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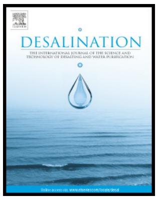

Antiscaling effect of polyaspartic acid and its derivative for RO membranes used for saline wastewater and brackish water desalination

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HIGHLIGHTS

- PASP and its derivate were investigated as greener RO antiscalants.
- PASP derivate showed better antiscaling effect than PASP and a commercial product.
- PASP derivate led to larger crystals and a less dense scale layer on the RO membrane.
- PASP and its derivative appeared to be cost-effective.

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ABSTRACT

Polyaspartic acid (PASP) and its derivative (PASP-SEA-ASP) were tested as environmentally benign scale inhibitors at lab scale for a polyamide reverse osmosis (RO) membrane in the desalination of a synthetic brackish water containing various scale-forming ions. Their performance was compared with a commercially available RO antiscalant which contains phosphonic acid. The addition of the scaling inhibitors to feedwater led to increase in water recovery and removal efficiency of inorganic matter for the RO unit operated under constant transmembrane pressure, with PASP-SEA-ASP giving greater water recovery (90%) than PASP (87%) and the commercial antiscalant (85%). PASP-SEA-ASP was superior to PASP and the commercial antiscalant in scaling inhibitor/fouling reduction due to the reduced deposition of the scale forming ions on the membrane. Examination of the used membranes with scanning electron microscopy and X-ray diffraction suggested the different effect of the antiscalants was related to the resultant crystalline morphology on the membrane surface. The PASP and its derivative appeared to be more cost effective in maintaining permeate flux and inhibiting the formation of a dense scale layer. The present study demonstrated the great potential of these non-phosphorus containing agents for scale inhibition in domestic and industrial wastewater reclamation and brackish water desalination applications.

1. Introduction

Membrane fouling caused by inorganic, organic and biological materials is a major problem limiting the efficiency of reverse osmosis (RO) based wastewater reclamation and brackish water desalination processes. Inorganic fouling, known as scaling, occurs after deposition of inorganic constituents on the RO membranes. The most common scale-forming constituents in membrane processes are $CaSO_4$, $CaCO_3$, $BaSO_4$, calcium phosphates, silica, aluminum and ferric hydroxides [1,2]. Scaling can reduce permeate flow due to formation of a cake layer by surface blockage and/or bulk crystallisation with the inorganic deposits [3], leading to significantly increased operational cost for the membrane systems. Scaling may also physically damage the membranes because of ineffective scale removal and occurrence of irreversible pore plugging during filtration. As such, scaling mitigation is a critical measure to ensure efficient RO operation for wastewater reclamation and brackish water desalination.

Several methods can be used to prevent the scaling of RO membranes, including (i) acidification of feedwater to reduce bicarbonate by converting it into carbon dioxide, (ii) scale inhibitor chemicals which change the physical and chemical nature of the depositor ions and hence the scale growth mechanisms, (iii) operating conditions of RO systems, and (iv) softening with lime or soda ash which react with bicarbonate in the feed to produce $CaCO_3$ sludge [4,5]. Antiscalants are used widely in RO processes due to their high effectiveness for preventing scaling. Antiscalants generally delay scale formation and allow higher water recovery by hindering scale growth under supersaturated conditions [6]. Reitz [7] investigated a number of commercial antiscalants for the control of scaling caused by $SrSO_4$, $CaSO_4$ and

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$CaCO_3$ in RO systems and found that they were effective for inhibiting $CaCO_3$ precipitation. Another study by Lisitsin et al. [8] reported that zinc ion was promising to mitigate scaling for membrane processes. However, many commercial antiscalants can enhance biofouling of RO systems as they contain nutrients such as phosphorus [9,10,11]. Moreover, phosphorus-containing antiscalants remaining in the RO concentrate/brine can contribute to eutrophication of the receiving water bodies and consequent blooms of harmful algae. It has been suggested that most of the commercially available antiscalants are expensive, and could account for approximately 10% of the total treatment cost for the production of clean water [12]. As such, the development of low-environmental risk and cost-effective antiscalants is required for improving the sustainability of RO-based water purification processes.

Polyaspartic acid (PASP) is a polyamino acid which does not contain phosphorus and is biodegradable. It was reported as being an environmentally friendly antiscalant in the freshwater environment [13]. The functional groups of PASP have a scale inhibition effect as they have a side chain generated through the aminolysis reaction with amine-group [14]. Gao et al. [15,16] synthesised a PASP derivative (PASP-ASP) with the aim of enhancing the chelating performance of PASP through the introduction of carboxylic acid to its side chain, and the experimental study demonstrated the improved scale inhibition effect of the derivative in freshwater applications. It was suggested that PASP could ionise and form molecular chains of negative charge, leading to the formation of water-soluble complexes with Ca^{2+} and hence reduced deposition of the scale causing ions on membrane surface [13]. They also synthesised a PASP derivative (PASP-SEA-ASP) for enhancing both chelation and dispersion performance by introducing sulfonic acid and carboxylic acid to the side chain of PASP, with a view to inhibiting scale formation in a saline water environment such as seawater [17]. As there is a sulfonic acid group in the molecular structure of PASP-SEA-ASP, and when PASP-SEA-ASP is adsorbed onto the small crystal particles, a double layer can be formed and the charge state of the particle surface is changed. This can result in enhanced dispersion of the crystal particles in water. Although PASP and its derivative exhibited a promising antiscaling effect on carbon steel in freshwater and seawater for potential industrial applications such as scale inhibition for heat exchangers and water pipes, their effect on scale inhibition for polymeric RO membranes used for wastewater and brackish water desalination has not been investigated.

The present study was aimed at examining the antiscaling effect of PASP and its derivative PASP-SEA-ASP on polyamide RO membranes used for the desalination of a synthetic saline water containing various scale-forming ions, and to compare them with a phosphorus-containing commercial RO antiscalant. The antiscaling effect was assessed by determining the filtration performance in terms of water recovery within the test period and removal efficiency of inorganic matter, the quantity and chemical composition of the scale on the membranes, and examining the scale crystals formed on the membrane surface using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Materials and methods

2.1. RO feedwater

The chemical composition of the synthetic feedwater used for the RO tests is shown in Table 1. The chemicals were selected based on their wide occurrence in the scale on RO membranes. The chemical reagents used for the preparation of the RO feedwater were of analytical grade, supplied by Sigma-Aldrich.

Table 1
Composition of the synthetic RO feedwater.

Composition/property	Unit	Concentration
NaCl	mg/L	15,000
$CaCl_2$	mg/L	8000
$MgSO_4$	mg/L	2000
SiO_2	mg/L	1000
pH	–	7.9
Conductivity	µs/cm	52,800

2.2. Antiscalants

A commercial RO antiscalant that is widely used for wastewater desalination in many countries including Australia was tested in this study. According to the manufacturer, the antiscalant is based on phosphonic acid and polycarboxylic acid. The PASP and PASP-SEA-ASP were synthesised in our lab with the methods described in Section 2.3. The purity of PASP and PASP-SEA-ASP was determined as 99% and 98.5%, respectively. The antiscalant dosage of 1 mg/L (1 ppm) was used for all RO antiscaling experiments.

2.3. Synthesis of antiscalants

2.3.1. PASP

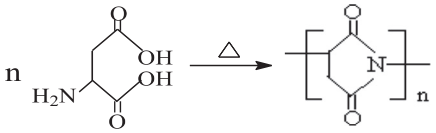
PASP was synthesised through two steps. The first step was the synthesis of polysuccinimide, which was carried out in an electric thermostatic drying oven through pyro-condensation of L-aspartic acid (Industrial grade, Sigma Aldrich) monomer at 240 °C for 4 h. The second step was the synthesis of PASP. Firstly, polysuccinimide was suspended in three times its weight of water. The aqueous polysuccinimide suspension was stirred at 12 °C, and then NaOH solution (15%, industrial grade) was added. The reaction was for 4 h at 12 °C and pH 8–9. Solid PASP was obtained through the separation process involving the addition of double volume of absolute alcohol, washing of the resultant precipitates with deionised water, and then drying at 80 °C for 48 h. PASP stock solution (36%) was prepared by dissolving the solid PASP in deionised water. The relevant synthetic reactions are expressed in Schemes 1 and 2.

2.3.2. PASP-SEA-ASP

Synthesis of PASP-SEA-ASP was through two steps. In the first step, polysuccinimide was synthesised as described in Section 2.3.1. The second step was the synthesis of PASP-SEA-ASP, in which polysuccinimide was first suspended in three times its weight of water. The polysuccinimide suspension was stirred at 25 °C, and then aspartic acid and 2-aminoethanesulfonic (Industrial grade, Sigma Aldrich) which were dissolved in NaOH solutions (15%) were added. The reaction was for 24 h at 25 °C and pH 8–9. The pH of the mixture was then dropped to 5.2 by adding 2 N HCl to remove the unreacted 2-aminoethane sulfonic acid through filtration. Unreacted aspartic acid was removed from the solution by further dropping the pH to 2.8 and then filtration. Solid PASP-SEA-ASP was obtained through a separation process in which a double volume of absolute alcohol was added to the filtrate and the resultant precipitate was rinsed using deionised water and dried at 80 °C for 48 h. The stock solution of PASP-SEA-ASP (30%) was made through dissolving the obtained solid in deionised water. The relevant synthetic reaction is expressed in Scheme 3.

2.4. RO tests

RO tests were performed using a flat-sheet membrane (Polyamide RO AG membrane, GE Osmonics) with a bench-scale cross flow RO rig (SEPA CF, GE Osmonics). Before the filtration tests, RO membranes



Scheme 1. Synthesis route of polysuccinimide.