Desalination 424 (2017) 95–101

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

# Inactivation of biofilms on RO membranes by copper ion in combination with norspermidine

Hye-Jin Lee, Jiwon Seo, Min Sik Kim, Changha Lee*

*School of Urban and Environmental Engineering, KIST-UNIST Ulsan Center for Convergent Materials (KUUC), Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, Republic of Korea*

ARTICLE INFO

*Keywords:*
Biofilm
Biofouling
Reverse osmosis membrane
Copper ion
Norspermidine

ABSTRACT

Biofouling is one of the most important factors that degrade the performance of reverse osmosis (RO) membranes during the desalination process. This study demonstrates that copper ion (Cu(II) or Cu(II) plus hydroxylamine (HA) to produce Cu(I)) in combination with norspermidine (Nspd) can effectively inactivate bacterial biofilms on RO membranes. The addition of Nspd inhibited the inactivation of planktonic *P. aeruginosa* cells by copper ion. However, with respect to the cells in biofilms (grown in CDC reactors), the use of Nspd enhanced the cell inactivation by copper ion; the addition of Nspd increased the inactivation efficacies of Cu(II) and Cu(II)/HA against biofilm cells from 2.4 to 3.1 and from 1.3 to 3.5 (log inactivation in 1 h), respectively. Nspd disrupted extracellular polymeric substances (as evidenced by the removal of proteins and polysaccharides from biofilms), and it is believed to facilitate the penetration of copper ion into the biofilm matrix. These results showed that the Cu(II)/HA/Nspd treatment also inactivated biofilms in pressurized cross-flow RO filtration units, resulting in partial recovery of permeate flux. However, pretreatment using Nspd (and the subsequent treatment by copper ion) was not as effective as the simultaneous use of Nspd and copper ion in both CDC reactors and cross-flow filtration units.

## 1. Introduction

Biofilms are formed by all microbial communities and they cause problems in a wide range of industrial facilities including membrane filters, heat exchangers, ship hulls, and water distribution systems [1]. Importantly, the development of biofilms on membrane surfaces leads to fouling of membranes (biofouling), causing a severe decline in the permeate flux and an increase in energy consumption. The biofouling of reverse osmosis (RO) membranes has been recognized as one of the most important factors that reduce the efficiency of the desalination process, and accordingly, various strategies to prevent or mitigate the biofouling of RO membranes have been developed [2–4].

Effective control of biofilms is a challenging task because extracellular polymeric substances (EPS) enclosing biofilm cells serve as a barrier to biocides [5]. Oxidative disinfectants such as chlorine and ozone limitedly penetrate into the interior of biofilms due to their consumable reactions with EPS [6]. Nonoxidative biocides such as silver ion relatively easily penetrate through the EPS barrier, but still a large proportion of biocides can be blocked by EPS through physical or chemical mechanisms. For this reason, biofilm cells are much more resistant to biocides than planktonic cells (e.g., 8300–10,000 times resistant to chlorine and 28–40 times resistant to silver ion) [7].

During the life cycle of biofilms, the dispersal of aged biofilms is induced by small signaling molecules that are produced by the cells [8–10]. Recently, it has been demonstrated that these signaling molecules (e.g., D-amino acids and polyamines) can be artificially used to disassemble the already grown biofilms as well as to inhibit biofilm formation [11,12]. These compounds were also shown to be applicable in the control of membrane biofouling [13,14]. Norspermidine (Nspd), a polyamine compound, has been found to be a biofilm disruptor in recent studies. Nspd at millimolar concentrations was shown to inhibit the formation of biofilms of different bacterial species including *S. aureus*, *B. subtilis*, *E. coli*, *S. enterica*, and *P. aeruginosa* [15–17]. However, Nspd has not been studied in terms of the control of membrane biofouling.

Meanwhile, copper ion has been reported as an effective biocide for planktonic and biofilm cells [18–20]. It is known that cuprous ion (Cu(I)) is more cytotoxic than cupric ion (Cu(II)), and the microbicidal action of Cu(II) originates from the toxicity of Cu(I) produced by the cellular reduction of Cu(II) [21]. Recent studies have demonstrated that the use of Cu(II) with hydroxylamine (HA) (a Cu(II)-reducing agent) results in enhanced inactivation of planktonic cells of *E. coli*, MS2

* Corresponding author.
*E-mail address:* clee@unist.ac.kr (C. Lee).

http://dx.doi.org/10.1016/j.desal.2017.09.034
Received 29 August 2017; Received in revised form 29 September 2017; Accepted 29 September 2017
Available online 05 October 2017
0011-9164/ 