

ORGANIC AND INORGANIC FOULING ON ULTRAFILTRATION MEMBRANES: EFFECT OF BACKWASHING AND CHEMICAL CLEANING

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ABSTRACT

UF membranes are periodically subjected to backwashing (BW), chemically-enhanced backwashing (CEB) and cleaning-in-place (CIP) episodes in order to remove foulants from their surface. The objective of this study was to quantify the fouling layer on a UF membrane and identify which foulants were best detached after BW and CIP episodes.

For this purpose, a bench-scale outside-in UF hollow fibre module operated under dead-end filtration mode at constant transmembrane pressure was employed. BW was periodically applied (with additional CEBs comprising NaClO and NaOH every 3 BW) (termed "BW(+CEB)"). On completion of the experiment, the UF membrane was consecutively subjected first to a CIP based on alkaline (NaOH) and oxidant (NaClO) agents (termed "CIP-B") and, second, to a CIP based on an acidic agent (citric acid) (termed "CIP-A"). TMP was monitored by a pressure gauge. Feed water, permeate, BW stream and CIP-B and CIP-A solutions were collected for analysis of turbidity, UV₂₅₄, Al, Fe, TOC and DOC fractions. DOC fractionation was carried out by high-performance size-exclusion chromatography (HPSEC).

Results showed a gradual decrease in permeability, with slight and momentary increases when BW was applied, indicating that irreversible foulants slowly accumulated onto and into the membrane.

Permeate analysis confirmed that UF membrane successfully removed turbidity (96%), Al (71%) and Fe (78%), whereas TOC and DOC were poorly removed (10% and 4%, respectively). With regard to the organic fractions, BP was preferentially removed (43%) over HS (7%), while other fractions with lower MW seemed to entirely permeate the UF membrane. The application of BW(+CEB) resulted in little detachment of foulants: 33% of BP, 9% of HS and 7% of Al and Fe, revealing that HS, Al and Fe were more rigidly attached to the membrane than BP. Larger detachment of foulants was achieved only when more aggressive cleaning strategies were applied. CIP-B detached 34% of the initial BP retained by the membrane, 41% of the initial Fe, 16% of the initial Al and 9% of the initial HS, and CIP-A a further 24% and 43% of the initial Al and Fe, respectively (with BP and HS detachments not quantifiable due to analytical limitations).

Keywords: dissolved organic carbon, fractionation, ultrafiltration, fouling, backwashing, chemical cleaning, reversibility.

1. Introduction

Application of ultrafiltration (UF) has expanded in recent years as an alternative technology for wastewater treatment and drinking water production. But like all membrane processes, UF suffers from fouling membrane. In order to remove it, UF membranes in full-scale plants are periodically subjected to backwashing (BW), chemically-enhanced backwashing (CEB) and cleaning-in-place (CIP) episodes. Fouling of UF membranes, both by inorganic and organic components, is gaining increasing attention of researchers in the water treatment field. It is acknowledged that different inorganic and organic constituents in feed water do not necessarily

foul UF membranes in the same way or degree, and therefore organic fouling composition also determines the cleaning strategy of the UF membrane. Within this context, the objective of this study was to quantify the fouling on a UF membrane and identify which foulants were best detached after backwashing (BW) and cleaning-in-place (CIP) episodes.

2. Materials and methods

2.1. Experimental set-up

A bench-scale outside-in UF hollow fibre module (MWCO 300 kDa, pore size 0.08 μm) operated under dead-end filtration mode at constant transmembrane pressure (TMP) was employed. BW with permeate was periodically applied (with additional CEBs comprising NaClO 7mg/L and NaOH pH=10-11 every 3 BW) (termed hereafter “BW(+CEB)”). On completion of the filtration experiment, the UF membrane was consecutively subjected first to a CIP step based on alkaline (NaOH pH=11-12) and oxidant (NaClO 200 mg/L) agents (termed hereafter “CIP-B”) and, second, to a CIP based on an acidic agent (citric acid pH=3-4) (termed hereafter “CIP-A”).

TMP was measured over the experiment by a pressure gauge. Feed and permeate were collected for analysis of turbidity, UV₂₅₄, Al, Fe, TOC and DOC fractions. These parameters were also analysed for the successive BW streams and CIP-B and CIP-A solutions.

2.2. Analytical techniques

Turbidity was analysed by nephelometry (Hach 2100 AN IS Turbidimeter), UV₂₅₄ by spectrophotometry (Hach DR 5000), Fe and Al by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer Optima 4300 DV) and TOC by oxidative combustion and infrared-detection (Shimadzu V CPH).

Fractionation of dissolved organic carbon (DOC) was performed by high-performance size-exclusion chromatography (HPSEC) using a Toyopearl TSK HW-50S column coupled to on-line UV₂₅₄, organic carbon and organic nitrogen detectors. The principles of the technique are reported in depth by Huber *et al.* (2011). Briefly, it is based on size exclusion liquid chromatography whereby organic compounds are fractionated into five sub-fractions according to their molecular weight (MW): (1) biopolymers (BP, with MW>20000 g/mol), (2) humic substances (HS, with MW of approx. 1000 g/mol), (3) building blocks (BB, with MW 300-500 g/mol), (4) low molecular weight acids (LMWA, with MW<350 g/mol) and (5) low molecular neutrals (LMWN, with MW<350 g/mol). The organic carbon retained in the chromatographic column is referred as to the non-chromatographic DOC.

3. Results

3.1. Feed water characterisation.

The feed water was settled water from the settling basin of the drinking water treatment plant in Sant Joan Despí (Spain). Average feed water quality was pH 7.6, conductivity 1490 $\mu\text{S}/\text{cm}$, turbidity 1.8 NTU, UV₂₅₄ 0.080 (abs/m), Al 364 $\mu\text{g}/\text{L}$, Fe 23 $\mu\text{g}/\text{L}$, TOC 4.0 mg/L and DOC 3.3 mg/L. With regard to the organic fractions, HS clearly predominated accounting for 51% of the total DOC, followed by the lower MW fractions BB and LMWN (18%) and at much lower levels BP (4%). The LMWA fraction was always found below limit detection. The non-chromatographic fraction accounted for 8%.

3.2. Permeability evolution over the experiment

Figure 1 shows the evolution of the normalised permeability (P/P₀) during the experiment. The P/P₀ profile showed successive decreases in permeability during the filtration step followed by short increases during BW. BW never restored permeability completely to the initial value, indicating that irreversible foulants slowly accumulated onto and into the membrane. The hydraulically reversible fouling are mainly associated to cake formation, while the persistent irreversible fouling on the long term may be due, at least partially, to blocking of the UF membrane pores. Only when a CIP was applied at the end of experiment, was the permeability restored to the pre-experiment value.

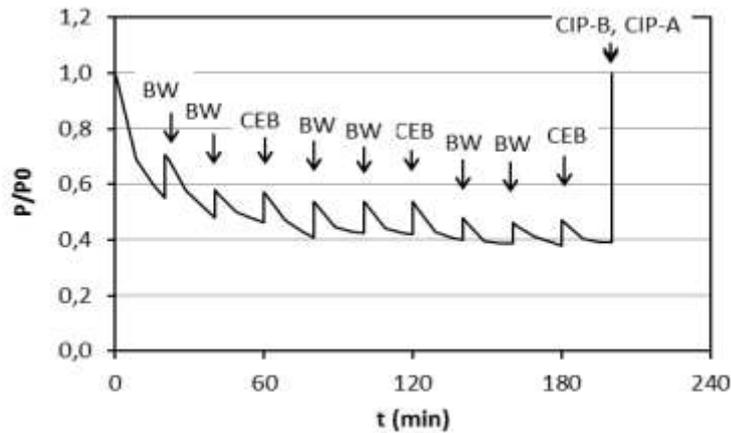


Figure 1: Evolution in the normalized permeability (P/P_0) of the fouled UF membrane

3.3. Removal of feed water constituents by ultrafiltration

Figure 2 shows variations in bulk parameters and inorganic ions and organic components by the passage of feed water through the UF membrane. Turbidity was removed at a very high percentage (96%). For particles smaller than the membrane pore size, this removal might occur initially by pore blocking, while for larger particles or additional small particles the removal might occur by cake formation (Guo *et al.*, 2012). Al and Fe ions were removed by 71% and 78%, respectively. Their removal is likely due to precipitation in the form of (oxy)hydroxides, which are known to form a slimy fouling layer, and to a lesser extent to complexation with organic matter which is in turn retained by the UF membrane (Shi *et al.*, 2014).

TOC and DOC were poorly removed (10% and 4%, respectively), since most of the organic matter present in feed water is in dissolved form and, of this, most (88%, which is the sum of HS, BB, LMW) has a size smaller than the UF membrane pore size. With regard to the organic fractions, UF membrane preferentially retained the highest MW fraction BP (removal percentage of 43%), while intermediate HS was retained at a percentage of 7% and smaller BB and LMWN seemed to entirely pass through the UF membrane. The pattern was expected from size exclusion effects. The mechanisms whereby BP and HS were retained by the UF membrane differ depending on the fraction: HS was likely adsorbed initially both inside the pores and on the membrane surface, while bigger BP was likely retained by size-exclusion forming a cake that in turns retained new arriving BP and HS. UV_{254} , often used as a surrogate for organic matter, was removed by 24%, suggesting that UV_{254} non-absorbing organic compounds were more retained than the UV_{254} absorbing ones.

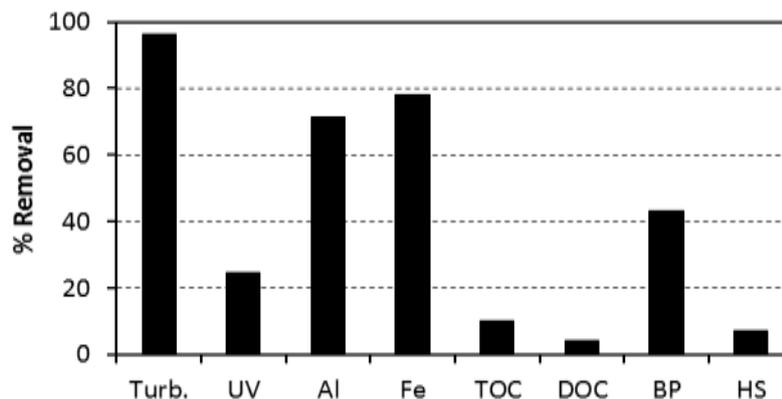


Figure 2: Removal percentages by the UF membrane

3.4. Fouling reversibility

Based on the flow rates of feed and permeate streams, the experiment duration and the concentrations of the foulants studied, the masses of Al, Fe, BP and HS retained on the membrane were calculated through a mass-balance (Figure 3). The fouling layer appeared to be largely comprised of Al (accumulated mass of 690 μg) and HS (469 μg) along with smaller amounts of BP (229 μg) and Fe (71 μg). Figure 3 also provides the mass remaining after applying BW (+CEB), CIP-B and CIP-A calculated through a mass-balance from the concentration of each foulant within each cleaning solution volume.

The application of BW(+CEB) resulted in little detachment of foulants, with sum of washed out masses of Al, Fe, BP and HS amounting 171 μg . In percentages referred to the initial mass in the foulant layer, the detachments were 33% (BP), 9% (HS) and 7% (Al and Fe), revealing that HS, Al and Fe were more rigidly attached to the membrane than BP. The preferential washing out of BP was likely due to its size relative to that of the membrane pores: organic substances much larger than the membrane pores led to cake formation, which is more readily detached, while lighter fractions such as HS or precipitates of Al and Fe can cause pore blocking or build-up a denser cake layer less readily washed out (Katsoufidou *et al.*, 2005).

CIP-B led to a larger detachment of foulants (363 μg). A further 34%, 41%, 16% and 9% of the initial BP, Fe, Al and HS retained by the membrane were extracted by the NaOH+NaClO solution. The detachment of BP and HS fractions may be explained by the fact that these fractions can be hydrolysed at high pH and oxidised, increasing their solubility and therefore being more prone to be detached from the membrane. The detachment of Al and Fe is explained by the formation of soluble inorganic hydroxy-complexes (e.g. $\text{Al}(\text{OH})_4^-$) and/or metal-NOM complexes (Kimura *et al.*, 2004).

Finally, the effect of applying the CIP-A solution resulted in the detachment of 166 μg Al (24% of the initial Al), and 30 μg Fe (43% of the initial Fe) by dissolution of Al- and Fe- precipitates. BP and HS detachment could not be quantified because the organic fractions detached, if any, might be in the HPSEC chromatograms overwhelmed by the very high concentration of citric acid employed as cleaning agent.

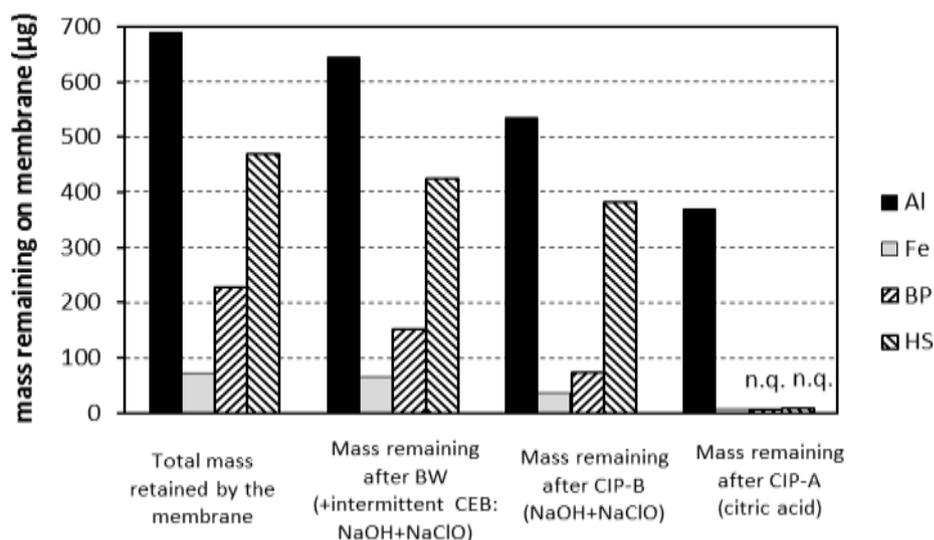


Figure 3: Masses of Al, Fe, BP and HS remaining on the UF membrane after the successive application of BW(+CEB), CIP-B and CIP-A.

4. Conclusions

The UF membrane successfully removed turbidity (96%), Al (71%) and Fe (78%), whereas TOC and DOC were poorly removed (10% and 4%, respectively). With regard to the organic fractions, BP was preferentially removed (43%) over HS (7%), while the other fractions with

lower MW seemed to entirely pass through the UF membrane. The application of BW(+CEB) resulted in little detachment of foulants: 33% of BP, 9% of HS and 7% of Al and Fe, revealing that HS, Al and Fe were more rigidly attached to the membrane than BP. Larger detachment of foulants was achieved only when more aggressive cleaning strategies were applied. CIP-B detached 34% of the initial BP retained by the membrane, 41% of the initial Fe, 16% of the initial Al and 9% of the initial HS, and CIP-A a further 24% and 43% of the initial Al and Fe, respectively (with BP and HS detachments not quantifiable due to analytical limitations).

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