Green Inhibitor as Antibacteria and Antiscaling in Reverse Osmosis Desalination Plants

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ABSTRACT

Today, reverse osmosis membranes are the leading technology for new desalination installations, however, a challenge facing widespread application of RO technology is membrane fouling. In the present study, we used an environmentally friendly green inhibitor as anti-scaling and anti-biofouling in reverse osmosis (RO) desalination plants. The influence of Sargassum sp., Corallina mediterranea, and Avicennia marina on RO membrane mineral scaling was evaluated using gypsum as a model scalar. Antibacterial properties for three marine extracts from Sargassum sp., C. mediterranea, and Avicennia marina were investigated with Gram-positive bacteria (ArthroberscherantesfuriciumYACS14, Staphylococcus aureus) and Gram-negative bacteria (VibrioanwirilurnMVM425, Escherichia coli). The antimicrobial results were detected for the two selected extracts as the most potent extracts (ethy acetate, methanol crude extracts of the Avicennia marina leaves). Data showed that ratios of 3 and 5% recorded the highest suppression percentages (100%) for all tested bacteria including bacterial community collected from Eastern Harbor. On the other side, data confirmed that the anti-scalant properties by 100 ppm of Avicennia marina leave extract giving 85% of scale inhibition. The effect of Avicennia marina leaves extract for calcium sulfate dihydrate (gypsum) scaling on selected reverse osmosis (RO) membrane surfaces was investigated. The effect of different concentrations of Avicennia marina leaves extract was observed in the extent of surface scale coverage and surface crystal size among the membrane studied. Keywords: Anti-microbial, Anti-scaling, Green inhibitor, RO membrane, Desalination.

INTRODUCTION

The rapid increase demands for water resources, fresh water shortage has become an important issue affecting the economic and social development in many countries. As one of the main technologies for producing fresh water from saline water and other wastewater sources, membrane desalination has been widely used so far. However, a major challenge facing widespread application of membrane technology is membrane fouling, which results in reduced production capacity and increased operation costs. Therefore, many researches have been focused on enhancing the membrane resistance to fouling (HOEK et al., 2001).

Fouling by microorganisms and mineral scaling require frequent chemical cleaning and ultimately shortens membrane life, thus imposing a large economic burden on RO membrane plant operation (up to 50% of the total costs) (Jasbir et al., 1999). There are mainly four types of foulants in membrane fouling: inorganic (salt precipitations such as metal hydroxides and carbonates), organic (natural organic matters such as humic acid), colloidal (suspended particles such as silica) and biological (such as bacteria and fungi). Because desalination membranes are nonporous, the formation of a fouling layer on the membrane surface is referred to as the dominant fouling mechanism (Amjad, 1985, Greenlee et al., 2009). Membrane fouling is closely related to the interaction between the membrane surface and the foulants.

Marine organisms are a rich source of structurally novel and biologically active metabolites (Lima-Filho, et al., 2002; Chong et al., 2008). Many chemically unique compounds of marine origin with various biological activities have been isolated and have been used to develop new pharmaceuticals (Lima-Filho et al., 2002). The cell extracts and active constituents of various algae have been shown to have antibacterial activity in vitro against Gram-positive and Gram-negative bacteria (Borowitzka et al., 1992). A wide range of results of in vitro anti-fungal activities of extracts of green algae, diatoms, and dinoflagellates have also been reported (Moreau et al., 1988; Borowitzka et al., 1992).

Mangroves have enormous ecological value. They protect and stabilize coastlines, enrich coastal waters, yield commercial forest products and support coastal fisheries. Mangrove forests are among the world’s most productive ecosystems, producing organic carbon well in excess of the ecosystem requirements and contributing significantly to the global carbon cycle. Extracts from mangroves and mangrove-dependent species have proven active against human, animal and plant pathogens (Kathiresan et al., 2001).

Biofouling is referred to as the unwanted deposition and growth of biofilms. A biofilm is an assemblage of surface-associated microbial cells that is irreversibly associated (not removed by gentle rinsing) with a surface and enclosed in a matrix of extracellular polymeric substances. The formation of biofilms may occur on a wide variety of surfaces including living tissues, indwelling medical devices, industrial or potable water system piping, or natural aquatic systems (Shamsuddin et al., 2013). Micro-organisms are present in nearly all water systems and are capable of colonizing almost any surface (Baker et al., 1992).

In the present study, the antimicrobial and hence anti-biofilm activity against indicator strains and bacterial
community were described using three marine extracts from *Sargassum* sp., *Corallina mediterranea*, and *Avicennia marina* obtained from the coast of Mediterranean Sea Alexandria Egypt and Red sea. In addition, the impact of *Avicennia marina* leaf extract as an antifouling and biosorbent in pretreatments of input feed water were used to decrease the rate of fouling formation and as a green technology for RO membrane in water desalination plants.

**MATERIALS AND METHODS**

**Reference bacterial strains**

Antibacterial properties were investigated with Gram-positive bacteria (*Arthrobacter sulfureus* YACS14, *Staphylococcus aureus*) and Gram-negative bacteria, (*Vibrio anguillarum* MVM425, *Escherichia coli*).

**Chemicals and Media**

All chemicals used for biochemical tests and extraction of antimicrobial activity were of pure grade and purchased from Sigma chemicals, USA. Ingredients of media were all of analytical grade and obtained from recognized chemical suppliers (mainly Oxoid Co.).

Media used throughout the work are described below. The composition is given in g l⁻¹. The pH value of the media was adjusted to 7.5 prior to sterilization. Autoclaving was occurred at 121°C for 15 min.

Nutrient agar medium (Atlas, 1997) composed of: yeast extract, 2; beef extract, 1; peptone, 5; sodium chloride, 5. Agar (15-20) was added for obtaining nutrient agar medium.

**Extracts from different marine material**

Different marine material (*Sargassum* sp., *Corallina mediterranea* and *Avicennia marina*), were used for the extraction of bioactive substances to be applied in the inhibition of bacterial film formed by reference bacteria and bacterial community as whole in seawater. Seaweeds were collected from Mediterranean Sea, Alexandria coastline. While, mangrove plant (*Avicennia marina*), especially leaves and fruits, were collected from Safaga region in the Red Sea. This type of mangrove plant was the most abundant species in such area of the Red Sea. Ten grams of each marine material were macerated with 50 ml of 70% aqueous methanol and ethyl acetate. After soaking for a week with gently shaking, they were filtered through whatman 542 filter paper. Methanol and ethyl acetate was evaporated using rotary evaporator to obtain aqueous soluble extracts (*Ballantine et al.*, 1987). The residues (crude extracts) obtained were finally dried under vacuum.

**Antibacterial activity**

**Well-cut diffusion technique**

The well-cut diffusion technique was used to test the ability of eight extracts from collected seaweeds and mangrove plant (*Avicennia marina*) to inhibit the growth of indicator bacteria. Fifty millimeters of nutrient agar medium were inoculated with indicator micro-organisms and then poured into each plate. After solidifying, wells were punched out using 0.5 cm cork borer, and each of their bottoms was then sealed with two drops of sterile water agar. Then 100 µl (200 µg) of each algal extract were transferred into each well aftersterilizing by ultra-filtration using 0.22 µm sterilized filters. A plate loaded with only solvent was similarly prepared as a control. All plates were incubated at 30°C for 24-48 hr.

After incubation period, the radius of clear zone around each well (Y) and the radius of the well (X) were linearly measured in mm, where dividing Y; over X² determines an absolute unit (AU) for the clear zone. The absolute unit of each crude extract, which indicates a positive result in the antimicrobial action, was calculated according to the following equation (*Yang et al.*, 1992):

\[
AU = Y^2/X^2 \quad (1)
\]

**Pouring technique**

Nutrient agar was prepared and then 24 h old -indicator strain was added in 0.1%. The crude extracts were added to yield 0.5, 1, 3, and 5% (v/v). Control was prepared without any crude. After incubation period, the count of indicator pathogen(s) used was determined. Comparing the treated with crude extracts to control, then the suppression percentages were calculated according to the following equation (*Al-Ajlani et al.*, 2006):

\[
\text{suppression} \% = \frac{C_{\text{control}} - C_{\text{moment}}}{C_{\text{control}}} \times 100 \quad (2)
\]

Where (C) refers to bacterial count as cfu/ml

**Solution preparation for antiscaling**

Double distilled water and analytical reagent-grade NaCl, Na₂SO₄ and CaCl₂.2H₂O were used for preparing synthetic brine solutions. Calcium brine solution was prepared according to the following salt concentration (7.5 g/l NaCl + 11.0 g/l CaCl₂.2H₂O) and Sulfate containing solution (7.5 g/l NaCl + 10.66g/l Na₂SO₄) (*Gouellec et al.*, 2002). The 0.7 M NaCl solution was chosen to produce the total ionic strength of natural seawater at 35000 ppm salinity.

Ten grams of each marine material were macerated with 50 ml of 70% aqueous methanol and ethyl acetate. After soaking for a week with gently shaking, they were filtered through whatman 542 filter paper. Methanol and ethyl acetate was evaporated using rotary evaporator to obtain aqueous soluble extracts. The extract solutions were then filtered to remove any contamination (Atlas, 1997). The concentration of the stock solution was determined by evaporating 10 ml of the filtrate and weighing the residue. The concentration of the stock solution was expressed in term of grams per liter.

The supersaturated solutions were prepared in (250 ml) bottles by mixing equal volumes (50 ml) of brine calcium chloride and brine sodium sulfate solutions. Then 12 bottles of the same supersaturated solutions with different concentration level of seaweeds and mangrove leaf extract from 0, 25, 50 and 100 mg/l are introduced in the calcium brine solutions before mixing with brine sodium sulfate solutions. The four bottles of
each additive were placed in constant temperature shaking water bath maintained at 50 - 60°C for 72 h and around pH of 6.5. After that the concentration level of calcium ions remained in the solution was evaluated according to Standard Test Method for Hardness in Water (Abdel-Gaber et al., 2008).

The percentage of scale inhibition can be determined from the following equation (Lin et al., 1988)

\[
\% \text{ Inhibition} = 100 \times \frac{(\text{Ca}-\text{Cb})}{(\text{Cc}-\text{Cb})} \quad (3)
\]

Where, \( \text{Ca}-\text{Ca}^{2+} \) concentration in the treated sample after precipitation, \( \text{Cb}-\text{Ca}^{2+} \) concentration in the blank after precipitation, \( \text{Cc}-\text{Ca}^{2+} \) concentration in the blank before precipitation.

Materials and Membrane test system

A commercial TFC (thin film composite) RO membrane TW30-1812-80 (Reverse Osmosis Element, USA) was used in RO scaling tests. The reverse osmosis performance of the PA-TFC membranes was evaluated through measuring both permeates flux (L/m².h) and salt rejection (%). Permeate flux and salt rejection were measured using ALFA LAVAL pilot-scale laboratory unit for membrane filtration laboratory unit M20 (Fig. 1) and aqueous feed solution containing 2000 ppm NaCl with pH range 7± 0.2 at 25°C. The flow rate was 1g/min and the applied pressure was 225 psi (15.5 bar). All flux and rejection measurements were evaluated after 90 min from the start of cross flow experiment to ensure that the filtration process had reached steady state.

All membrane samples were extracted from an 8 spiral wound module, stored at 4°C. These samples were then thoroughly rinsed it with MilliQ water and soaked in MilliQ water baths for 24h to remove preservation agents prior to characterization and/or ageing. Water baths were periodically renewed and a final bath was stored overnight at 4°C. The minimum number of membranes that can be used is 2 and the maximum is 20. The effective membrane area is 0.018 m².

The permeate flux (\( JW \)) through a membrane area (\( A \)) was calculated as the volume (\( \Delta V \)) collected during a time period \( \Delta t \)

\[
JW = \frac{\Delta V}{A \cdot \Delta t} \quad (4)
\]

Also, the salt rejection (Rs %) was calculated by measuring the electric conductivity of both feed and permeate solutions using a conductivity meter. The salt rejection percent (Rs %) was calculated as follows:

\[
Rs\% = \frac{(Cf - Cp/Cf) \times 100}{(5)}
\]

Where, Cf and Cp are the concentrations of the feed and permeate water (product), respectively.

Membrane mineral scaling tests

The feed-water was prepared by rapidly mixing equimolar solutions of calcium chloride (\( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \)) and anhydrous sodium sulfate (\( \text{Na}_2\text{SO}_4 \)), with targeted chemical composition of the final solution close to its saturation index (SI₂). All solutions were prepared with analytical grade chemicals purchased from Sigma-Aldrich Co and DI water. The feed solution was well characterized, prior to filtration tests, by measuring pH and Total dissolved salts (TDS) via a laboratory multi-parameter meter (ino Lab 750 pH/ION/Cond multi lab, WTW-GmbH, Germany) and the feed water composition for membrane scaling test was 4880 mg/L total dissolved solids with a bulk gypsum saturation index (SI₂ = 0.94 and pH = 7.1. The bulk supersaturation ratio of the precipitate for the feed water source and scaling solution were calculated as:

\[
s = \sqrt{\frac{\Delta C}{K_sp}} \quad (6)
\]

Where \( \Delta C \) - \( K_sp \) are the activities of calcium and sulfate ions, respectively, computed by the PHREEQC code (version 2.18.00) (Parkhurst et al., 1999) using the “Pitzer” database. The value of thermodynamic solubility product \( K_sp \) was also obtained through that software. The supersaturation index SI₂ alternatively employed in some publications, is defined as:

\[
SI₂ = 2 \log S. \quad (7)
\]

GC-MS analysis

Identification of the chemical moiety of crude extracts of mangrove leaves and mangrove fruits which showed highest antibacterial activities was carried out using GC-MS (Trace DSQ II MS). The maximum peaks representing mass to charge ratio characteristics of the antimicrobial fractions were compared with those in the mass spectrum library of the corresponding organic compounds. The concentration of such compound was also obtained through that software. The supersaturation index SI₂ alternatively employed in some publications, is defined as:

\[
SI₂ = 2 \log S. \quad (7)
\]

Morphology characterization

The change of crystal habits and morphology of the calcium sulfate dihydrate were examined through SEM and XRD studies, using JOEL JSM 840 S Scanning microscope and using JOEL-8030 X-ray diffract meter for these scales formed without and with the presence of algae and the mangrove leaf extract were taken.
**Results and discussion**

**Antimicrobial activity of marine extracts**

Eight crude extracts from (algae and mangrove) were screened for antibacterial activity against indicator strains and marine bacterial community using well-cut diffusion technique. The data in Table (1) reveal that, the antibacterial activity ranged between 1.2 and 25 AU. In addition, the methanol and ethyl acetate extracts of *A. marina* leaves exhibited broad spectra of antibacterial activity and recorded the highest AU values. The most indicator bacteria affected were: *S. aureus* (AU=24) by methanol extract and *V. anguillarum* (AU=25) by ethyl acetate. The lowest activities were observed against *S. aureus* (AU=1.2) by methanol extract of *Sargassum sp.* Regarding the bacterial community, it was little affected by the eight crude extracts, since its AUs ranged between 1.8 and 5.8. The methanol extract of *Avicennia marina* leaves yielded activity (AU=5.8) against bacterial community.

| Table (1): Screening the antibacterial activity of several marine natural extracts expressed as absolute unit (AU) |
|--------------------------------------------------|--------------------------------------------------|------------------------------------|------------------|------------------|
| **Marine substrate (CE)** | **Extraction solvent** | **Indicator bacteria/Suppression %** | **S. aureus** | **A. sulfureus** | **V. anguillarum** | **E. coli** | **Bacterial community** |
| Sargassum sp. | Methanol | 1.2 | 1.6 | ND | ND | ND | ND |
| Sargassum sp. | Ethyl acetate | ND | ND | 2.4 | ND | ND | ND |
| *A. marina* (L) | Methanol | 24.0 | 9.0 | 13.0 | 5.8 | 5.8 | 5.8 |
| *A. marina* (L) | Ethyl acetate | 16.0 | 17.8 | 25.0 | 16.0 | 4.3 | 4.3 |
| *A. marina* (S) | Methanol | 3.4 | ND | 4.8 | ND | 1.8 | 1.8 |
| *A. marina* (S) | Ethyl acetate | ND | 1.6 | ND | 2.8 | ND | ND |
| *C. mediterranea* | Methanol | 3.2 | ND | 3.2 | ND | ND | ND |
| *C. mediterranea* | Ethyl acetate | ND | 1.3 | ND | 2.4 | 2.4 |

L= leaves of mangrove (*A. marina*), while S= stem of mangrove (*A. marina*).

On the other side, applying pouring technique in order to detect the antibacterial activity of the most potent crude extracts (CE) revealed that, the two extracts (methanol and ethyl acetate extracts of *Avicennia marina* leaves) were selected. In such manner, to optimize the crude extract addition, each crude extract was added to the medium of bacterial growth (indicator strains and bacterial community) in four identified concentration percentages (0.5, 1, 3, and 5%).

Data shown in Table 2 conducted that; ratios of 3 and 5% recorded the highest suppression percentage (100%) for all tested bacteria. Other high suppression percentage (90%) was recorded at 1% amendment of ethyl acetate extract of *A. marina* leaves. Moreover, addition of 0.5% of both crude extracts and 1% of methanol extract of *A. marina* leaves, showed wide variations in the suppression of tested bacteria ranging from 10-100%. From all previous data, the present investigation confirmed the antibiofilm properties of *Avicennia marina* leaves (*A. marina*) extracts either Shamsuddin et al., 2013 by ethyl acetate or methanol solvents.

**GC - MS analysis**

The GC-MS patterns of the major constituents in the powerful crude extract (both aqueous ethyl acetate and methanol extracts of *Avicennia marina* leaves). Actually, the GC-MS patterns confirmed extraction of several groups of compounds such as; fatty acids and their derivatives, carboxylic acids and terpenoids (Table 3 and 4). The dominant fatty acids detected in the crude extracts were palmitic acid and oleic acid, while fatty acids derivatives were methyl ester of hexadecanoic. However, the recorded terpenoids were mainly determined as carotenoids like; lupeol (ex: triterpene). Moreover, cinnamic acid was detected as an unsaturated carboxylic acid.

| Table (2): Screening the antibacterial activity of the most effective extracts in different percentages and response was expressed in the count of indicator bacteria treated with different extracts in corresponding to controls and bacterial community (2x10^5 CFU/ml) |
|--------------------------------------------------|--------------------------------------------------|------------------------------------|------------------|------------------|
| **Marine substrate** | **Extraction solvent** | **Ratio (%) (CE)** | **Indicator bacteria/Suppression %** | **S. aureus** | **A. sulfureus** | **E. coli** | **V. anguillarum** | **Bacterial community** |
| *A. marina* (L) | Ethyl acetate | 0.5 | 50 | 40 | 45 | 55 | 40 | 40 |
| *A. marina* (L) | Ethyl acetate | 1 | 75 | 65 | 100 | 90 | 100 | 100 |
| *A. marina* (L) | Ethyl acetate | 3 | 100 | 100 | 100 | 100 | 100 | 100 |
| *A. marina* (L) | Ethyl acetate | 5 | 100 | 100 | 100 | 100 | 100 | 100 |
| *A. marina* (L) | Methanol | 0.5 | 55 | 20 | 50 | 60 | 35 | 35 |
| *A. marina* (L) | Methanol | 1 | 60 | 60 | 85 | 100 | 85 | 85 |
| *A. marina* (L) | Methanol | 3 | 100 | 100 | 100 | 100 | 100 | 100 |
| *A. marina* (L) | Methanol | 5 | 100 | 100 | 100 | 100 | 100 | 100 |

L= leaves of mangrove (*A. marina*).

| Table (3): GC - MS of major components of *A. marina* leaves extract in ethyl acetate. |
|--------------------------------------------------|--------------------------------------------------|------------------------------------|------------------|------------------|
| **No.** | **Compound** | **Molecular formula** | **Molecular weight** | **Retention time (min)** | **Area (%)** |
| 1 | Cinnamic acid (2-propenoic acid, 3-phenyl) | C_{10}H_{8}O_{2} | 148 | 12.8 | 65.9 |
| 2 | Hexadecanoic methyl ester | C_{16}H_{32}O_{2} | 270 | 20.9 | 18.6 |
| 3 | Palmitic acid (n-Hexadecanoic acid) | C_{16}H_{34}O_{2} | 256 | 21.7 | 67.7 |
| 4 | Oleic acid | C_{18}H_{34}O_{2} | 282 | 25.0 | 33.4 |
| 5 | Lupeol | C_{26}H_{46}O_{2} | 426 | 50.4 | 49.0 |
Effect of some Green additives on scale formation of CaSO₄.2H₂O (gypsum)

Mineral scaling tests were performed with gypsum as the model scalant in order to illustrate the impact of some green additives on mineral scaling. Currently plants extracts are employed as inhibitors in order to develop new cleaning chemicals for a green environment. The precipitation behavior of supersaturated calcium sulfate solutions with different dosage of additives was shown in table (5). The precipitate was collected after filtering and drying the sample at the end of the experiment. The XRD and SEM of the collected precipitate indicate that the scale formed is gypsum (CaSO₄.2H₂O).

The impact of antiscalants on local morphology of surface crystals is of interest for direct assessment of antiscalant effectiveness. From the data in the table (5), we noticed that the most effective concentration of antiscalants is 100 ppm and it was found that Avicennia marina (L) is the most effective green inhibitor. As shown in the table (5), it can be seen that the degree of inhibition of the antiscalant on gypsum decreased in the following order:

Avicennia marina (L) extract > C. Mediterranean extract > Sargassum sp. extract.

Table (4): GC–MS of major components of A. marina leaves extract in methanol.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Retention time (min)</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cinnamic acid (2-Propenoic acid, 3-phenyl)</td>
<td>C₉H₈O₂</td>
<td>148</td>
<td>12.7</td>
<td>11.75</td>
</tr>
<tr>
<td>2</td>
<td>Palmitic acid (n-Hexadecanoic acid)</td>
<td>C₁₆H₃₂O₂</td>
<td>256</td>
<td>21.2</td>
<td>48.1</td>
</tr>
<tr>
<td>3</td>
<td>Oleic acid</td>
<td>C₁₈H₃₄O₂</td>
<td>282</td>
<td>25.6</td>
<td>11.1</td>
</tr>
<tr>
<td>4</td>
<td>Lupeol</td>
<td>C₃₀H₅₀O₄</td>
<td>426</td>
<td>51.5</td>
<td>26.8</td>
</tr>
</tbody>
</table>

Table (5): Effect of some green additives on scale formation of (gypsum).

<table>
<thead>
<tr>
<th>Name of additives</th>
<th>Conc. of additives (ppm)</th>
<th>Inhibition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicennia marina extract (L)</td>
<td>100</td>
<td>85.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>72.47</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>63.22</td>
</tr>
<tr>
<td>Corallina Mediterranean extract</td>
<td>100</td>
<td>68.29</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>60.00</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>52.15</td>
</tr>
<tr>
<td>Sargassum sp. extract</td>
<td>100</td>
<td>55.09</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>48.78</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>39.85</td>
</tr>
</tbody>
</table>

The calcium sulfate dihydrate scale in the blank and with additives deposit were observed by scanning electron microscope (SEM) to examine direct images as shown in figure (2). It reveals that the shape of calcium sulfate dihydrate crystal is regular needle-like, the surface is smooth and compact without additives (Fig. 2a).

Anti-scalants is one of the most effective methods for controlling scale formation in either thermal or RO desalination processes. Sargassum sp. extract inhibition effect on gypsum scaling was the same as Corallina Mediterranean extract as shown in figure (2b and c).

Figure (2): SEM of Gypsum a) without additives, b) after treatment with Sargassum sp, c) after treatment with Corallina Mediterranean, d) after treatment with Avicenния marina extract. Avicennia marina leaves extract (M) had the best effect on the number of crystals formed. The numbers of crystals with the treatment of three extracts were very less than the blank. Avicennia marina extract made distortion to the crystal morphology which formed during the test, and this was shown in figure (2d).
Green Inhibitor as Anti-bacteria and Anti-scaling in Reverse Osmosis Desalination Plants

In calcium sulfate dihydrate supersaturated solution containing the antiscalants were adsorbed towards the crystal growth point, inhibiting or retarding the growth of crystals to enable the supersaturated solution to achieve a state of temporary stabilization. However, (Hamdona et al., 2008) slow growing faces without adsorbed inhibitors can achieve a certain amount of growth in the induction period and covered the inhibitor molecules adsorbed on active sites such that the crystal can grow again but with poor directionality (Amjad, 1985). In this case, the crystal habit was also distorted and deformed. Thus, after the addition of inhibitors, the crystal morphology of the precipitates changes and their lattice is distorted. This also contributes with the result of Amjad and Hamdona who studied influence of additives on the precipitation of gypsum (Sahoo et al., 2012).

Effect of Green Antifouling for gypsum scale on RO membrane

Scaling by inorganic compounds such as calcium carbonate and sulfate is formed in the feed spacers and on the membrane surface and block the flow. This type of fouling may be controlled by injecting an anti-scalant and/or acid Liu et al., 1973.

Batch tests were carried out to demonstrate the effect of antiscalant Avicennia marina leaves extract (M) to prevent or reduce membrane fouling. SEM indicated that the crystallization of gypsum was highly reduced in presence of 100 ppm of the antiscalants (M). A few rod like crystals were seen on the membrane, which had typical hexagonal prism shape of gypsum crystals. Each crystal was found with one end fractured looking like a broom which might be possible due to drying and/or vigorous growth resulting in bursting out of the parent crystal at one end into a bunch of small crystals. The mechanism of crystallization was understood as the particulate fouling, which was very apparent as the crystals were seen as if formed in the bulk and settled on the membrane. They were not observed as if rooted to the membrane surface. However, the general understanding demonstrates that the antiscalant adsorbs onto the formed crystals or complexes with incipient nuclei, there by inhibiting salt crystal growth (Liu et al., 1973, Azuma et al., 2002). The presence of big gypsum crystals on the membrane surface may be possible due to the inception of gypsum nuclei at the start of the test when the antiscalant concentration was decreased in the solution. With time, these small crystals grow in size in the supersaturated CaSO₄ solution.

In this study, data of permeate flux and salt rejection of the antiscalant solution test (M) with different concentrations 25, 50, 100 ppm are presented in figures (3,4 ), showing decreased in membrane performance in comparison with scaling test without additive addition, the water flux and salt rejections showed slighter changes compared with blank (M = 0).

![Comparison of permeate flux at different concentrations of additive (M).](image1)

![Comparison of salt rejection % between different concentrations of additive (M).](image2)

![SEM images of calcium sulphate particles on the desalination membrane, a) Without additive, b) With additive M (25 ppm), c) With additive M (50 ppm), d) With additive M (100 ppm). Desalination time 90 min.](image3)
CONCLUSION

The results showed that methanol is an efficient solvent for extracting the bioactive materials and the significant inhibition zones were observed for methanol extracts. The efficiency of Avicennia marina leaf extracts (M) as antibacterial agents and hence inhibiting the bacterial film formation, which is considered the main starter in biofouling problem. Preliminary experiments have been initiated to study the precipitation behavior of (gypsum) without and with some green inhibitors at saturation Index level (SIg = 4.1), pH = 6.5 and temperatures 60°C. The degree of inhibition of gypsum scale in the presence of these inhibitors in the following order: Avicennia marina (M) > C. Mediterranean > Sargassum sp. extract at different dosage.

Mitigation of membrane mineral salt scaling (saturation Index levels SIg = 0.94) by antiscalant addition to the feed (M = 25, 50,100 ppm) demonstrated a significant reduction in surface crystals size and less defined facets of rosette needlelike arms with increased antiscalant dosage. SEM indicated that the gypsum scaling was highly reduced in presence of 100 ppm of the antiscalants (M).

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Pharmacy and Pharmaceutical Sciences, 5(8): 672-675.


المثبتات الخضراء كمضاد للبكتيريا ومكافحة التكلسات في محطات التحلية باستخدام التناظح العكسي

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الملخص العربي

اليوم نجد أن أغشية التناظح العكسي هي التكنولوجيا الرائدة في مجال التحلية للمناطق الجديدة، ومع ذلك، فإن التحدي الذي يواجه التطبيق الواقعي لتقنية التناظح العكسي هو القطرانات التي تتكون على الغشاء. في الدراسة الحالية، استخدمنا مثبتات من البيئة البحرية وهي مصدرة للبيئة كمضاد للتكتل والبكتيريا في محطات تحلية المياه بتقنية التناظح العكسي RO (Reverse Osmosis). تم تقييم تأثير سارجاموس، كورالينا ميديتيرانيا، ونباتات الافيسينيا على معدل تكون القطران المعدني على غشاء RO باستخدام الجرب حماة نموذجية. تم فحص خصائص مضادة للجراثيم ثلاثة مستخلصات بحرية من سارجاموس، ميديتيرانيا، ونباتات الافيسينيا مع البكتيريا جرام موجب (Arthrobacter sulfurificus YACS14) والبكتيريا سالبة الجرام (Staphylococcus aureus, Vibrio anguillarum MVM425). تم تسجيل النتائج للميكروبات للمضادة للمستقبلين المختارين (Escherichia coli, Vibrio anguillarum MVM425).

AVICENNA MARINA

كمستخلص أقوى (خلات الاميل، مستخلصات الميثانول الخام من أوراق Avicenna marina) وأظهرت البيانات أن نسبتي 3 و 5% سجلت أعلى نسب كمبلتة (100%) لجميع البكتيريا المختبرة بما في ذلك المجتمع البكتيري الذي تم جمعه من Eastern Harbour. على الجانب الآخر، أكدت البيانات أن خصائص المضادة للتكثت بمعدل 100 جزء من المليون من مستخلص أوراق "الافيسينيا" تمنع 85% من تكوين التكتلات. تم دراسة تأثير مستخلص أوراق الافيسينيا المستخرجة من مستخلص ورق هذا النبات على سطح غشاء التناظح العكسي. ولاحظ تأثير تركز مختلفة من مستخلص أوراق نبات في مدى تثبيط النمو البلوري وأيضا التأثير على حجم البلورة على سطح الغشاء محل الدراسة.