On-Line Anti Scaling System for RO Membrane Pretreatment

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Abstract: The primary goal of this research was to investigate the effectiveness of using a certain chemical compound viz. ammonium bifluoride (ABF) to enhance or improve the performance of the RO membrane which means it can operate long with the same efficiency by using (ABF) as online dosing with different doses to reverse osmoses membrane (RO) for mitigation of scaling caused by silica (SiO2) and choosing the optimum dose of (ABF). The main parameters measured silic, TDS, Fe, Flux loss was observed for the cross-flow UF membrane after filtration. To study the effciency of antiscalant Scanning Electron Microscopy & Energy Dispersive X-ray Spectroscopy (SEM-EDS) was done for all phases to know the effect of silica before and after using anti scaling on the used UF membrane surface. This paper studied the effect of ABF as antiscalant for silica by different doses 2, 4, 6 mg/l at constant pH = 6 to know the effect of the removing of silica only and the optimum dose was 4 mg/l.

Key words: Reverse osmosis · Membranes · In-line antiscalant · Ultrafiltration · Ammonium biflouride

INTRODUCTION

Obtaining potable, irrigation and high quality industrial waters from high salinity water sources using reverse osmosis is technically and economically feasible. Nevertheless some of the ions that are present in the water can be limiting factors for applying this technology. This paper deals with operational practices in a pilot plant study where silica is the limiting factor for increasing recovery rates [1].

Silicon is a very common element in nature, as earth crust contains approximately 25% of this element. Silica (SiO2) content in water usually varies between 10-40 mg/L, but in some places (Chile, México, Canary Islands, Rassedr-Egypt) concentrations can reach up to 100 mg/L [1].

Silica scaling is a common problem encountered in membrane separation processes due to its low solubility of about 120 mg/L in amorphous form. Presence of silica in water is due to the dissolution of silica to become silicate based on the following reaction: SiO2 + 2H2O → Si (OH)4. The most common method of silica removal is by precipitation with polyvalent metal hydroxide, such as: Fe (OH)3, Al(OH)3 and Mg(OH)2, indicating both softening and coagulation are capable of removing silica.

Although softening is capable of removing silica, it is not feasible unless raw water contains enough hardness. Coagulation is one the best options due to its low cost. However, applying coagulation along with sedimentation facilities requires a lot of footprints, which offsets the benefit of fewer footprints required for RO membrane process. Consequently, on-line coagulation/RO is a significant methodology for silica pretreatment, where optimum silica removal was achieved in the in-line coagulation process, the remaining particle was removed by RO and fewer footprints were required [2].

The research conducted in this paper is based principally on the operation of pilot using membranes and various antiscalant doses. Membrane autopsies have been carried out which are a unique tool for characterizing the state of membranes and it is fundamental to guarantee the efficiency of chemical treatments. The results that are presented in this paper refer to diverse studies related to problems with dissolved silica (also called "reactive silica") and not to alumino-silicates (clays in colloidal form) also called "non-reactive silica" [1].

Silica Scale Inhibition Mechanisms: The objective is to avoid scaling formation and to increase recovery rate. For this purpose, a complete water analysis of raw water was

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carried out and critical parameters used for scaling tendency calculation are considered as silica, calcium, bicarbonates, iron, aluminum, magnesium and the water pH. Analysis of these parameters and using specialized scaling prediction software allows the optimum product and dosage rate to be calculated. Raw water acidification should be avoided as in many cases this can reduce silica solubility.

It is also crucial to prevent iron, aluminum and manganese to form scaling on membrane surface as even at very low concentrations (0.05 mg/L) as they have a high anti-scalant demand which acts as a contaminant if it used with high concentration.

The Antiscalant of silica deposits and the optimum dose of Antiscalant (ABF) has been used in this research as Silica Antiscalant to prevent forming scales and deposits, as fluorine is generated in an acidic medium. Fluorine can dissolve silica crystals but its use has important disadvantages related to handling by operators and oxidative properties. Fluorine can also oxidize the polyamide layer even faster than chlorine.

ABF was the selected antiscalant in this study since it is a promising material used by several companies and in several countries.

Very few studies have reported silica removal by coagulation and none of them applied in-line coagulation. Precipitation aids such as alum and ferric chloride were found necessary for improving performance of the lime-soda ash process to reduce silica to the acceptable level [3]. Enhanced coagulation and UF process and found out that silica was removed from 10 mg/L to less than 2 mg/L [4]. Using coagulation process for industrial wastewater containing silica and silica was reduced from 30 mg/L to 10 mg/L, demonstrated that coagulation is effective in a jar testing experiment to enhance the silica removal and coagulation along can remove silica to 50 % at medium pH to significantly reduce the possibility of silica scaling. All the evidence demonstrates that coagulation is a feasible process for silica removal [5].

MATERIALS AND METHODS

Materials and Module Description: The pilot module is an RO system consisting of:

- The RO feed tank PET (polyethylene) capacity 35 L.
- PET Cartridge filters hosing containing one cartridge 5 micron.
- Two high pressure pumps, Headon Model no HF-9050. Each one capacity (1.2 l/min)

Table 1: Raw water analysis for the tested city tap (feed) water and synthetic water

Parameter	City tap water	Synthetic water
Calcium mg/l	39	39
Magnesium mg/l	11.4	11.4
Sodium mg/l	7.2	7.2
Potassium mg/l	4.9	4.9
Strontium mg/l	0.0	0.0
Barium mg/l	0.0	0.0
Ammonia mg/l	0.0	0.0
Alkalinity mg/l	93	93
Bicarbonate mg/l	25.3	25.3
Sulphate mg/l	24	24
Chloride mg/l	80	80
Fluoride mg/l	0.65	0.65
Iron mg/l	0.12	0.12
Manganese mg/l	0.0	0.0
Nitrate mg/l	0.0	0.0
Total PO4 mg/l	3.6	3.6
Silica mg/l	0.0	100
Carbonate mg/l	0.0	0.0
TDS mg/l	180	180
Conductivity us/cm	270	270
pH	7.8	6

- One PET membrane pressure vessels containing one membrane element Filmtech membrane model TW30-1812-100.
- RO skid & piping connection with valves on the reject line to control membrane pressure, 4 pressure gauges (two before and after cartridge filter, one on membrane inlet and other on the membrane out let)
- Set of flow meters on membrane feed, brine water pipe and permeate water pipe

The pilot plant was located at The Pipe Laboratory, Sanitary and Environmental Engineering Institute (SEI), Housing and Building National Research center (HBRC), Dokki, Giza, Egypt.

Feed Water Preparation: The feed water used in this study is synthetic water, the source of water is city tap with increased silica concentration by adding sodium-meta silicate (Na2O3Si.9H2O) to increase the silica concentration and increase the tendency of silica scale formation. The required dose of the silica was calculated using Permacare scaling program (Nalco. Co.).

The original and synthetic water analysis is shown in Table 1.

Experimental Methodology: Permacare program (Nalco. Co.)was used to predict and adjust the required silica dose to create scaling on the membrane to know the effect of antiscalant on silica only, Fig. 3.
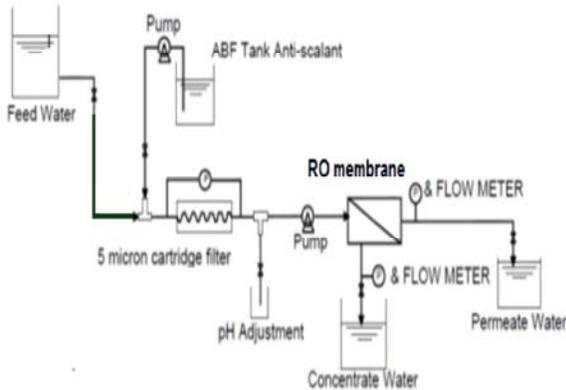
Fig. 1: Schematic diagram for In-line anticipant/RO membrane process

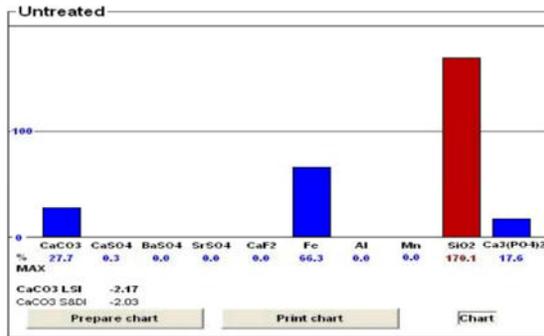Fig. 2: Shows a photo of the entire membrane pre-treatment system

Fig. 3: Graph indicating silica scaling after adding silica to membrane system

The following was conducted in every phase of the experimental work: the RO unit was operated at constant membrane feed pressure at 6 bar, feed flow 0.03 m3/hr, feed water temperature20-27°C, feed water pH constant at 6,and SDI15 = 3. Permeate, reject (brine) flow and pressure were measured, the recovery of the system was calculated and recorded till it reached minimum recovery of 32%. The time spent to reach this recovery was also recorded. The membrane was removed and anatomy of the membrane was conducted to identify the changes in the membrane surface and type of scaling formed. Some coupons 5x5 cm were taken from the membrane for analysis the scaling and others for SEM scanning.

These steps were repeated for each phase, with the same operating conditions on new membranes except for the ABF dose: first phase was without the addition of ABF and then the doses were 2, 4, 6 mg/l for the following phases respectively by using dosing pumps with concentration 3% of ABF.

Repeat the same work for new other membrane elements separately at the same parameter on batch water mixing with ABF, the water solution was analysis to adjust the ABF concentration in the water to be 4 mg/l with retention time 5, 10, 15 minutes and running RO and recorded the time spent to reach minimum recovery 32%, Comparing all the data recorded in each case

Silica was measured according to the method 4500-SiO2 listed in the 20th edition of the Standard Methods (APHA, 2005) using a T70+ UV/VIS spectrometer by PG Instruments Ltd. Scanning electron microscopy & Energy dispersive X-ray Spectroscopy (SEM-EDS) is EDAX inspect S 2007 model, manufactured by Philips, Ltd.

The Recovery of the System Calculated As:

Recovery = Q permeate / QFeed

Where:
Qfeed = Water flow enter to the plant.
Qpermeate = Treated water flow exit from the plant or membrane

RESULTS AND DISCUSSION

The highest recovery for RO membrane plant was 58.5 %, it decreased with time to reach 32.5%.Time taken to reach this recovery was140 hours which indicates the formation of silicate scaling on the membrane surface, SEM scanning was conducted on the membrane surface as shown in Fig. (4, 5) which shows scaling of silica on the membrane surface. The analysis of the sample taken from this scaling indicates the content of silica in sample is 91.96% silicate 8.04% of silt.

In case of no ABF added (phase 1), the time spent for the recovery of the system to decrease from 58% to 32.5 % is130 hrs as shown in Fig. 6 and this number of hours will be constant in all phases of the experiments to know the effect of using ABF as anti scaling, the curve of

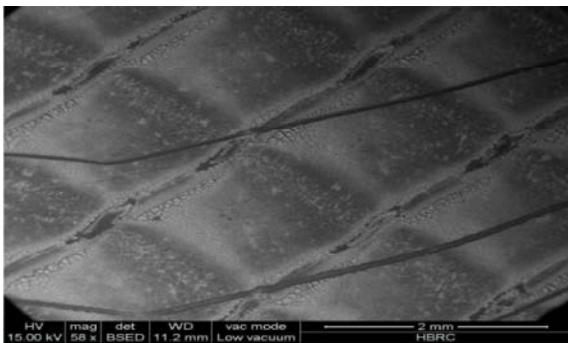Fig. 4: Sodiummetasilicates detected on membrane surface.

Fig. 5: SEM-EDX Micrograph membrane surface fully covered by sodiummetasilicates and zoomed 58 times.
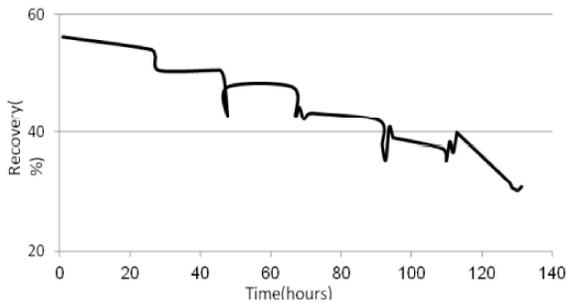

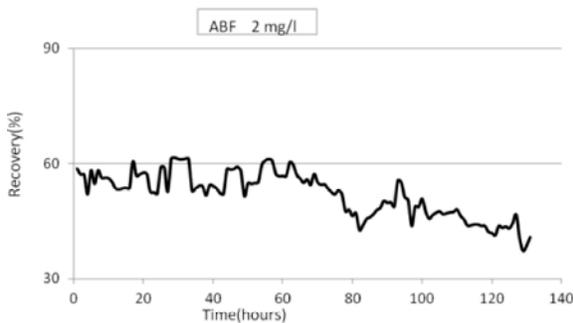Fig. 6: Membrane recovery Vs time with no ABF dose

Fig. 7: Membrane recovery vs. time with ABF dose 2mg/l

recovery in the figure also shows a sequence of sharp fluctuations which result from stopping the RO unit and then operating it again. The parameters which need to be adjusted like (pressure, flow …) when starting the unit after any stop takes some times be adjusted.

In the following phase of the experiment, ABF was added in continuous flow mode with dose 2 mg/l (phase 2)using anew membrane, the time spent for the decrease in the recovery of the membrane system from 58% to 40.8 % was130 hrs at the end of this phase as shown in Fig. 7. After 80 hours of the RO unit operation, the pressure of the feed water dropped with no ability to increase the feed of membrane pressure again, which lead to decrease of membrane productivity and as a result the feed flow and recovery decreased and to know the main reason for this decrease of pressure all components of the RO unit were checked and noticed that the cartridge filter was blocked so after replacing it and operating the system the recovery increased again to the same reading before the drop [5-7].

Starting new phase of the experiment with new membrane the system and water have the same data at the same parameters to continuous flow mode with dose 4 mg/l (phase 3) of ABF was added as shown in Fig. (8), after 130 hrs at the end of this phase the recovery of the system was decreased from 58.8% to 56.7%, Some coupons 5x5 cm were taken from the membrane for analysis. While the analysis of this sample of this scaling on the membrane is 98% silt and 2% gelatin material no silica found or fluoride.

Starting new phase of the experiment with new membrane, the system and water have the same data at the same parameters to continuous flow mode to 6 mg/l (phase 4) of ABF was added after 130 hrs at the end of this phase. The recovery of the system decreased from 58.5% to 52.06%as shown in Fig. 9. Some coupons 5x5 cm were taken from the membrane for analysis, the microscope scan for scaling at dose 6 mg/l show the fouling is colloidal fouling not silica fouling as shown in Fig.5. while the analysis of this sample of this scaling on the membrane is 95% silt and 3% gelatin material 2% calcium florid, no silica found.

Starting new phase of the experiment with new membrane the system and water have the same data at the same parameters to continuous flow mode with adding ABF on water in batch mode with retention time 6 hours at ABF dose 4 mg/l as shown in Fig. 10, show that the recovery was decrease from74.8% to 70.1% in time 130 hrs at the end of this phase.
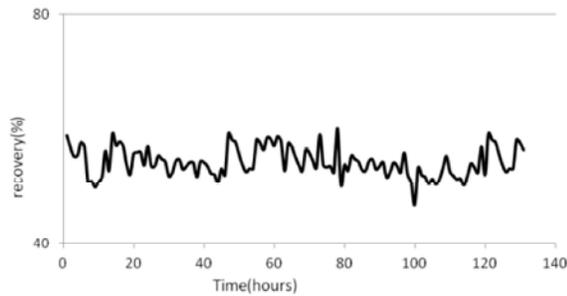
Fig. 8: Recovery of membrane unit treating water with High silica treated by antiscalant (ABF) dose 4 mg/l versus time.
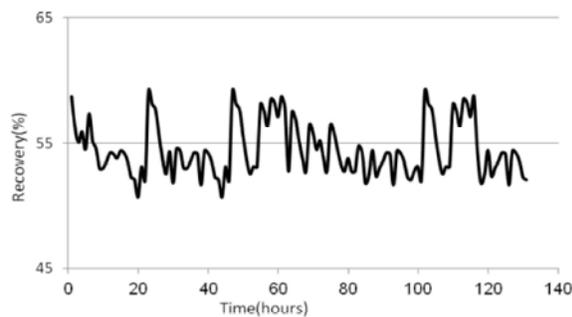

Fig. 9: Recovery of membrane unit treating water with High silica treated by antiscalant (ABF) dose 6 mg/l.
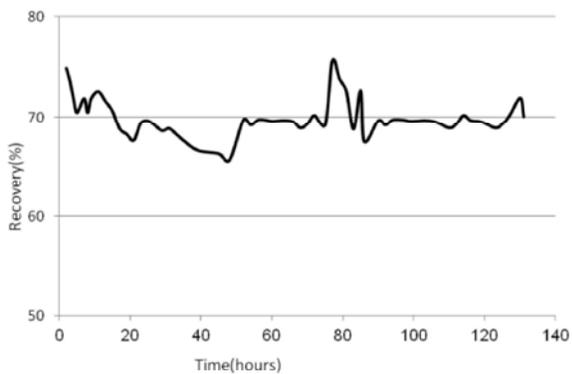

Fig. 10: Recovery of membrane unit treating water with High silica treated by antiscalant (ABF) dose 4 mg/l versus time but with retention time from 1 to 6 hours.

In the final phase of the experimental work, ABF was used as a cleaning agent for scaled membrane and the recovery of this membrane decreased from 58.7% to 32% used in a previous phase of the experiments,. By cleaning this membrane (reduce silica scaled on membrane surface as much as possible) by operating the unit with dose100 mg/l of ABF for two hours, then flushing for
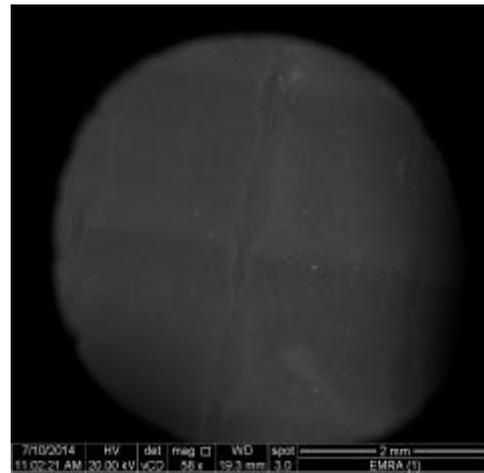

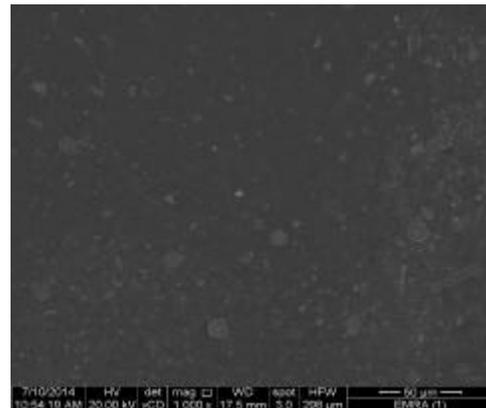Fig. 11: SEM photo of membrane scaled with silica and washed by ABFdose 10 mg/lzoomed x 58 times.

Fig. 12: SEM photo of membrane scaled with silica and washed by ABFdose 10 mg/lzoomed x 1000 times.

10 mints with distilled water, then running RO system, we found that the recovery of the system was increased from 32% to 55.3% the recovery increased by about 23.3 % after cleaning, see Fig. 11, 12, 13, 14. of SEM of this membrane after cleaning for two hours [5].

The effect of ABF in preventing the formation of silica scaling can be explained as follows: the ABF increase the solubility product of the silicate than ionization constant of the silicate so, at high recovery and increase the silicate concentration in brine water with increase also concentration of ABF in brine which will increase the solubility of Silicate before ionization so, prevent formation of silica layer on membrane surface as scaling in case of increase the ABF dose to 6 mg/l leads to increase of florid in brine water which became to form fluoride scaling on membrane surface [6, 7].
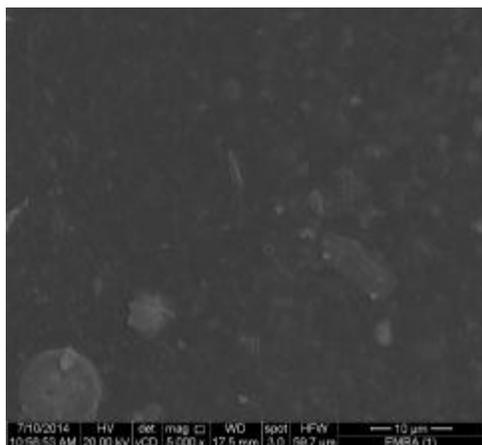
Fig. 13: SEM photo of membrane scaled with silica and washed by ABF dose 10 mg/l zoomed x 5000 times.
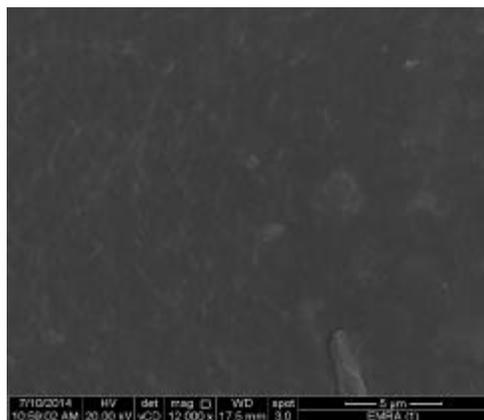

Fig. 14: SEM photo of membrane scaled with silica and washed by ABF dose 10 mg/l zoomed x 12.000 times.

CONCLUSIONS

- Silica was successfully removed in these in-line coagulation/ultrafiltration processes. The removal efficiency of silica depends on pH value and coagulant dose are critical factors on silica removal. The optimum silica removal at best recovery of 55 % was after 140 hours determined with pH=6 and antiscalant dosage=4 mg/L as ABF, corresponding to a maximum of 55 % recovery for RO membrane plant. Flux loss was observed for the cross-flow UF membrane after filtration.

- Dosing a silica specific antiscalant prevents silica scale and deposits on membrane surfaces without having to reduce the feed pH through acid dosing but in case of ABF it should be lower than 6.5.
- It is possible to increase recovery rates and make substantial savings in water and energy consumption this can be achieved by adding 4 mg/l of ABF as anti scaling.
- Even in case of forming silica scaling on the membrane surface, this scaling can easily be removed with cleaning of the membrane with a 100 mg/l dose of ABF to increase the membrane efficiency with 55% and reuse this membrane again.

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