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Sustainable antiscalant for municipal reverse osmosis plants

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ABSTRACT

Restrictions on the discharge of reverse osmosis brines containing phosphorus compounds that promote eutrophication are continuously increasing, and the related regulations are becoming more stringent. The low biodegradability and the phosphorous content of the phosphonate-based antiscalants are some of the first reasons for the growing concern about their environmental impact when discharged into natural ecosystems. To address this issue, a broad-spectrum biodegradable and phosphorus-free antiscalant has been developed for inhibiting scale formation in municipal reverse osmosis applications in both brackish water and seawater plants. The study evaluated the biodegradability of the green antiscalant, demonstrating it is inherently biodegradable. A dosing model for the green antiscalant and a scaling potential reduction model for sparingly soluble species model were developed. These models cover a wide range of scaling potentials applicable to both brackish water and seawater conditions, enabling precise calculation of the minimum required antiscalant dosage for effective protection against scaling. Experimental tests in a reverse osmosis pilot plant validated the effectiveness of the green antiscalant in preventing scaling. Membrane autopsies confirmed the successful prevention of scaling. The results evidenced that the green antiscalant is a sustainable and cost-effective solution for membrane scaling control in municipal reverse osmosis applications. Its use can contribute to reliable and efficient water supply while reducing the environmental impact compared to antiscalants containing phosphorous compounds.

Keywords: Green antiscalant; Phosphorous-free; Biodegradable; Scale inhibition; Municipal reverse osmosis plants; Brackish water; Seawater

1. Introduction

Water scarcity and the recurrence of droughts have become critical concern with extensive consequences, particularly in the Mediterranean region, where the limited rate of rainfall poses significant challenges to water availability. For this reason, water authorities need to consider alternative water sources to satisfy the increasing demand of drinking water caused by the population growth and development of economic activities [1,2]. Reverse osmosis is currently taking a fundamental role in seawater and brackish water desalination for providing drinking water. With the increasing demand for safe and sustainable drinking water sources in water-stressed regions, reverse osmosis has become a preferred method for meeting these challenges [3–5].

Under certain operating conditions it is usual that the surface of the reverse osmosis membranes and spacers become fouled. Membrane fouling is a persistent problem throughout reverse osmosis systems which reduces plant efficiency, increases operating and energy costs and reduce membrane lifetime. The membrane fouling causes a decrease of permeate water production, a decrease of salt rejection and an increase of drop pressure. In these cases, is essential to reduce membrane fouling for optimum operation of reverse osmosis plants. The decrease in the efficiency of the osmosis membranes is mainly due to four types of fouling:

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adsorption of organic matter, microbiological contamination due to the growth of microorganisms on membrane surface, plugging of the membrane surface due to deposition of particulate matter and colloidal particles, and scaling and metal oxide fouling due to the precipitation of sparingly soluble salts and metal hydroxides and oxides in the concentrate water [6]. Sparingly soluble salts can exceed the solubility limits in the concentrate water leading to precipitation of insoluble salts on the membrane surface. The most common scaling and fouling are calcium carbonate, calcium sulfate, calcium fluoride, calcium phosphate, strontium sulfate, barium sulfate, iron, aluminium, manganese and silica.

To prevent scaling in the concentrate water and maintain plant efficiency, antiscalant dosing is commonly employed. Phosphonate-based antiscalants are widely used for scaling control in reverse osmosis plants. However, their low biodegradability is one of the main reasons of growing concern for the environmental impact that represents the discharge of these compounds into the natural ecosystems. These compounds can act as a nutrient source for algae and bacteria promoting eutrophication [7]. As a result, restrictions on the discharge of reverse osmosis brines containing phosphorus compounds are continuously increasing, prompting stricter regulations in municipal water policies.

To address this issue, a broad spectrum green antiscalant has been developed. It is a biodegradable and phosphorus-free antiscalant developed to inhibit scale formation in municipal reverse osmosis applications in both brackish water and seawater plants. It is a blend that contains sustainable active agents with excellent antiscalant performance comparable to non-biodegradable phosphorous compounds. Other properties of the green antiscalant are its non-toxicity effect to humans and aquatic systems, its compatibility with reverse osmosis membranes and its competitive cost compared to traditional antiscalants.

The aim of the study is to measure the biodegradability and evaluate the effectiveness of the green antiscalant in preventing the inorganic scales in municipal reverse osmosis applications for both brackish and seawaters.

2. Materials and methods

2.1. Biodegradability tests

The biodegradability of the green antiscalant was measured using the Organisation for Economic Cooperation and Development OECD 302B procedure [8]. The biodegradability test assessed the green antiscalant's susceptibility to microbial degradation under environmental conditions, ensuring its safety when discharged into aquatic systems. The biodegradation process during experimental tests was monitored by determining the chemical oxygen demand (COD). The tests were carried out in 1 L glass bottle containing an aqueous mixture of the green antiscalant, mineral nutrients and activated sludge. The bottles were agitated and aerated in the dark at 20°C–25°C for a test time of up to 28 days. The extent of green antiscalant biodegradation was evaluated by analysing the COD at regular intervals throughout the test and comparing it with the biodegradation rate of sodium acetate which is a standard substance that degrades in this test. In OECD 302B a test compound is classified as inherently biodegradable if the extent of biodegradability is over 20% within the 28 d.

2.2. Scaling prediction software

To design the optimal green antiscalant treatment it is essential to accurately simulate the behaviour of the water inside the membranes in terms of composition and ionic strength, with the aim to predict the formation of scaling with precision. As well as, it is crucial to develop a dosing model for the green antiscalant. The ADICRO scientific software allows to achieve these objectives by providing knowledge and effective treatment to reverse osmosis plants, reducing operating costs and environmental impact. It is an innovative and constantly improving software, that incorporates the knowledge acquired in laboratory and pilot plant tests, experience in real plants and scientific literature. It allows to determine scaling potential of concentrate water with great accuracy. The input variables are the feedwater composition, temperature, plant recovery and membranes used. Software calculates osmotic pressure, ionic strength and the values of the solubility products for sparingly soluble species corrected according to ionic strength. These values are used to calculate saturation levels, Langelier Saturation Index, Stiff and Davis Index, fouling index and scaling potentials in the concentrate water to predict the risk of membrane scaling or fouling. The software also recommends the most effective antiscalant and calculates the minimum dosage of this antiscalant to ensure complete membrane protection against scaling. The program determines the optimal operating range, and indicates whether the treated water will be within allowable limits for the different scaling potentials. It also calculates the amount of sulphuric or hydrochloric acid or base required to decrease or increase the feedwater pH to reach the desired pH.

2.3. Reverse osmosis pilot plant tests

Dynamic tests were conducted in a continuous flow reverse osmosis pilot plant to evaluate and validate the effectiveness of the green antiscalant in preventing scaling in concentrate water from municipal reverse osmosis plants under both brackish and seawater conditions. Pilot plant is composed of one pressure vessel housing a 2540-size element. Assays were carried out with a total recycle of both the concentrate and permeate to the feed vessel, so as to maintain a constant composition. Two types of water were tested: brackish water and seawater. For the tests with brackish water, the Hydranautics ESPA-2540 element was used, and for seawater, the Hydranautics SWC-2540 element was used. Synthetic water was used to work in totally controlled conditions. Separate solutions containing anions and cations were added to a matrix of brackish water or seawater, to obtain a water that simulated the concentrate water operating at recovery of 75% and 45%, respectively. The reverse osmosis pilot plant operated at a recovery of 8%. The water pH and temperature were controlled. Two tests were conducted for each type of water: (1) without antiscalant treatment and (2) dosing the green antiscalant. During the tests the following operating parameters were monitored: normalized permeate flux, normalized salt rejection, feed pressure, pressure drop between feed and brine streams (Delta P), pH and temperature. The normalized parameters are the best indicators of membrane fouling. The evaluation is carried out analytically by standardizing operating data in accordance with the standard method ASTM D 4516 Standard Practice for Standardizing Reverse Osmosis Performance Data [9]. A complete chemical analysis of the feedwater and permeate was periodically performed.

2.4. Membrane autopsy

Membrane autopsies were performed at the end of each reverse osmosis pilot plant test to investigate the scaling formation on the membrane surface. The measurements of the inorganic fraction were performed using a scanning electron microscopy (SEM; JSM-6510, JEOL Ltd.) combined with energy-dispersive X-ray (EDX) analysis (INCA Energy Serie200, Oxford Instruments). SEM allows obtaining high resolution images of the chemical and topographical features of the foulants and particles on the membrane surface. The captured images are analysed in terms of different elements, EDX is used for elemental analysis and chemical characterization at a specific location in a sample. During treatment of the membrane samples for SEM-EDX analysis, samples were coated with graphite to make them conductive, therefore carbon peak in the EDX spectrum was not taken into account when fouling composition was studied.

3. Results and discussion

3.1. Biodegradability tests of green antiscalant

Fig. 1 shows the biodegradation percentages of both the green antiscalant and sodium acetate over a 28-d period, following the OECD 302B procedure for biodegradability testing. As expected, the sodium acetate biodegraded rapidly, reaching 100% biodegradability in the OECD 302B test within 28 days. This result confirmed the activity of the microorganisms and validated the reliability of the test.

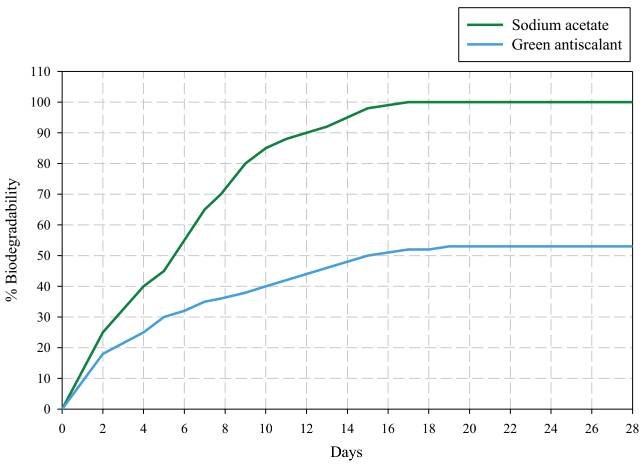

Fig. 1. Biodegradability of green antiscalant and sodium acetate in OECD 302B test.

The results show that in 28 days, the green antiscalant has a biodegradability of 53% and can be classified as inherently biodegradable. The results evidenced its potential to break down over time when discharged into aquatic systems.

3.2. Green antiscalant dosing model

A dosing model for green antiscalant was developed. The model calculates the optimum effective antiscalant dosage to inhibit the formation of scales in the concentrate water. The mathematical model was developed from data obtained from reverse osmosis pilot plant experimental runs. The antiscalant was tested under various solution supersaturation conditions and antiscalant dosages. The model covers a wide range of scaling potentials applicable for both brackish water and seawater characteristics. The model predicts the dosage for scale control based upon water chemistry and operating parameters. The experimental results allowed modelling the reduction of scaling potentials for sparingly soluble species as a function of the concentration of antiscalant. The dosage of green antiscalant model, the scaling potential reduction model and the knowledge acquired in the experimental stage were incorporated into the ADICRO scaling prediction software. The program calculates scaling potentials and recommends the optimal dosage of green antiscalant to ensure the effective protection against scaling and fouling. The dosage of the minimum effective antiscalant concentration reduces operating costs for chemical treatment, minimizes chemicals discharge to the environment and prevents the over and under dosing of the antiscalant.

A study using ADICRO software was conducted to determine the scaling potential and design the treatment with the dosage of the green antiscalant to inhibit scale formation in municipal reverse osmosis applications for both brackish water and seawater plants.

3.3. Simulation study for brackish water

Based on the analysis of the feedwater, which corresponds to a well water after pre-treatment and operating at 75% recovery for a municipal brackish water reverse osmosis plant, a study of the scaling potential for sparingly soluble species in the concentrate water was conducted using ADICRO software. Table 1 shows the chemical composition of the feedwater and concentrate water at 75% recovery.

Fig. 2a shows the scaling potentials in the concentrate water without antiscalant treatment at a temperature of 18°C. The scaling potentials are expressed as the percentage of the maximum admissible limit for the saturation levels and fouling indexes. A scaling potential higher than 100% indicates the saturation level for a compound is greater than the maximum permissible limit for this saturation level, and the compound will tend to precipitate. The simulation results indicated that the solubilities of calcium carbonate ($CaCO_3$) and iron (Fe) would be exceeded in concentrate water without antiscalant treatment. For other compounds, scaling potentials were within admissible limits and the plant could be operated without risk of scale formation.

The ADICRO software calculates the optimal dosage of the green antiscalant to inhibit the formation of scaling using the developed dosing model. Fig. 2b shows the reduction of scaling potentials in the concentrate water when dosing the recommended dose rate of green antiscalant. The scaling potentials for the calcium carbonate and iron were reduced to values below 100% with antiscalant dosing. The reverse osmosis membranes were fully protected against scale formation on the membrane surface by dosing the green antiscalant.

Table 1
Water chemistry of feedwater and concentrate water at 75% recovery for the municipal brackish water reverse osmosis plant

Parameter	Feedwater	Simulation of concentrate water at 75% conversion
pH	7.55	8.03
Calcium (Ca), mg/L	98	389
Magnesium (Mg), mg/L	40	159
Sodium (Na), mg/L	221	882
Potassium (K), mg/L	67	266
Barium (Ba), mg/L	<0.001	<0.001
Iron (Fe), mg/L	0.027	0.107
Aluminium (Al), mg/L	0.108	0.429
Manganese (Mn), mg/L	0.049	0.195
Sulfate (SO_4), mg/L	166	659
Chloride (Cl), mg/L	441	1,752
Bicarbonate (HCO_3), mg/L	209.7	718.4
Carbonate (CO_3), mg/L	1.1	18.8
CO_2, mg/L	12.5	12.5
Nitrate (NO_3), mg/L	8.8	34.9
Silica (SiO_2), mg/L	15.0	59.6
Phosphate (PO_4), mg/L	<0.05	<0.05
Total dissolved solids, mg/L	1,256	4,939
Ionic strength	0.024	0.088

3.4. Simulation study for seawater

Based on the analysis of the feedwater, which corresponds to seawater after pretreatment for a municipal seawater desalination plant located on the Mediterranean coast, a study of the scaling potential for sparingly soluble species in the concentrate water operating at 45% recovery was conducted using ADICRO software. Table 2 shows

Table 2
Water chemistry of feedwater and concentrate water at 45% recovery for the municipal seawater desalination plant

Parameter	Feedwater	Simulation of concentrate water at 45% conversion
pH	8.20	8.33
Calcium (Ca), mg/L	526	954
Magnesium (Mg), mg/L	1,474	2,675
Sodium (Na), mg/L	12,382	22,465
Potassium (K), mg/L	453	822
Barium (Ba), mg/L	0.014	0.025
Strontium (Sr), mg/L	6.7	12.2
Iron (Fe), mg/L	0.067	0.122
Aluminium (Al), mg/L	0.019	0.034
Manganese (Mn), mg/L	0.319	0.578
Sulfate (SO_4), mg/L	2,927	5,311
Chloride (Cl), mg/L	22,452	40,740
Fluoride (F), mg/L	0.65	1.18
Bicarbonate (HCO_3), mg/L	182.0	302.5
Carbonate (CO_3), mg/L	11.7	34.3
CO_2, mg/L	1.3	1.3
Silica (SiO_2), mg/L	1.8	3.3
Ionic strength	0.736	1.301

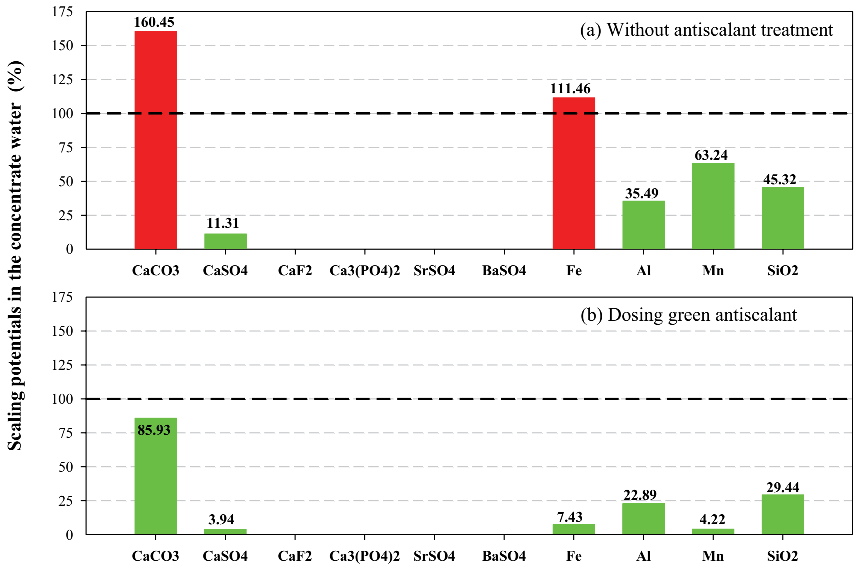

Fig. 2. Scaling potentials in the concentrate water for the municipal brackish water reverse osmosis plant at 75% recovery and 18°C temperature (a) without antiscalant treatment and (b) dosing green antiscalant.

the chemical composition of the feedwater and concentrate water at 45% recovery.

Fig. 3a shows the scaling potentials in the concentrate water without antiscalant treatment at a temperature of 20°C. The simulation results indicated that the solubilities of calcium carbonate ($CaCO_3$), barium sulfate ($BaSO_4$), iron (Fe) and manganese (Mn) would be exceeded in concentrate water without antiscalant treatment. For other compounds, scaling potentials were within admissible limits. Fig. 3b shows the reduction of scaling potentials in the concentrate water when dosing the recommended dose rate of green antiscalant. The scaling potentials for the calcium carbonate, barium sulfate, iron and manganese were reduced to values below 100% with antiscalant dosing. The reverse osmosis membranes were fully protected against scale formation on the membrane surface by dosing the green antiscalant.

3.5. Experimental study in reverse osmosis pilot plant to evaluate the effectiveness of the green antiscalant in preventing scaling

To evaluate the effectiveness of the antiscalant in preventing scaling, tests were conducted in the pilot plant using brackish water and seawater. For each type of water, two tests were conducted: one without antiscalant treatment and the other with green antiscalant dosing.

3.6. Effectiveness of the green antiscalant in brackish water

The effectiveness of the green antiscalant in brackish water was evaluated during the tests conducted in the reverse osmosis pilot plant fed with synthetic water that simulated the concentrate water operating at 75% recovery. The composition of the concentrate water is shown in Table 1. The pilot plant operated for 7 days. Figs. 4 and 5 show the evolution of normalized permeate flow per unit of membrane area (permeate flux) and Delta P without antiscalant treatment and with green antiscalant dosing. The results show that without antiscalant treatment, normalized permeate flux decreased by 60% and the Delta P increased by 385% over a period of 1.8 days. The decrease in flux and the increase in Delta P were due to the formation and deposition of scaling on the membrane surface. With the dosage of green antiscalant, the normalized permeate flux and Delta P remained constant, demonstrating its ability to prevent membrane scaling.

To validate the effectiveness of the antiscalant, an autopsy of the reverse osmosis elements was performed at the end of the tests, and membrane samples were analysed using the SEM-EDX technique. The membrane surface of the element used during the test in the absence of antiscalant was covered with a thick layer of deposit composed of calcium carbonate, as illustrated in Fig. 6a. The autopsy results of the element used during the test with the dosage of the green antiscalant indicated that no inorganic deposits were present on the membrane surface, as shown Fig. 6b. The sulphur peak detected in EDX spectrum of the membrane surface with green antiscalant dosing corresponds to the polysulfone support of the reverse osmosis membrane structure.

3.7. Effectiveness of the green antiscalant in seawater

Figs. 7 and 8 present the normalized permeate flow rate and Delta P for a 15 days operation of the pilot plant when fed with synthetic seawater concentrate at 45% recovery, respectively, comparing test results under untreated conditions and with green antiscalant dosing. The composition of the concentrate water is shown in Table 2. The results revealed that, without antiscalant, calcium carbonate precipitated on the membrane surface, leading to significant

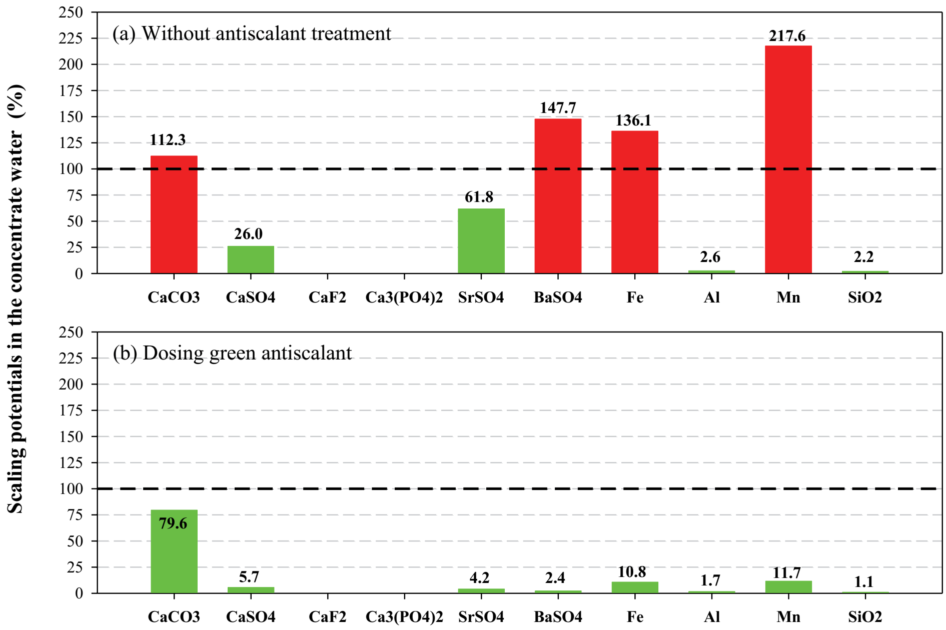

Fig. 3. Scaling potentials in the concentrate water for the municipal seawater desalination plant at 45% recovery and 20°C of temperature (a) without antiscalant treatment and (b) dosing green antiscalant.

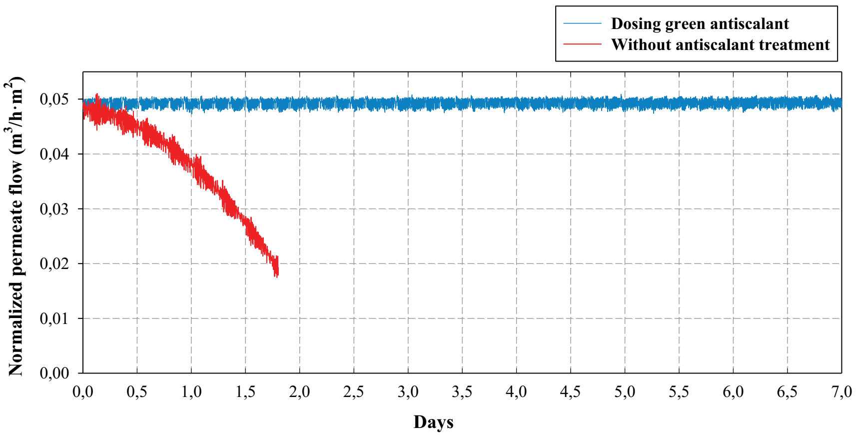

Fig. 4. Normalized permeate flux for the brackish water tests without and with green antiscalant dosing.

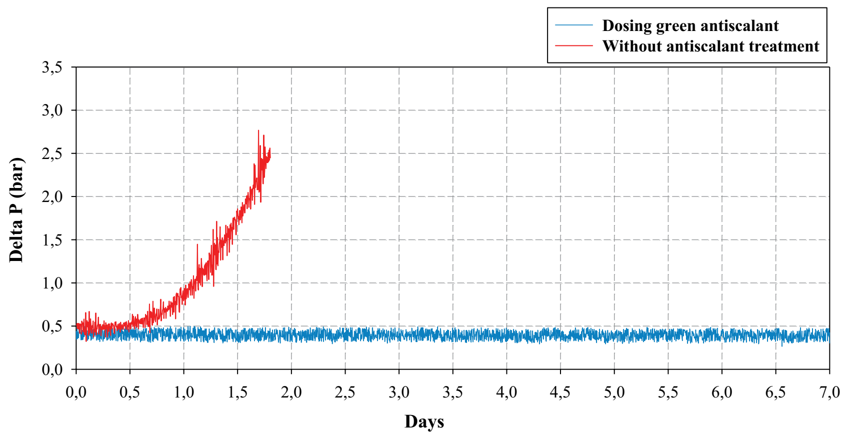

Fig. 5. Delta P for the brackish water tests without and with green antiscalant dosing.

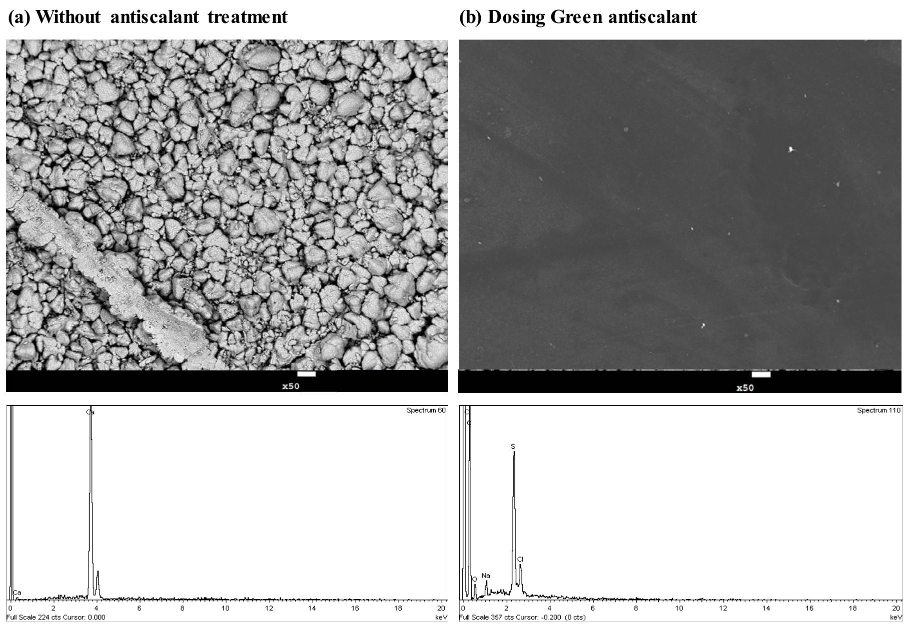

Fig. 6. Scanning electron microphotographs (50x magnification) and energy-dispersive X-ray analysis of the surface of reverse osmosis membranes used during the brackish water tests (a) without antiscalant treatment and (b) with green antiscalant dosing.

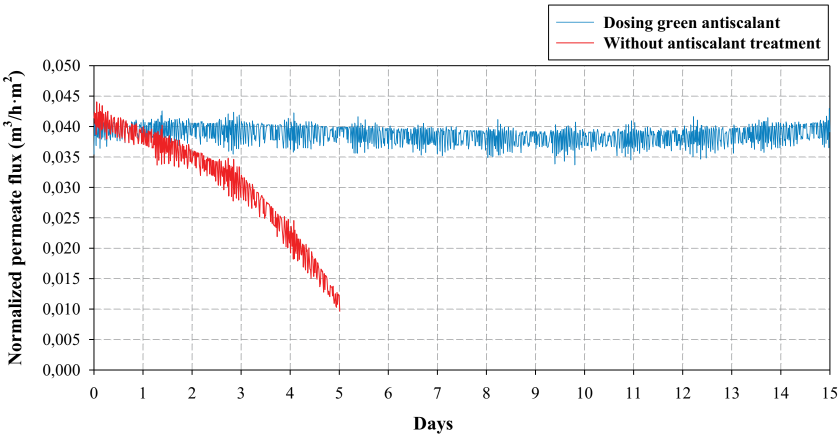

Fig. 7. Normalized permeate flux for the seawater tests without and with green antiscalant dosing.

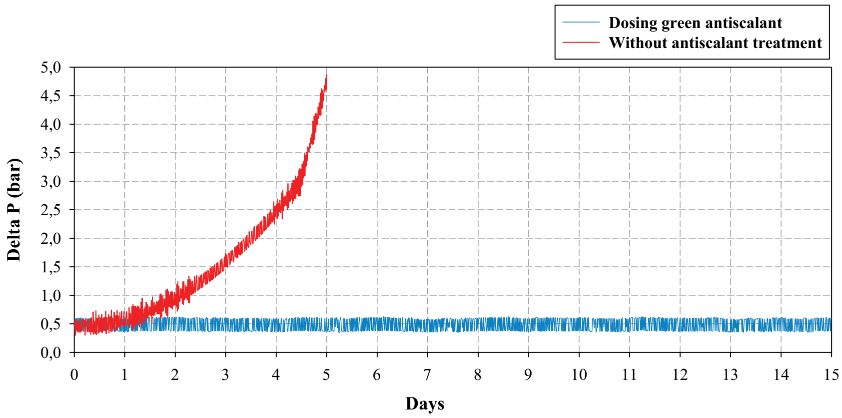

Fig. 8. Delta P for the seawater tests without and with green antiscalant dosing.

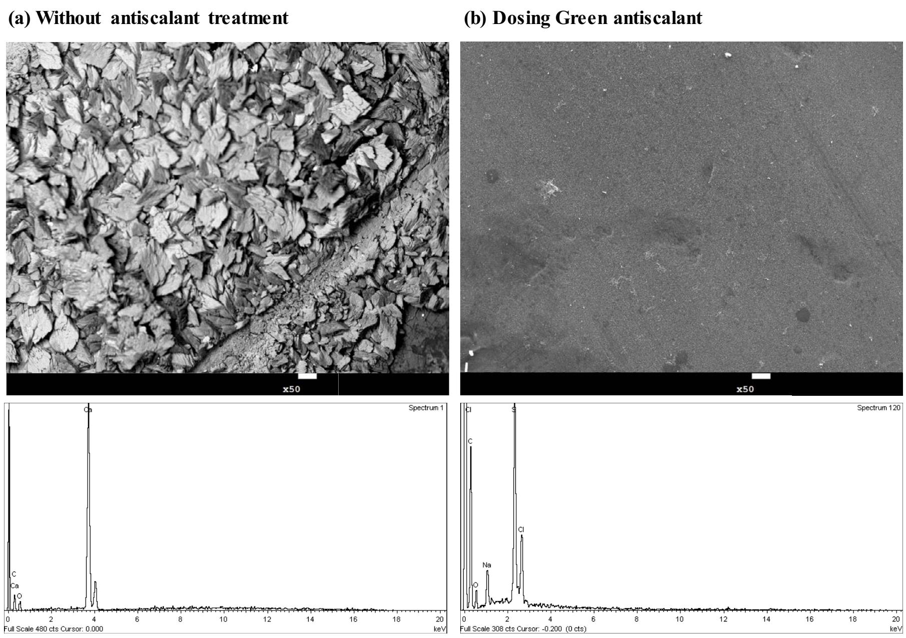

Fig. 9. Scanning electron microphotographs (50x magnification) and energy-dispersive X-ray analysis of the surface of reverse osmosis membranes used during the seawater tests (a) without antiscalant treatment and (b) with green antiscalant dosing.

decrease in normalized permeate flux and an increase in Delta P. The normalized permeate flux decreased by 76%, and the Delta P increased by 952% over a 5 d period. The loss of membrane performance without antiscalant treatment in seawater tests occurs over a longer time compared to brackish water, because the calcium carbonate scaling potential is lower, as shown in Figs. 2 and 3. However, green antiscalant dosing is effective in controlling scaling in seawater reverse osmosis systems, because the normalized permeate flux and Delta P remained constant.

Fig. 9 shows the SEM images and EDX analysis of the membrane surfaces from the tests conducted without and with green antiscalant treatment. As illustrated in Fig. 9a, without antiscalant treatment, the membrane surface was covered by a thick layer of deposits composed mainly of calcium carbonate, while no scaling was observed on the membrane surface when green antiscalant was dosed (Fig. 9b).

4. Conclusions

A broad-spectrum green antiscalant was developed. It is biodegradable, phosphorous-free, and highly effective in inhibiting scaling in both brackish and seawater municipal reverse osmosis plants. The study evaluated the biodegradability of the green antiscalant using OECD 302B standard method and confirmed that it is inherently biodegradable, making it suitable for municipal plants discharging to surface waters or offshore.

A dosing model for the green antiscalant was developed. The mathematical model was incorporated into the software ADICRO. The model was tested for both brackish water and seawater reverse osmosis plants. The software accurately predicts scaling potential and recommends optimal antiscalant dosages to ensure effective membrane protection against scaling.

Experimental tests in a reverse osmosis pilot plant confirmed the effectiveness of the green antiscalant in preventing scaling. In both brackish water and seawater tests, without antiscalant treatment, membrane scaling occurred, leading to decreased permeate flux and increased pressure drop. However, when dosing the green antiscalant, the membranes remained fully protected, and scaling was inhibited. Membrane autopsies confirmed the successful prevention of scaling with the green antiscalant, confirming its ability to maintain membrane efficiency and extend membrane lifetime.

Overall, the results of the study demonstrate the potential of the green antiscalant as a sustainable and cost-effective solution for membrane scaling control in municipal reverse osmosis applications. The use of the green antiscalant can contribute to ensuring a more reliable and efficient water supply in water-scarce regions, while also reducing the environmental impact associated with traditional antiscalants containing phosphorous compounds.

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