Annals of R.S.C.B., ISSN:1583-6258, Vol. 25, Issue 6, 2021, Pages. 12814 - 12819
Received 25 April 2021; Accepted 08 May 2021.

Relationship between Reverse Osmosis Membrane Fouling and Pretreatment in the Khenifra City Plant in Morocco

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ABSTRACT
Reverse osmosis (RO) is considered the most important and optimized membrane desalination process currently dominating the desalination market to help meet the growing need for water, especially in water-stressed countries. The major problem associated with RO is membrane fouling which is frequently related to the interaction between the feed water quality and the pretreatment process. This article deals with the problem of reverse osmosis membrane clogging at the Khenifra plant. This problem was coupled with the increase in operating pressure, pressure drop and permeate conductivity. To identify the causes of these problems, different investigations are being done. A membrane autopsy, chemical analyses of the feed water and monitoring of the operating parameters are performed. The autopsy of the membrane was performed by SEM/EDS(Scanning Electron Microscopy /energy-dispersive spectrometer).The results show that the film is mainly composed of: $CaCO_3$ (38.70 %), Al_2O_3 (17.42 %), Ba $(SO_4)_2$ (15.23 %), $MgCl_2$ (15.02 %) and SiO_2 (13.64 %).
Keywords: Demineralization, Reverse Osmosis, Membrane, Permeability, Water, Fouling.

1 INTRODUCTION
Pretreatment is an essential part of the membrane desalination process. The pretreatment system for reverse osmosis units is designed to produce feed water with reduced fouling potential by removing particulate matter, micropollutants, and microorganisms, and preventing the formation of inorganic deposits (Farhat, 2018; Schwaller, 2021). Scaling and fouling are the most serious problems related to the efficient operation of reverse osmosis systems. Foulants can be classified into four broad categories: poorly soluble inorganic compounds, colloidal or particulate matter, dissolved organic substances and microorganisms(Chun, 2017; Talantikite, 2020). Fouling results in a loss of membrane performance, such as increased pressure drop, poor product quality, and decreased flow, to a point where it may become necessary to replace the membrane. Point where it may become necessary to replace the membranes (Ray, 2017).Inorganic scaling occurs when the soluble components exceed the solubility limit (Kumar, 2019). Particles fouling is caused by convective and diffusive transport of suspension or colloidal material (Ray, 2017). Organic fouling is partly governed by interactions between the membrane surface and organic foulants and between the organic foulants themselves(Daly, 2020). Biological fouling is caused by the attachment and proliferation of microorganisms to the membrane surface (Motsa, 2014) leading to the formation of biofilms, consisting of microbial cells implanted in a matrix of extracellular polymeric substances produced by the microbes (Thamaraiselvan, 2019). The best approach to membrane autopsy today is to develop more in situ tools that allow non-destructive analysis of membrane materials (Firouzjaei, 2020).
The objective of this study is to evaluate the impact of the feed water quality and the chemicals used to control membrane fouling. The determination of the chemical

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characteristics of the scale was done in order to study a possible relationship between this scale and the concentrations of the chemicals used in the plant. For this, a systematic approach based on the application of an autopsy of a membrane element and an analysis of the fouling layer was realized.

2 CASE STUDY

2.1 Desalination plant by reverse osmosis in Khenifra city

Morocco, located in a semi-arid area, is classified among the countries with the least water resources in the Mediterranean basin. Water resources in Morocco are characterized by scarcity and pronounced irregularity. The lack of good quality water, especially in the Middle Atlas regions, has necessitated the desalination of brackish water to supply these regions with drinking water.

The city of Khenifra located in the Middle Atlas. It is one of the most important tourist poles of the country. It is characterized by a seasonal fluctuation from cold in winter to hot in summer. The creation of the reverse osmosis desalination plant in Khenifra marked a new experience in the use of desalination of brackish surface water in Morocco (Boulahfa, 2019; Ennouhi, 2021).

The desalination plant of Khenifra was built in 2013 with nominal capacity of 36,290 m³/d and a conversion rate (80 %). The Pretreatment is designed using coagulation-flocculation employing recirculation of aluminum sulfate, polyelectrolyte and settled sludge at the flocculation level (Fig.1).

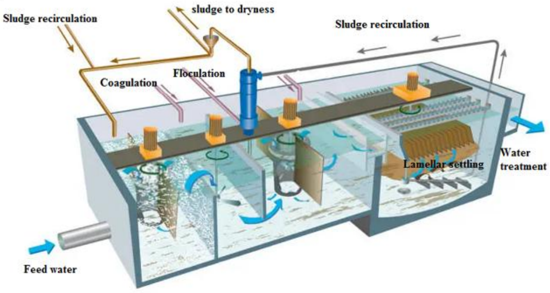

Figure 1: Diagram of the water treatment plant.

The system of reverse osmosis is composed of three lines, each osmosis plant is composed of 75 pressure tubes divided into two stages, which are 56 tubes in the first stage and 19 tubes in the second stage. Every tube is loaded with 7 membranes (XLE-440 from Filmtec), which gives a total of 525 membranes by osmosis plant. The mode of association of the two stages of pressure tubes is the series-rejection mode.

1.2 Feed water characterization

The composition of the OumRbiâa feed water is presented in (Table 1). The feed water has a salinity of 2500 mg.L^{-1}, a high hardness typical of surface waters of the OumRbiâa, a variable concentration of sulfate and bicarbonate reaching respectively 117 mg.L^{-1} and 214 mg.L-1 and a high concentration of chloride 866 mg.L^{-1}.

Table 1: Feed water characteristics at the inlet of the reverse osmosis demineralization plant.

Chemical Composition	Amount
pH	8.5
Alkalinity (°F)	17.6
Calcium (mg.L^{-1})	95

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Magnesium ($mg.L^{-1}$)	32.5
Sodium ($mg.L^{-1}$)	422
Potassium ($mg.L^{-1}$)	2.9
Manganese total ($mg.L^{-1)}$	0
Aluminium ($mg.L^{-1}$)	< 0.2
Ammonium ($mg.L^{-1}$)	0
Iron ($mg.L^{-1}$)	< 0.03
Barium ($mg.L^{-1}$)	0
Bicarbonnate ($mg.L^{-1}$)	214
Chloride ($mg.L^{-1}$)	866
Sulphate ($mg.L^{-1}$)	117
Nitrate ($mg.L^{-1}$)	6.49
Fluoride ($mg.L^{-1}$)	0
Silica ($mg.L^{-1}$)	15

The molar classification of water will provide a useful tool for determine the type of scale that may be present and the scaling potential of a concentrated solution that comes into contact with the reverse osmosis membrane surface. The relationship between chloride and the molar ratio of $CaSO_4/HCO_3$(Sarfraz, 2021) indicates that the natural water from Khenifra has a moderately high scaling potential for carbonates and moderately high for sulfates. The molar classification of water will provide a useful tool to determine the type of scaling potential of a concentrated solution that comes into contact with the RO membrane.

The relationship between chloride and $CaSO_4/HCO_3$ molar ratio (Ayoub, 2019) indicates that natural water from Khenifra has a high scaling potential for carbonates and medium-high for sulfates. This classification covers the carbonate and sulfate scales of Mg and Ca. However, regular study of the limestone deposits formed and generated by the water types proves that Sr and Ba are always associated with calcium deposits over the whole range of proposed water types(Amy, 2017; Baghbanzadeh, 2017; Able, 2018).

Dalvi et al (Dalvi, 2000)reported general considerations regarding the comparison of different pretreatment processes in RO desalination operations. They detailed that the pretreatment process must be adapted to the quality of the water to be treated. In the reverse osmosis plant of Khenifra, the addition of sulfuric acid to control $CaCO_3$ scaling and a phosphonate-based antiscalant (flocon 135) is used to control other salts, in particular sulfates and calcium fluorides.

1.3 Pre-treatment process of khénifra city

Reverse osmosis systems had widely carried out pretreatment technologies. These technologies had the advantage of enhancing the feed water quality mainly toensure reliable reverse osmosis exploitation as well as to prolong membrane life (Ennouhi, 2020). Among all the processes, conventional water treatment methods include coagulation, flocculation, and sedimentation processes, usually followed by filtration and disinfection (Koók, 2019).

Coagulation–flocculation is considered the most crucial method in surface water treatment, and it can be used as a pretreatment, post-treatment, or even main treatment (Luo, 2018; Fortunato, 2020). Some parameters may affect the aggregation of colloids, pH, turbidity, chemical composition of the raw water samples, coagulant dosage, water temperature, surface area of colloids, and mixing conditions(Abushaban, 2021).Coagulation is the process of destabilizing suspended solids. Coagulant sand colloids possess adverse electrical charges in water and thus when they meet the charges could be neutralized, resulting in fast aggregation

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of small suspended particles to form microflocs(Liu, 2019).In addition, coagulants are extensively used in the treatment of public water supply systems (Baghbanzadeh, 2017).

Among all the coagulants, Al-based coagulants have been used most widely, and they can change surface charge properties to promote agglomeration and/or enmeshment of smaller particles into larger flocs(Ennouhi, 2020). However, it raised more concerns due to the increase of residual aluminum in treated water, which can cause even more issues(Su, 2019).

3 MEMBRANE AUTOPSY

After six years, the exploitation of the membrane process with aluminum sulphate pretreatment showed in all three reverse osmosis membrane lines an increase in pressure drop and a decrease in quality. pressure drop and decreased permeate quality. The permeate quality also decreased rapidly, Cleaning in place (CIP) increasing at the same time [20]. This decrease in performance requires an autopsy in order to know the reasons and to find solutions (Fig. 2 and Fig. 3).

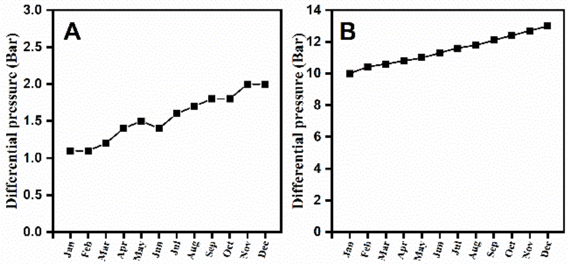

Figure 2: First (A) and second (B) stage pressure drops during 2017 [20].

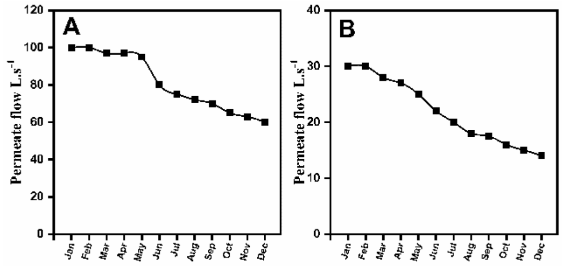

Figure 3: Decrease in permeate flow at the first (A) and second (B) floors during 2017.

In order to identify the causes of these difficulties, analytical technique such as the Scanning Electron Microscope - Energy Dispersive X-ray Spectrometry (SEM/EDS) are used to determine the nature of membrane foulant present on the membrane surface. The key steps of membrane autopsy procedure are selection of representative element, dissection, analysis, identification and remediation (Fig.4)(Su, 2019).

The membrane element is removed from the first stage which presents the majority of problems. The surface of the membrane element removed is visually inspected and found to be covered with a dark brown gelatinous looking deposit.

Figure 4: Appearance of membrane surface.

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EDS analyses indicate a result comparable to that of Boubakri et al. (Luo, 2020) according to which the chemical compounds presented relatively high levels of: Ca, S, Na, Cl and Mg (Fig.5). Fairly low levels of organic matter C, O, N, Fe, Si, P are also present. The C and O peaks are probably due in part to organic compounds present in the feed water and in the organic antiscalant[24]. J.P van der Hoek et al (Van der Hoek, 2018) report that the use of an antiscalant (flocon 135) in combination with H_2SO_4 controlled scaling. However, this mode of operation resulted in significant biofouling, as the antiscalant acted as a nutrient for microbial regrowth in the water.

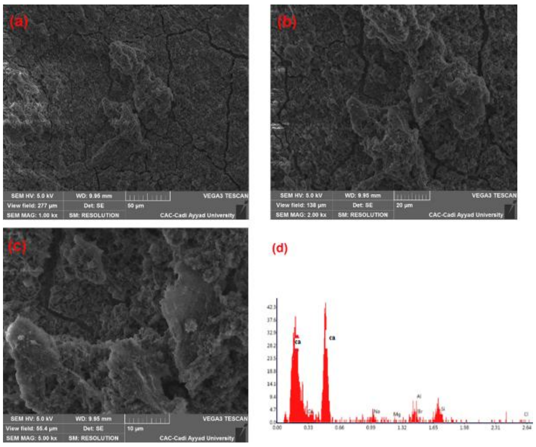

Figure 5: (a) SEM images of a reverse osmosis membrane structure x 1000; (b) x 2000; (c) x 5000; (d) EDS spectrum result [20].

The levels of Al and Si in the particulate matter suggest that it is primarily aluminum precipitate that causes common fouling in reverse osmosis operation [17]. Since cartridge filtration with 5 μm filters is used to pretreat the reverse osmosis feed water is likely to be free of larger silicates. However, finer particles could remain in the feed and then become part of the fouling layer [25].

The use of a phosphateantiscalant in this case may also contribute to the relatively high levels of P. In the Khenifra plant, the antiscalant addition is about 2.4 $mg.L^{-1}$.Since organic phosphonates are much more resistant to hydrolysis or converted to orthophosphate (PO_4^{3-}), it is possible that the P on the membrane results from the reaction of the inhibitor with Ca present in the feed water.

4 CONCLUSIONS

The quality of the feed water supplied to the Khenifra reverse osmosis desalination plant is subject to temporal variations. This change is due to the deviation of rainfall and seasonal temperature fluctuation leading to evaporation of water from the river. The feed water is subject to strong seasonal variations which leads to the precipitation of salts on the membrane surface inducing membrane scaling. The use of scale inhibitors must take into account the salinity of the feed water during the seasons and adjust its dosage according to the salinity. The use of chlorinated products in the treatment of surface water, may leave traces of chlorine in the waterfeeding the membrane and may damagethe surface of the membrane. Indeed, for improving the functioning of the Khenifrareverse osmosis Plant and achieving high performance, pre-treatment of the feed water is highly recommended.

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