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Effect of chemical cleaning and membrane aging on membrane biofouling using model organisms with increasing complexity

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ABSTRACT

A major obstacle in the widespread application of membrane microfiltration for activated sludge wastewater treatment is the rapid decline of the permeation flux with time as a result of membrane fouling. Nowadays, fouling is mostly controlled by optimal operational conditions, and physical and chemical cleaning. In this study, the efficiency of chemical cleaning and the impact of these chemicals on the membrane structure (membrane aging) has been evaluated and linked to properties of the microbial community present in the feed. Three polymeric microfiltration membranes (polyvinyldifluoride, polyethylene and polysulfone) and 3 model biofoulants with increasing complexity were used in a cross-flow filtration set-up. The cleaning efficiency was measured in terms of bacterial cell density and exopolymeric substance concentration. Membrane cleaning by 1% NaOCl and 2% citric acid had a cleaning efficiency ranging from 57 to 100% and 41 to 100% respectively, depending on the concentration and the complexity of the used biofoulants. Membrane aging by NaOCl and citric acid was reflected in an increased membrane pore size and surface porosity, while the membrane hydrophobicty and surface chemistry of the membrane surface remained unaffected. Differences in bacterial cell densities were found on aged membrane, but the results were strongly biofoulant dependent. On the other hand, significantly higher exopolymeric substances concentrations were detected on the aged membranes, suggesting that the biofoulants behave differently on aged membranes.

1. Introduction

To avoid fast pore blocking of the membrane, sustainable operation relies on physical cleaning, supplemented with periodic chemical cleaning. Physical cleaning is performed at very regular time points (orders of minutes) and removes most of the reversibly bound particles from the membrane surface. However, the effectiveness tends to decrease with operation time as more irreversible fouling accumulates on the membrane surface [1]. Therefore, in addition to the physical cleaning, different types/intensities of chemical cleaning may also be recommended on a weekly/monthly/yearly basis. The prevalent cleaning agents are sodium hypochlorite (NaOCl), and citric acid (CA) which remove organic and inorganic foulants, respectively [1]. NaOCl oxidizes the organic molecules and, therefore, the particles and biofilm attached to the membrane can be loosened. CA has strong solubilization, chelation and hydrolyzation capacities and is effective in removing metal oxides and organic compounds. Nevertheless, the extensive use of chemicals has not only an important financial aspect (membrane replacement, interruption filtration process, corrosion, energy and chemical cost) but also environmental consequences (formation of carcinogenic byproducts such as trihalomethanes, chemical discharge in nature, selection for unwanted resistant organisms, etc.) [2–4]. Moreover several studies reported changes in membrane properties (such as changes in streaming potential, hydrophobicity, pore size) after chemical treatment, a process called “membrane aging” [5–10].

The effect of membrane cleaning in terms of plant performance has been well documented in both reverse osmosis system as well as in membrane bioreactors (MBRs) [11–13]. However, only a few studies focused on the cleaning efficiency from a microbiological point of view, notwithstanding that microorganisms and their microbial products are the main cause of irreversible fouling [14–17]. Numerous biofilm related studies have highlighted the survival of microorganisms after cleaning and disinfection in food, medical and domestic environments, and recently on membranes [14,18–20]. The resistance of microorganisms to disinfection is attributed to their ability to produce exopolymeric substances (EPS) and to form biofilms [21]. It was also found that biofilm formation and resistance to antimicrobial agents is species dependent and enhanced by synergetic interactions in multispecies biofilms [22,23].

Previous studies demonstrated that bacterial adhesion and biofilm formation on membranes was strongly species dependent [24,25]. Moreover, it was shown that environmental factors, such

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as the presence of other species, oligotrophic conditions, and the species acclimatization influenced the biofouling behavior. Following this study, the current research investigated the effect of the cleaning efficiency by NaOCl and CA treatments on 3 types of microfiltration membranes. For this purpose, membranes were fouled using biofoulant model organisms with increasing complexity (monospecies, duospecies and complex community). In a first approach, the biofouling resistance after chemical cleaning was analyzed in terms of permeability decrease, cell viability and EPS content. In a second approach, membrane aging and the subsequent consequences on the biofouling formation and removal were investigated.

2. Material and methods

2.1. Experimental design

Biofouling was generated in a cross-flow filtration cell containing 6 replicate filtration channels. Three microfiltration membranes, commonly used in MBR systems [26], were tested: polyvinyldifluoride (PVDF), polyethylene (PE) and polysulfone (PSF) membranes. Three biofoulants with increasing complexity were used in every experiment: monospecies *Pseudomonas aeruginosa*, duospecies *P. aeruginosa* and *Escherichia coli,* and activated sludge spiked with *P. aeruginosa*.

Two experiments were performed to study (1) the effect of chemical cleaning by NaOCl and CA, and (2) the effect of membrane aging by NaOCl and CA on the membrane biofouling.

The cleaning efficiencies of both chemicals were evaluated in terms of remaining bacterial cells after treatment. Biofouling associated cells were enumerated by traditional plate count and visualized by confocal laser scanning microscopy (CLSM) and scanning electronic microscopy (SEM). Membrane characteristics were measured by SEM, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and contact angle.

2.2. Membranes

Two lab-made and one commercial membrane were used. PVDF and PSF microfiltration membrane sheets were prepared via phase inversion [27,28]. 12 wt% PVDF (Sigma-Aldrich) and 10 wt% PSF (BASF-Ultrason) solutions were prepared in dimethylacetamide (Sigma-Aldrich) and N-Methyl-2-pyrrolidone (ACROS) solutions, respectively. Subsequently, the membranes were cast (250 μm thickness) on a polypropylene/polyethylene support (Viledon Non-woven FO 2471, kindly supplied by Freudenberg, Germany). The solvents were allowed to evaporate during 60 s, followed by coagulation of the polymer film in deionized water (dH_2O). The PE membrane was purchased from Kubota® (cartridge type 203). These flat sheet membranes were made of chlorinated polyethylene on a non-woven cloth and had a nominal pore size of 0.4 μm as reported by the manufacture. Out of every membrane sheet, replicate coupons of 26 cm^2 were cut. Each coupon was sterilized during 3 h in 70% EtOH, followed by two rinsing steps using sterile dH_2O to remove the remaining EtOH. Each sterile membrane coupon was stored in a 50 ml falcon tube filled with 40 ml sterile dH_2O water at 4 °C until further use. Each membrane coupon was used only once.

The nominal pore size and porosity of the membranes were determined using scanning electron microscopy (SEM, Philips SEM XL30 FEG with Adax dx-4i system) and image processing software (ImageJ) and were compared with data from the literature [29,30].

The membrane surface hydrophobicity was determined using contact angle goniometry (VCA Optima video camera system, AST Products, Billerica) with the sessile drop method (2 μl). The contact angle was measured at least at 5 different positions and at different time points: immediately after the drop had reached the membrane and after 10 min (Table 1).

ATR-FTIR spectroscopy was performed to analyze the changes in the chemical functional groups after membrane aging. ATR-FTIR spectra were collected on dried membranes using a Bruker ALPHA-P FT-IR spectrometer (Bruker) with a diamond crystal. Forty scans were collected at a resolution of 4 cm^{-1}. Every membrane was measured at least at 3 different positions.

2.3. Model microorganisms and culture conditions

P. aeruginosa and *E. coli* have been chosen as model organisms because they are both Gram-negative, have approximately the same growth rate and hydrophobicity, are commonly present throughout aquatic environments [31] and activated sludge [32], and are well studied as model organisms for biofilm formation [33–35]. *P. aeruginosa* (PA14) green fluorescent protein (gfp) labeled and *E. coli* (LMG 2092^T) red fluorescent protein (rfp) labeled were cultivated at 28 °C in Lysogeny Broth (LB) (10 g tryptone, 5 g yeast extract and 5 g NaCl per liter). *P. aeruginosa* culture was supplemented with 100 mg/l ampicillin, 10 mg/l gentamycin, 25 mg/l kanamycin and 25 mg/l streptomycin [36]. *E. coli* was cultured with 50 mg/l kanamycin and 100 mg/l nalidixic acid. At the start of each experiment, cells from a 24 h culture were harvested and suspended in sterile Ringer's solution (Oxoid). The initial cell concentration was spectrophotometrically determined ($\lambda_{650\ nm}$) and, additionally, countable 10-fold dilutions were plated as a control [37].

Activated sludge was harvested from a lab-scale MBR that was treating molasses wastewater. The operational parameters of the MBR and the sludge characteristics are described in detail by

Table 1
Characteristics of the membranes used in this study.

	Type	Treatment	Pore size (μm)	Surface porosity (%)	Contact angle (°) 5 s	10 min	J_w (L/m² h bar)
PSF	Labmade	Pristine	[a]	[a]	74 ± 1	71 ± 2	1071 ± 536
		NaOCl pretreated	[a]	[a]	74 ± 2	[b]	466.7 ± 146
		CA pretreated	[a]	[a]	77 ± 4	[b]	602.9 ± 71.3
PVDF	Labmade	Pristine	[a]	[a]	73 ± 7	49 ± 2	1308 ± 863
		NaOCl pretreated	[a]	[a]	68 ± 3	[b]	762.5 ± 546
		CA pretreated	[a]	[a]	68 ± 2	[b]	462.5 ± 173
PE	Kubota	Pristine	0.119 ± 0.011	13.78 ± 1.375	103 ± 2	73 ± 3	816.8 ± 350
		NaOCl pretreated	0.211 ± 0.012	15.22 ± 2.154	104 ± 1	[b]	444.2 ± 67.4
		CA pretreated	0.223 ± 0.002	18.31 ± 1.375	102 ± 1	[b]	440.3 ± 115

[a] Not possible to measure with Image J.
[b] Not determined.