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Impact of feed spacer and membrane modification by hydrophilic, bactericidal and biocidal coating on biofouling control

P.A. Araújo [a], D.J. Miller [b], P.B. Correia [a], M.C.M. van Loosdrecht [c], J.C. Kruithof [a], B.D. Freeman [b], D.R. Paul [b], J.S. Vrouwenvelder [a,c,d,*]

[a] Wetsus, centre of excellence for sustainable water technology, Agora 1, P.O. box 1113, 8900 CC Leeuwarden, The Netherlands
[b] University of Texas at Austin, Department of Chemical Engineering, Center for Energy and Environmental Resources, 10100 Burnet Road, Building 133, Austin, TX 78758, USA
[c] Department of Biotechnology, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands
[d] King Abdullah University of Science and Technology, Water Desalination and Reuse Center, Thuwal, Saudi Arabia

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ABSTRACT

The influence of polydopamine- and polydopamine-*graft*-poly(ethylene glycol)-coated feed spacers and membranes, copper-coated feed spacers, and commercially-available biostatic feed spacers on biofouling has been studied in membrane fouling simulators. Feed spacers and membranes applied in practical membrane filtration systems were used; biofouling development was monitored by feed channel pressure drop increase and biomass accumulation. Polydopamine and polydopamine-*g*-PEG are hydrophilic surface modification agents expected to resist protein and bacterial adhesion, while copper feed spacer coatings and biocides infused in feed spacers are expected to restrict biological growth. Our studies showed that polydopamine and polydopamine-*g*-PEG coatings on feed spacers and membranes, copper coatings on feed spacers, and a commercial biostatic feed spacer did not have a significant impact on feed channel pressure drop increase and biofilm accumulation as measured by ATP and TOC content. The studied spacer and membrane modifications were not effective for biofouling control; it is doubtful that feed spacer and membrane modification, in general, may be effective for biofouling control regardless of the type of applied coating.

1. Introduction

Membrane filtration processes like ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) produce high-quality drinking water from sources such as seawater and sewage. Because the global demand for clean freshwater is growing, these membrane technologies are increasing in importance. Biofouling – excessive growth of biomass which impacts membrane performance [1] – is one of the most serious problems in membrane applications, influencing (i) the amount and quality of purified water, (ii) reliability of water production, and (iii) operating costs [2]. Numerous authors have described biofouling problems in membrane installations [3–9]. The study of membrane biofouling and its control has recently intensified [10].

Presently, several strategies to prevent and control biofouling are pursued: (i) nutrient removal by biological pre-treatment (e.g. sand filtration), (ii) metabolic inactivation of bacteria (e.g. biocide dosage or UV radiation), (iii) membrane surface modification, and (iv) chemical cleaning [11]. In most cases, these strategies realize a short term effect only and are unsuitable for biofouling prevention or complete control [2,10,12]. If biofouling cannot be prevented, biomass must be removed from the module upon cleaning; otherwise rapid bacterial regrowth may occur [9,13–15]. Membrane modification has focused on the membrane surface itself despite the results of several studies showing that feed spacers play an important role in membrane system biofouling. Baker et al. [16] reported that initial fouling deposits were found accumulating alongside the membrane feed channel spacer; these deposits eventually encroached upon the remaining free membrane area. Van Paassen et al. [17] observed an exponential increase of the feed channel pressure drop caused by biofouling on the membrane module feed spacers. The biofilm accumulation they observed proved to be caused by impure hydrochloric acid dosed to the feed water to prevent scaling. Tran et al. [18] found that fouling occurred most readily in the vicinity of the feed spacer strands. Feed spacer biofouling has been addressed by periodic air/water cleaning [19] and altering feed spacer geometry [20]; spacer modification may provide an alternate means of preventing or controlling biofouling.

The objective of this study was to determine the potential of feed spacer and membrane modification to control biofouling. Membrane fouling simulators (MFS), which mimic the flow conditions and fouling patterns found inside commercial spiral-wound modules [9], were used to carry out studies of (i) polydopamine- and poly(ethylene

* Corresponding author at: Department of Biotechnology, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands. Tel.: +31 15 2784169; fax: +31 15 2782355.
E-mail address: j.s.vrouwenvelder@tudelft.nl (J.S. Vrouwenvelder).

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Nomenclature

ATP	adenosine tri phosphate (measure for active biomass) [pg ATP cm^{-2}]
FCP	feed channel pressure drop [mbar]
MFS	Membrane Fouling Simulator [−]
NF	nanofiltration [−]
PD	polydopamine [−]
PDPEG	polydopamine-*graft*-poly(ethylene glycol) [−]
PEG	poly(ethylene glycol) [−]
PP	poly propylene [−]
PSf	polysulfone [−]
PVC	poly(vinyl chloride) [−]
RO	reverse osmosis [−]
SMO254	austenitic stainless steel [−]
TOC	total organic carbon [mg cm^{-2}]
UV	ultraviolet radiation [−]
UF	ultrafiltration [−]

glycol)-coated feed spacers and membranes, (ii) a copper-coated feed spacer and (iii) a biostatic (triclosan containing) feed spacer. Polydopamine is a hydrophilic surface modification agent which spontaneously precipitates from buffered, alkaline dopamine solution under aerobic conditions [21]. Hydrophilic surfaces have previously shown resistance to protein and bacteria adhesion [22]. Poly(ethylene glycol) (PEG) may be grafted to polydopamine-modified surfaces as polymer brushes [23]. Decreases in microbial adhesion are thought to reduce the proliferation of biofilm and, thereby, prevent or control biofouling [24,25]. Copper ions are known to possess bactericidal effects and, therefore, application of a copper coating is proposed as an antifouling strategy [26]. The biostatic feed spacer comprises a biocidal agent to control biofouling [27]. The effect of feed spacer and membrane modifications for biofouling control is discussed based on results with these three modification techniques.

2. Materials and methods

2.1. Experimental set-up

An overview of the three biofouling control studies is shown in Table 1. Polydopamine, polydopamine-*g*-PEG, and copper coatings were applied in our laboratory; the commercial biostatic feed spacer was modified by the manufacturer and used as received. Previous studies have shown significant improvement in organic fouling by polydopamine and polydopamine-*g*-PEG modifications on ultrafiltration membranes used for oil water separation. Because the polydopamine coating is extraordinarily thin and conformal, it may be applied to the porous membrane without significantly decreasing the membrane flux; polydopamine and polydopamine-*g*-PEG modifications were therefore applied to both the ultrafiltration and nanofiltration membranes and feed spacers. Copper-coated feed spacers and the commercial biostatic feed spacer were used in conjunction with unmodified nanofiltration membranes.

2.2. Materials

NF and UF membranes were used in the studies. NF polyamide membranes and polypropylene (PP) feed spacers were harvested from a spiral-wound TS80 element obtained from Trisep Corp (Goleta, CA). A flat-sheet PS20 polysulfone (PSf) UF membrane was purchased from Sepro Membranes, Inc (Oceanside, CA). The NF membranes were used in the studies of Sections 3.1, 3.2 and 3.3 (Table 1); UF membranes were used in the study of Section 3.1 (Table 1). The polypropylene feed spacer was 31 mil (787 μm) thick with strands intersecting at 90° and a porosity of ~0.85; these specifications match most commonly-used feed spacers in spiral-wound modules for water treatment in The Netherlands. This spacer was used for the coating studies described in Sections 3.1, 3.2 and 3.3 (Table 1). Only new membranes and spacers of all types were used. All membrane and feed spacer coupons (40.0 mm × 200.0 mm) were cut with a punch and hydraulic press.

Dopamine, Trizma HCl, isopropanol, ethanol, sodium acetate, sodium dihydrogen phosphate, and sodium nitrate were purchased from Sigma-Aldrich (St. Louis, Mo.). Sodium hydroxide was obtained from Fisher Scientific (Pittsburgh, PA). Poly(ethylene glycol) monoamine (5000 Da) was purchased from JenKem Technology (Allen, TX). All chemicals were used as received. Tris buffer (15 mM), used in the polydopamine coating and poly(ethylene glycol) grafting (Sections 2.3.1 and 2.3.2), was prepared by dissolving Trizma HCl (2.634 g/L) in deionized water and the pH of the resultant solution was adjusted to 8.8 using sodium hydroxide.

2.3. Coated membranes and feed spacers

2.3.1. Polydopamine coating

PSf UF and NF membrane coupons were prepared by soaking in isopropanol for 10 min followed by deionized water for 30 min. To coat membranes with polydopamine, the selective side of membrane coupons was put in contact with dopamine solution (2 g/L in Tris buffer) for 1 h with gentle agitation to aerate the solution and to ensure complete surface coverage. PP feed spacer coupons (0.04 m × 0.20 m) were coated by immersion in stirred dopamine solution (2 g/L in Tris buffer) for 1 h. Modified membranes and feed spacers were soaked in ethanol for 10 min to remove residual, weakly-bound polydopamine and stored in deionized water until use. The characteristic brown colour of the polydopamine coating was imparted on membranes and feed spacers as shown in Fig. 1.

Table 1
Scheme for the experimental conditions of studies on modification of feed spacers and membranes to evaluate effectiveness for biofouling control. The feed water flow rate was the same for all experiments. The substrate was dosed to a concentration in the monitor feed water of 0.1 mg/l acetate C for the experiments with copper coated spacers and to a concentration of 0.5 mg/L acetate C for the other experiments: polydopamine and polydopamine-*g*-PEG and the commercial biostatic spacer.

Study	Modified material	Membrane type	Spacer material	Water temperature °C	Linear flow velocity m s^{-1}	Substrate load mg c m^{-2} s^{-1}	Feed spacer thickness mil*	Section
Effect of PD and PD-g-PEG coating#								
In situ coating	Membrane + spacer	UF + NF	PP	12	0.16	Constant	31	3.1
In situ coating	Membrane + spacer	UF + NF	PP	20	0.16	Constant	31	Supplementary material
Ex situ coating	Membrane + spacer	UF + NF	PP	20	0.16	Constant	31	Supplementary material
Effect of copper coating	Spacer	NF	PP	20	0.16	Constant	31	3.2
Effect of commercial biostatic spacer	Spacer (as delivered)	NF	PP + 0.5 wt.% triclosan	20	Varying	Varying	31, 34	3.3

* 1 mil = 25.4 μm; 31 mil = 787 μm; # PD = polydopamine; PDPEG = polydopamine-*g*-poly(ethylene glycol); PP = polypropylene; UF = ultrafiltration; NF = nanofiltration.