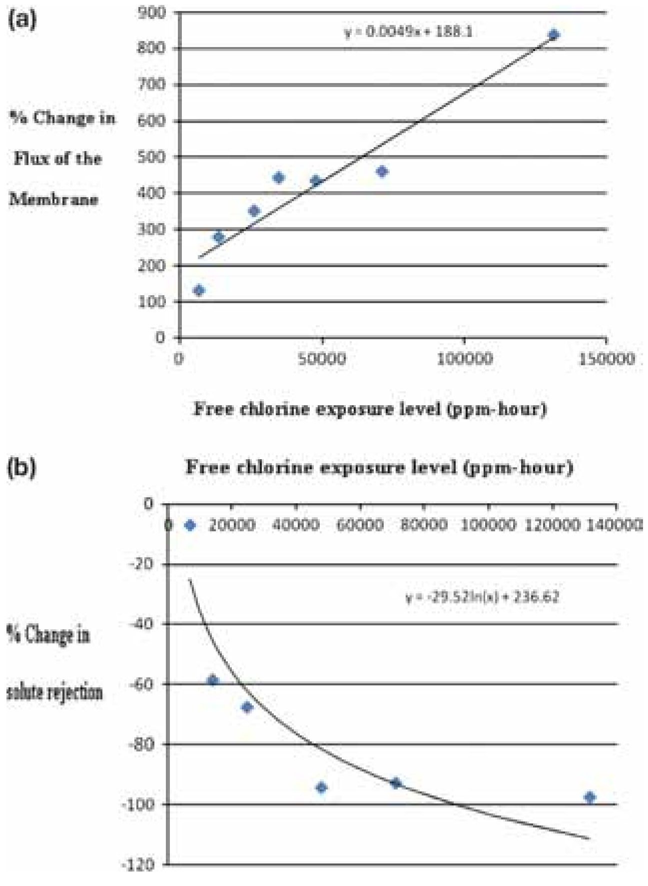

Fig. 1. (a) % change in flux vs. free chlorine exposure level (ppm h). (b) % change in solute rejection vs. free chlorine exposure level (ppm h).

level is logarithmic. This indicates there is a possibility to tune the characteristics of TFC RO membrane by free chlorine exposure in the controlled environment.

Following membranes are with prolonged exposures (see Table 3 and Fig. 2).

It is explicit from the above results that TFC RO membrane can be converted to ultrafiltration membrane with prolonged exposure to free chlorine. The above chart indicates linear relationship between pure water permeability @ 50 psi pressure versus chlorine exposure level in ppm h. Polyamide layer of TFC RO membrane gets deteriorated by such a long exposure and the membrane is converted to ultra-filtration membrane.

Molecular weight cut off of membrane as mentioned in Sr. No. 2 is 97.18 kD. Molecular weight cut off degraded chlorine treated membrane closely resembles MF/UF membrane and performance of degraded membrane also at par with fresh MF/UF membrane. This study indicates that there is a scope of reversibly converting RO into MF/UF as far as performance is concerned.

The chlorine treated membranes were evaluated for micro-organism removal from drinking water. The separation performance is as shown in Table 4:

The above results indicate that the membranes degraded by chlorine exhibit good bacterial separation performance and the performance are comparable with that of fresh MF/UF membrane e.g. Zee Weed 1000 ultrafiltration membrane claims log 4 removal of bacteria, Hydranautics HydraCap MF membrane.

The above results indicate controlled hypochlorite treatment can enhance the membrane productivity by up to three times increase in flux with fall in solute rejection by about 4% as indicated in Sr. No. 3 of Table 5. Hypochlorite exposure for longer time will continue to increase flux; however there will be substantial fall in solute rejection as explicit from the results in Table 5. These results indicate that there is potential of utilizing the discarded seawater RO membrane for alternate

Table 3
Prolonged exposure of free chlorine to TFC RO membrane

Sr. no.	Exposure time (h)	Concentration (mg/l)	Exposure level (ppm h)	Initial flux (gfd)	Initial solute rejection (%)	Pure water permeability (gfd)
1	24	3000	72,000	18.87	90.75	85
2	48	3000	144,000	18.87	90.75	153
3	72	3300	237,600	14.3	90.87	185
4	72	1000	72,000	18.82	91.18	103
5	96	3286	315,456	14.63	91.94	257
6	144	1000	144,000	18.82	91.18	145

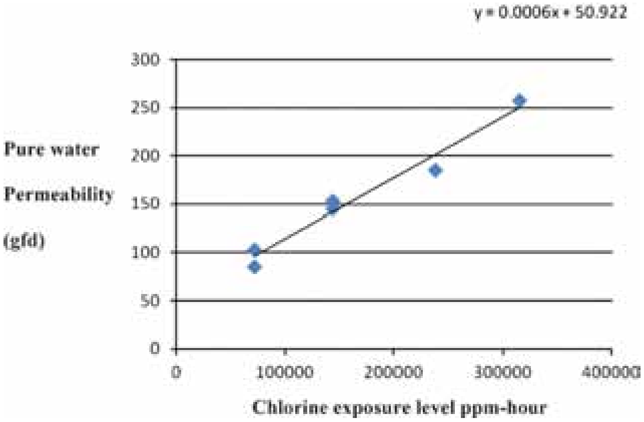

Fig. 2. Pure water permeability of converted MF/UF membrane vs. chlorine exposure level.

applications such as brackish water RO and there by create a substantial value addition.

The above results indicate that although the flux and rejection follow the similar pattern with chlorine for new and discarded TFC RO membrane, the rise in flux and fall in rejection are more pronounced in case of discarded RO membrane e.g. Sr. No. 1 of Table 2 indicates that with 7000 ppm hr of exposure the new membrane flux was improved 2.3 times and solute rejection decreased 7.11% whereas Sr. No. 8 of Table 5 indicates that with the same exposure level of chlorine to discarded membrane resulted in 3.4 times rise in flux and 32.24% fall in solute rejection. This indicates increased reactivity of chlorine with fouled membrane.

Table 6 indicates that rejuvenation of discarded seawater reverse osmosis membrane module can be done by systematic and controlled hypochlorite treatment. The membrane module with initial solute rejection efficiency 97.21% and product water flow 3.36 l/min has been converted to the membrane module with solute rejection efficiency 84.67% and product water flow 24 l/min. The objective of the study was to achieve the product flow close to the commercial brackish water RO membrane module. In this way, the permeability of the discarded membrane module was increased seven times by successive treatment. This type of membrane module can find applications in low pressure RO where feed water salinity is lower. It is also explicit from Table 6 that solute rejection efficiency falls merely 1% while product water flow becomes five times initial flow as shown in Sr. no.10 of Table 6. This opens up a possibility of making a step change in membrane performance with essentially the same selectivity.

Table 4
Performance of hypochlorite treated membrane for micro-organism removal

Sr. no.	Exposure time (h)	Concentration (mg/l)	Treated membrane exposure level (ppm h)	% Removal of *E. coli* by treated membrane
1	24	2000	48,000	99.9997
2	24	2500	60,000	99.9994
3	24	3000	72,000	99.9981
4	Fresh UF membrane			99.9974

Table 5
Performance enhancement of discarded SWRO membrane by hypochlorite treatment

Sr. No.	Time of exposure (h)	Conc. of free chlorine (mg/l)	Exposure level (ppm h)	Flux (gfd)	Solute rejection (%)
1.	Nil	Nil	Nil	9.88	92.63
2.	0.5	2000	1000	21.05	89.18
3.	1.0	2000	2000	30.25	88.96
4.	1.5	2000	3000	29.13	83.98
5.	2.0	2000	4000	26.93	75.41
6.	2.5	2000	5000	26.25	78.49
7.	3.0	2000	6000	27.83	80.11
8.	3.5	2000	7000	33.63	62.76
9.	4.0	2000	8000	33.58	63.27
10.	4.5	2000	9000	41.75	63.72

Table 6
Rejuvenation of discarded seawater reverse osmosis membrane module

Sr. no.	Initial olute rejection %	Initial flow (LPM)	Final solute rejection(%)	Final flow (LPM)	Free chlorine concentration (mg/l)	Time (min)	Treatment level (ppm h)
1	97.21	3.36	–	–	–	–	–
2	97.21	3.36	97.21	4.62	1115	30	557.50
3	97.21	4.62	97.64	4.80	566	30	283
4	97.64	4.80	98.24	6	300	30	150
5	98.24	6	98.53	7.20	264	30	132
6	98.53	7.20	98.39	7.44	182	30	91
7	96.19	7.44	97.50	12.84	1167	60	1167
8	97.50	12.84	96.24	14.28	969	60	969
9	96.24	14.28	94.56	16.32	1544	30	772
10	94.56	16.32	96.15	16.80	1018	30	509
11	96.15	16.80	94.01	18	2036	30	1018
12	94.01	18	92.36	19.10	2830	30	1415
13	92.36	19.10	84.67	21.73	2830	30	1415
14	84.67	21.73	82.37	24	946	30	473

ATR-FTIR spectra of chlorine exposed membranes are as shown in Fig. 3.

Kang and co-workers have proposed re-arrangement in the structure by converting CO–NH bond into CO–NCl bond and subsequent orton rearrangement to shift chlorine to benzene ring, which gives rise to degraded product [18]. The authors feel that there must be scission of the polymer structure into depolymerization which leads to loosened structure increasing the pore size and ultimately total break out of the polymer structure,

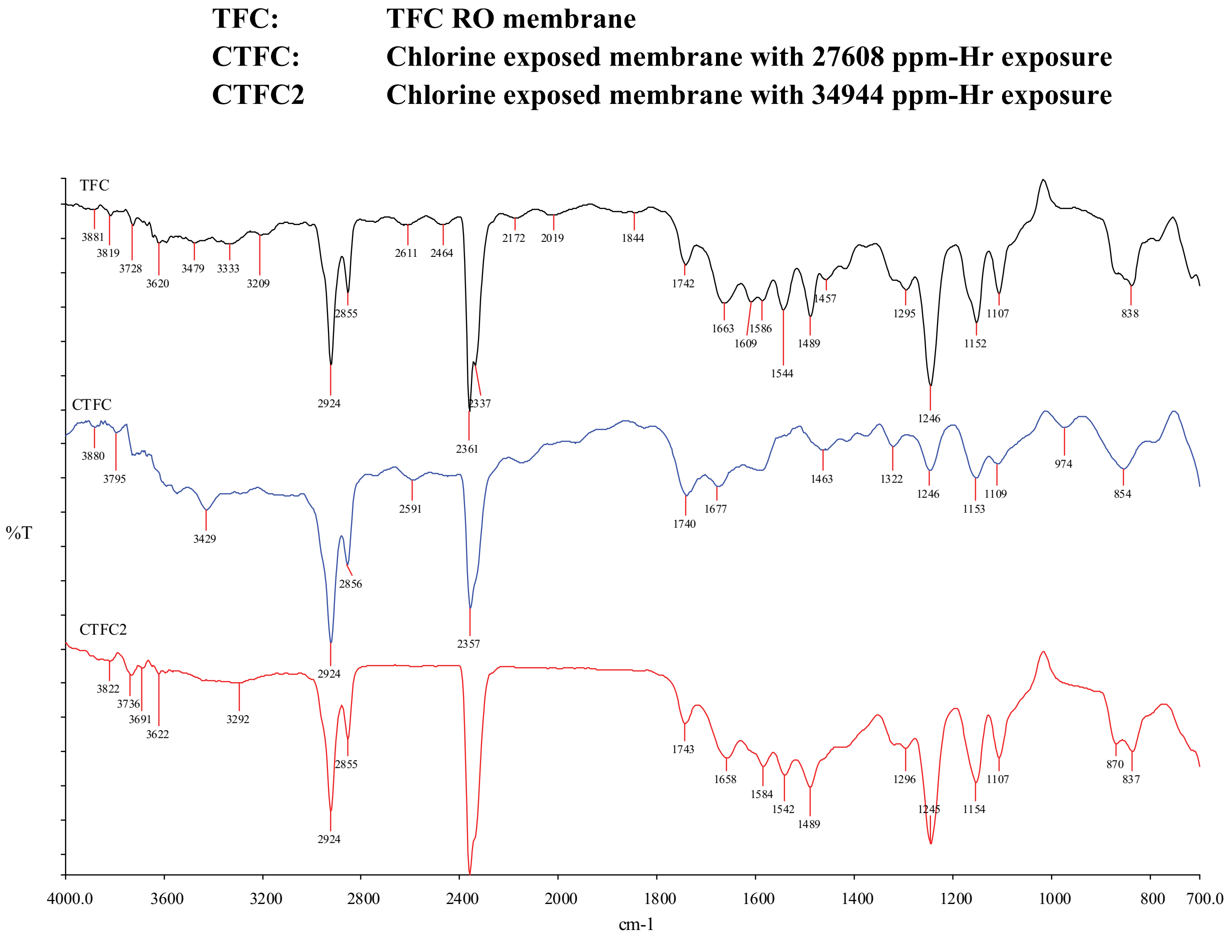

Fig. 3. ATR-FTIR spectra. TFC: TFC RO membrane; CTFC: chlorine exposed membrane with 27,608 ppm h exposure; CTFC2: chlorine exposed membrane with 34,944 ppm h exposure.

which leads to the membrane similar to ultra-filtration membrane.

Infrared spectroscopy was used to evaluate the chemical structure modification/degradation by free chlorine exposure. Comparison is made between the TFC membrane and chlorine treated membrane in each of Fig. 3. The stretching vibration of NH group in the band 3479 cm^{-1} to 3333 cm^{-1} is assigned to free and hydrogen bonded N–H bond stretching, respectively [19]. The peaks at 1663 cm^{-1} and 1544 cm^{-1} correspond to amide I and amide II, respectively. Amide I is considered to comprise of CO stretching, the amide II band is mainly contribution from the N–H in plane bending. A small peak at 1609 cm^{-1} is associated with C=C ring stretching vibration.

From the above spectra, it can be judged that the peak at 3333 cm^{-1} is getting suppressed in chlorinated TFC which indicates that hydrogen bonded N–H bond stretching is converted to N–Cl type bond structure. A small peak at 1609 cm^{-1} gets disappeared in chlorine exposed membrane which indicates that C=C ring stretching vibrations are getting affected as a result of chlorination which may in turn lead to ring opening. As a result of ring opening, the drastic rise in flux can be observed.

3.1. *Scanning electron micrographs and contact angle*

Scanning electron micrographs of virgin TFC and hypochlorite treated TFC are shown in Fig. 4.

The SEM images (Fig. 4A–C) indicate the increase in porosity of membrane by free chlorine exposure, moreover the reaction by-product are seen as white dots in Fig. 4B. The energy dispersive X-ray has been taken as indicated in Fig. 4C for those white dots, which indicates that sodium meta bisulfite has neutralized sodium hypochlorite (because of presence of sulfur).

The contact angle analysis was conducted at five different locations in the same membrane and the average has been taken into consideration.

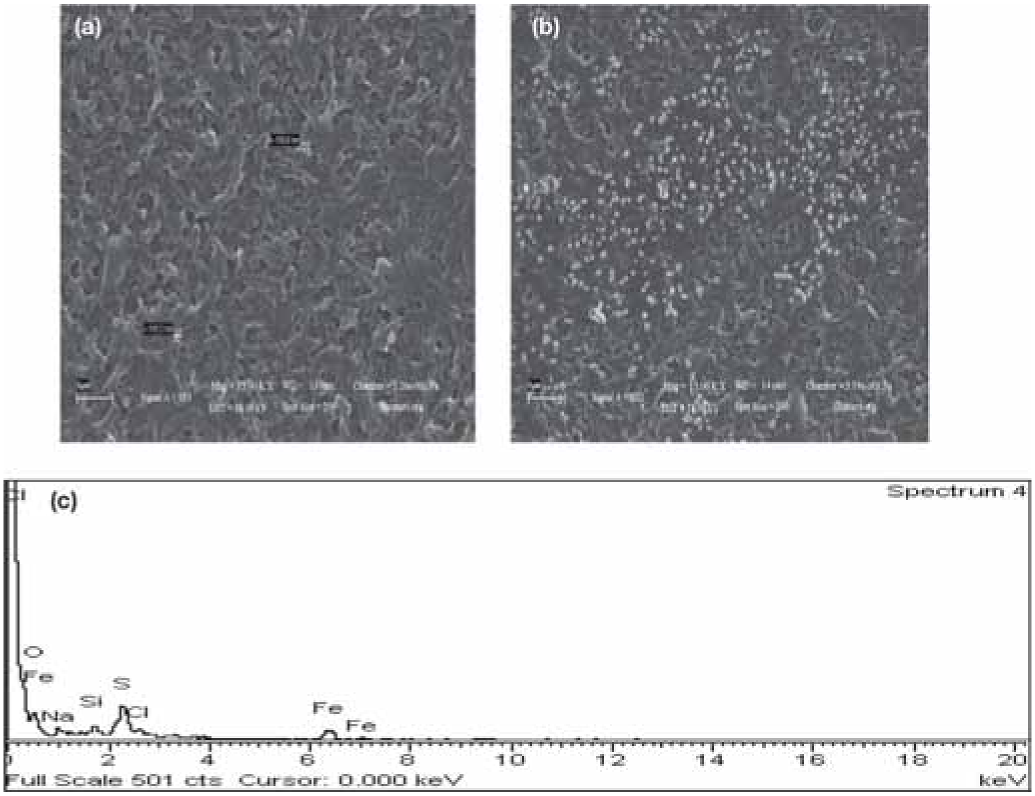

Fig. 4. (A) SEM image of TFC RO membrane; (B) SEM image of 1000 ppm h chlorine treated TFC RO membrane; (C) Energy dispersive X-ray of 1000 ppm h chlorine treated TFC RO membrane.

Table 7
Contact angles of TFC RO membrane and chlorine treated TFC RO membrane

Sr. no.	Membrane	Contact angle left	Contact angle right
1	TFC	45.65	48.25
2	1000 ppm h chlorine treated TFC	40.63	41.37

The results in Table 7 indicate hydrophilic nature of chlorine treated membrane as getting reflected by decrease in contact angle, which confirm with the high flux of treated membrane.

The results in Table 8 indicate that bio film formation and performance change because of the same varies widely for treated and untreated membrane. Membrane flux and solute rejection have fallen drastically with bacillus bio-film for untreated membrane whereas the performance has not been severely affected for treated membrane. In case of *E. coli* and *Pseudomonas* also, the performance decrement is less for treated membrane.

In this way, there are structural modifications in TFC RO membrane because of the free chlorine exposure. And hypochlorite treatment in a systematic manner opens up a possibility of reuse of fouled membrane and performance enhancement. The study indicates the recycle of TFC RO for rejuvenating performance of the membrane can open new dimension towards prolonging membrane life and reduced life cycle cost of membrane processes.

4. Conclusion

The rejuvenation of discarded TFC RO membrane can be done by free chlorine treatment in a controlled fashion. Various grades of TFC RO membrane of different solute rejection and flux can be tailor made by treating the TFC RO membrane to different free chlorine exposure level. This novel approach opens up new possibility of making different grades of TFC RO membrane suiting niche applications e.g. drinking water from less saline/brackish water. It has been demonstrated that discarded sea water RO membrane module

Table 8
Performance of hypochlorite treated TFC RO membrane for bio-film formation

Sr. no.	Time of exposure (h)	Concn. of free chlorine (mg/l)	Solute rejection (%)	Flux (gfd)	After biofilm formation *E. coli*		After biofilm formation *Bacillus* sp.		After biofilm formation *Pseudomonas* sp.	
					Solute rejection (%)	Flux (gfd)	Solute rejection (%)	Flux (gfd)	Solute rejection (%)	Flux (gfd)
1	Nil	Nil	80.86	10.5	48.78	12	31.71	17	56	2.7
2	1	1717	87.93	10.75	40.5	15	76.25	23	41.03	5.6
3	2	1717	74.4	12.5	42.5	24	82	15	42.05	3.8
4	3	1717	75.61	20	40	20	58.75	31	43.59	11.4
5	4	1717	73.54	21.5	45	26	68.75	26	41.03	9

can be converted to a useful brackish water RO membrane module by successive hypochlorite treatment. The membranes with prolonged exposure to chlorine were found suitable for applications in micro-organism removal from water. The performance decline because of bio-film formation is lower in case of hypochlorite treated membrane with *E. coli*, *Pseudomonas* sp. and *Bacillus* sp. bio films.

Symbols

TFC	thin film composite
RO	reverse osmosis
gfd	gallons per square feet per day
O.D.	optical density
UF	ultra-filtration
MF	micro-filtration
MPD	meta phenylene diamine
TMC	trimesoyl chloride
Psig	pounds per square inch (guage)
cm	centimetre
ATR FTIR	attenuated total reflectance Fourier transform infrared spectroscopy
E. coli	*Escherichia coli*
SEM	scanning electron microscope
mg/l	milligrams per litre equivalent to ppm
sq .ft	square feet
sp.	species
s	second

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