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Biofouling and scaling control of reverse osmosis membrane using one-step cleaning-potential of acidified nitrite solution as an agent

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ABSTRACT

Biofouling is generally regarded as a major issue in reverse osmosis (RO) membrane filtration. Two-step chemical cleanings with alkaline and acidic agents are typically applied to restore the treatment capacity. In this study, the feasibility of one-step cleaning using free nitrous acid (FNA) was investigated as a novel low cost cleaning agent. The FNA cleaning solution was prepared by acidification of a sodium nitrite solution with hydrochloric acid. Seven fouled RO membranes collected from full-scale wastewater recycling and desalination plants were used to perform lab-scale cleaning trials. Membrane fouling characterisation revealed six of out of seven membranes were mainly bio-fouled, while one membrane was severely fouled by calcium carbonate. This study showed the feasibility of using FNA at pH 3.0 for biomass removal as well as for calcium carbonate scaling removal. The results from the lab-scale cleaning tests suggested that FNA can be used as a single cleaning agent for both biofouling and scaling removal. Cost analysis showed that FNA is a cost-effective solution for biofouling and scaling removal in RO filtration applications.

1. Introduction

With the number of reverse osmosis (RO) membrane plants rapidly increasing worldwide for water recycling and seawater desalination, optimisation for sustainable operation of the membranes is essential [1]. Reverse osmosis membranes have been shown to consistently produce very high quality water independent of source water quality and can be used for a wide range of applications, including potable use. However, membrane fouling and more specifically biofouling, remains one of the major operating challenges [1,2]. Biofouling is defined as the adhesion, growth and multiplication of bacteria present in the water on membrane surfaces, and was shown to have a negative impact on operation. The main consequences observed are decreased membrane flux, increased pollutants passage through the membranes and increased loss of pressure across the membranes train. This can eventually result in biodegradation of the membrane polymer and other components of the modules [2–4]. These effects ultimately result in increased energy and chemical costs, loss of both water production and water quality as well as reduced membrane life. Overall, membrane biofouling critically reduces the process efficiency and cost-effectiveness. The preventative measures to alleviate biofouling in the desalination industry is estimated to cost approximately 15 billion $US yearly worldwide [5].

Current strategies to control biofouling include feedwater pretreatment to remove bacteria before they reach the RO membranes and nutrients to limit bacterial development, and dosing of biocides such as chlorine and monochloramine [6,7]. Chlorine is a strong biocide, and has been widely used for biofouling control in membrane systems. However, its application to RO membrane is restricted as it can damage the polyamide active layer of RO membranes [8–10]. Monochloramine was found to be less detrimental to the membranes; however it has also been shown to have a limited impact on bacteria removal. Indeed, even with continuous dosing, biofouling formation has been observed [2]. In recent years, research studies investigating membrane biofouling control have focused on optimisation of pre-treatment for the limitation of nutrients in feed water [7,11], development of novel membrane materials (chlorine resistant [12] or anti-fouling [13]), determination of novel biocides such as DBNPA [14] or nitric oxide [15] and development of novel biological methods such as inhibition of biofilm growth by quorum sensing, biomass dispersion by cell wall hydrolase or bacteriophage and enzymatic disruption [16,17]. Although some of these novel techniques are promising none of them have proved to dramatically improve biofouling control, and none can be implemented for full-scale plant

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operation in the medium term. In general, these methods do not allow complete/satisfactory removal of the microorganisms present in the feedwater and even if a process is very efficient, there is still enough cells remaining which can grow in the system [2,18]. Over time, biofouling will develop on the RO membranes, and chemical cleaning of the RO membranes is regularly required to restore their treatment capacity.

Typically, chemical cleanings are a sequence of cleanings with alkaline (e.g. sodium hydroxide) and acidic (e.g. citric acid, hydrochloric acid) agents. Alkali cleaning is used to remove organics and biofilm present on the membranes, while acid cleaning is generally used to target scaling. However, biofilm removal using the current strategies was never found to be complete [2,11,19]. In addition, the commonly used cleaning agents, used in large quantities, contribute significantly to operational costs and environmental issues for their disposal.

Recent studies carried out on sewer biofilms and waste activated sludge at both laboratory and full scales, have demonstrated that free nitrous acid (FNA) is a strong biocidal agent at parts per million concentrations (0.2–2 mgN/L), causing deactivation of microorganisms by inducing substantial cell death and biofilm detachment [20–23]. The FNA technology is currently being applied for sulphide and methane control in sewer networks. In a recent trial of the technology for sewer biofilm control, it has been shown that the activities of sewer biofilms were completely suppressed, accompanied by a substantial loss of biofilm after 24 h treatment [24]. Although sewage provided ample substrates for biofilm to regrow, the recovery of sewer biofilm activities one week after treatment was less than 20%. Given the very low substrate concentration in feedwater in an RO system (in comparison to raw sewage), it is reasonable to expect that the recovery of RO membrane biofilm would be much slower in comparison to sewer biofilms.

The aim of this study was to investigate feasibility of FNA as a novel low cost cleaning agent. Its utilisation was assessed for the removal of biofouling in RO membranes for water recycling and seawater desalination. As an acid, it is anticipated that FNA will also be effective at removing inorganics from the membrane surface. Therefore, the potential of using FNA to remove RO membrane biofilm and scaling was evaluated at bench-scale without (soak cleaning tests) and with cross-flow recirculation (cross-flow cleaning tests).

2. Material and methods

2.1. Chemicals

FNA is related to the total nitrite concentration, the pH and the temperature and is calculated as follows [25]: $\text{FNA} = \text{NO}_2^{-}\text{–N}/(\text{Ka}\text{x}10\,\text{pH})$, where Ka is the ionisation constant of the nitrous acid ($\text{Ka}=e^{-2300/(T+273)}$) and T is the temperature (°C). The FNA concentration was achieved by varying the nitrite concentration and pH. The pH was adjusted with hydrochloric acid (HCl). Sodium nitrite (≥ 99%, Sigma Aldrich) and HCl (32%, Univar) were used to generate FNA solutions. The others cleaning solutions were prepared using sodium hydroxide (pallets, Univar), HCl solution (32%, Univar) and citric acid (99.5%, Chem-supply).

2.2. Reverse osmosis modules and fouling characterisation

The cleaning trials were conducted using fouled RO modules collected from full-scale plants (Table 1). All RO membranes are commercial thin-film composite polyamide membranes.

Membrane autopsies were conducted on the seven fouled membranes to characterize the fouling layer. Chemical (loss on ignition, elemental analysis, polysaccharide and protein content) and microbial (ATP) analysis were used to describe the fouling deposit. Loss of ignition (LOI) is used to determine the proportion of inorganic versus organic fraction in the fouling layer. The amount of adenosine tri-phosphate (ATP), an energy-rich biomolecule present in all active microorganisms [26], was measured to quantify the active bacterial biomass in the fouling layer. The applicability of ATP concentration as a parameter for the assessment of active biomass present in the RO membrane fouling layer has been previously reported as a robust parameter [27]. Polysaccharides and proteins have been reported as extracellular polymeric substances (EPS) indicators [27]. EPS are abundant in biofilms and therefore protein and polysaccharide content were measured as proxy of microbial concentration. Elemental analysis via inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the metals content in the fouling deposit. Autopsy methodologies and data can be found in the Supporting information (SI) (Tables A.1 and 2).

Table 1
List of RO membranes used for the cleaning trials.

Reference no.	Source	Fouling type	Cleaning conditions
RO1	Municipal water recycling plant	Biofouling	Soak cleaning tests[*]
RO2	Industrial water recycling plant	Biofouling	Cross-flow cleaning tests[**]
RO3			
RO4	Municipal water recycling plant	Biofouling	
RO5	Municipal water recycling plant	Biofouling	
RO6	Seawater desalination plant	Biofouling	
RO7	Coal seam gas water recycling plant	Scaling	

[*] Without cross-flow recirculation.
[**] With cross-flow recirculation.

2.3. Lab-scale cleaning trials

2.3.1. Protocol for chemical cleaning

Cleaning trials were carried out at lab-scale without cross-flow recirculation (soak cleaning) and with cross-flow recirculation (cross-flow cleaning). The soak cleaning tests were used for prescreening the optimum FNA concentrations and pH for biomass removal only, while cross-flow cleaning tests were used for assessing the impact of FNA on biomass and scaling removal.

The first set of experiments was performed by soaking membrane coupons (42 cm^2) in 300 mL of cleaning solution for 24 h. Three replicate experiments were conducted using RO1 membrane. The beakers were placed on an orbital shaker (Ratek large orbital shaker) and agitated at 120 rpm.

The second set of experiments was conducted with cross-flow recirculation using cleaning cells made of Perspex and RO2–RO7 membranes. Both membrane coupons (150 cm^2 of membrane active surface) and the respective feed spacer were placed in the cleaning cells. Cleaning cells were designed to simulate the configuration of RO filtration system and were operated with cross-flow, without permeate production. The hydraulic performance of RO membranes were conducted in a separate cross flow filtration set-up using Sterlitech CF042 cells and described in detail in SI, Table A.1. The cleaning solutions were pumped (Cole Parmer, Masterflex L/S economy drive pump) through the cleaning cell for 24 h according to the following protocol:

- Rinse with DI water (2 h) to remove biomass or scaling at the external layer of biofilm.