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Effect of storage of NF membranes on fouling deposits and cleaning efficiency

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ABSTRACT

The aim of this work was to investigate changes of the foulant deposit during storage and the impact of storage onto cleaning efficiency of a nanofiltration membrane. ATR-FTIR analysis and chemical cleaning tests were performed on membrane pieces cut from a NF spiral wound module extracted from a drinking water plant just after sampling or stored for 4 or 8 weeks in distilled water at 4°C. Membrane permeability of flat sheets was measured before and after cleaning with a cross flow lab-scale pilot. For the non stored membrane, an homogeneous biofouling deposit was observed on the membrane surface by ATR-FTIR analysis. During membrane storage, some heterogeneity between the spectra, corresponding to different areas of the membrane appeared. A decrease of IR signals of foulants was observed after the first 4 weeks of storage; thereafter the IR signals remained approximately the same. The membrane permeability of the fouled flat sheets increased slightly after 4 weeks and remained stable after 8 weeks of storage. After cleaning, the biofilm IR signals of the membrane samples analyzed immediately after sampling or stored for 4 weeks decreased significantly. Cleaning had no significant effects on the biofoulant deposit after a storage of 8 weeks. Increases in permeability of 10, 5, and 5% were obtained after cleaning of the fouled flat sheets not stored, stored for 4 or 8 weeks, respectively. In conclusion, the storage of fouled NF membrane cuts in distilled water at 4°C conducted to alterations of the biofouling deposit but was compatible with cleaning efficiency tests after a storage period of 4 weeks at the most.

Keywords: ATR-FTIR; Chemical cleaning; Fouling; Nanofiltration; Permeability

1. Introduction

Membrane fouling is the major problem in membrane filtration applications [1]. Fouling of membranes for drinking water production results mainly from the accumulation of a biofilm at the membrane surface [2–4]. Chemical cleaning is the most common method to clean nanofiltration (NF) membranes. The selection of the appropriate agents for a particular cleaning situation is essential. Indeed, fouling is influenced by the feed water but also by the nature of the filtration membrane [5]. In spiral-wound modules, the dynamics and the complex feed flow fields with recirculation zones play a major role in the existence of zones of preferential fouling and deposits due to poor mass transfer [6,7]. The deposit formed at the NF membrane surface is heterogeneous [2,3,8]. Heterogeneity of foulants has been described as a succession of compact and less dense areas of deposit, and as a succession of different layers in depth. Several studies have been published about chemical cleaning efficiency in specific membrane filtration applications [4,6–8]. The variety of membrane and foulant characteristics in processes reduces the applicability of published studies in different situations. Further research is usually

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needed to find an ideal cleaning procedure for each specific application. Determining the efficiency of chemical cleaning requires to perform extensive tests, and cleaning processes may be continuously adapted depending on the evolution of the foulant deposit. Instead of proceeding to full scale cleaning tests, chemical cleaning can first be experimented on fouled membrane samples cut from industrial modules. After extracting one fouled module from the plant, cleaning experiments of the stored membranes can be done over a period of time, allowing to compare the efficiency of different chemical agents toward identical fouled membrane cuttings. Thus, the potential storage impact on cleaning results needs to be assessed.

A biofilm is constituted by microbial cells and a matrix of exopolymers, mainly exopolysaccharides (EPS). All these biofilm constituents may be modified during storage: microorganisms can grow and die, EPS can be degraded and be produced, some biofilm parts can detach from the membrane, etc. Kosutic and Kunst have tested the storage of membrane cuts in a preserving solution to prevent biological growth without any real evaluation of the impact of storage onto the biofilm constitution [9].

The aim of our work was to investigate changes of the foulant deposit during storage and the impact of storage onto cleaning efficiency. We decided to store the fouled membrane pieces in distilled water, a nutrient free solvent, incubated at 4°C, a temperature that prevents the growth and enzymatic activities of many microorganisms.

2. Experiments

2.1. Membrane autopsy

In November 2006, a NF module was extracted from the drinking water plant of Méry-sur-Oise, France, after seven years of operation. This 8 inches spiral wound module produced by DOW Filmtec (Delft, The Netherlands) contains NF200B membranes composed of an ultra thin top layer made of polypiperazine and a polysulfone and polyester microporous support. The nominal active surface area of a NF200–400 module is 37 m^2. Membrane samples (16.5 cm × 16.5 cm, effective membrane area of 140 cm^2) cut from randomly chosen areas of the module were air dried and analysed by ATR-FTIR or stored at 4°C in distilled water for 4 or 8 weeks before analysis. At least four different membrane samples cut were analysed for each storage duration.

2.2. Analysis of membrane foulants by ATR-FTIR

Samples of air-dried fouled membrane were analyzed by ATR-FTIR. IR spectra were recorded using a Tensor 27 IR spectrophotometer with a 45° diamond/ZeSe flat plate crystal and an average depth penetration of 2 μm. Each spectrum presented is the result of 32 accumulations obtained with a resolution of 2 cm^{-1} with air as the background. All the samples were pressed with the same force to obtain equivalent intimate contact between ATR crystal and sample surface.

2.3. Membrane cleaning and permeability measurement

Cleaning tests as well as permeability measurements were performed on a cross flow lab-scale unit (Osmonics, Minnetonka, USA) provided with flat sheet membrane samples cut from NF spiral wound modules. The membrane test unit accommodates any 16.5 cm × 16.5 cm (6.5″× 6.5″) flat-sheet membrane for a full 140 cm^2 (22″^{2}) of effective membrane area. During this study, cleaning procedure consisted in a two step operation using first a commercial alkaline-enzymatic solution then an acidic solution (Ecolab, Issy les Moulineaux, France). Between these two operations, membrane was rinsed with ultra pure water under dynamic conditions.

The cleaning efficiency was partially evaluated by measuring membrane permeability before and after cleaning through filtration of a synthetic solution of $MgSO_4$ under standard conditions (25°C, 70 psi). This measure was repeated at least 3 times.

2.4. Statistical analysis

Comparisons of significance were done by the equal-variance Student's *t* test, following the variance test with Fisher *F* statistics. *P* values below 0.05 were considered significant.

3. Results and discussion

3.1. Foulant deposit characterization

The ATR-FTIR spectra of the fouled membranes revealed the presence of biological matter at the membrane surface, mainly composed of polysaccharides, nucleic acids and proteins (Fig. 1). Biomass signals were detected near 1650 cm^{-1} (amide I), 1550 cm^{-1} (amide II), and from 1200 to 900 cm^{-1} (due in part to C–O–C, C–O, ring-stretching vibrations of polysaccharides and the P=O stretch of phosphodiesters). The majority of the peaks of the membrane were not observed except signals near 700 and 850 cm^{-1}, indicating that the membrane surface was largely covered by the fouling layer. The spectra corresponding to different areas of the membrane were similar, demonstrating that, from a chemical composition point of view, the fouling deposit was homogeneous on the membrane. The FTIR profiles were very similar to spectra obtained from fouled membranes extracted from the same plant in 2005 but some differences appeared: relative IR signals of foulants were weaker in 2005, quantitative heterogeneity between different membrane areas and more membrane signals were observed in 2005

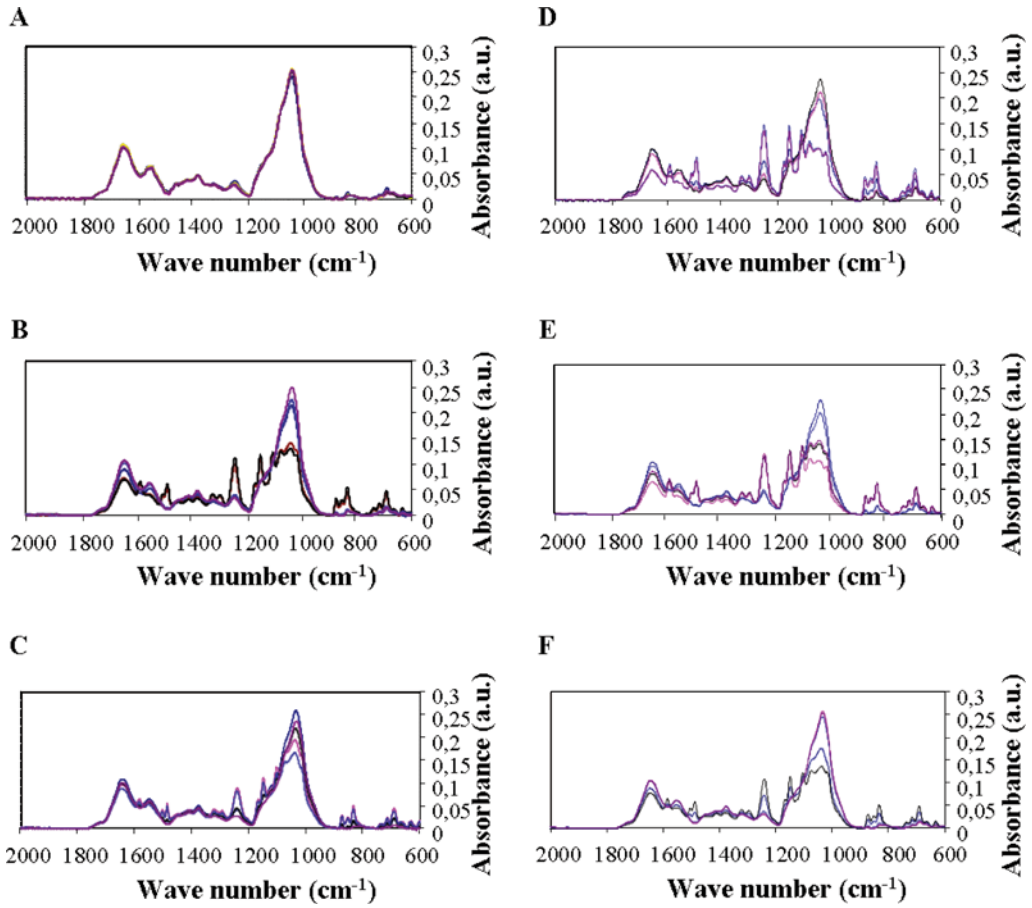

Fig. 1. ATR-FTIR spectra of the fouled membranes. The different spectra observed in each box differ from their localization onto the membrane surface. A, B and C spectra obtained before cleaning. D, E and F : spectra obtained after cleaning. A, D : no storage. B, E : storage of 4 weeks. C, F : storage of 8 weeks. a. u., arbitrary units.

[2]. Thus, the foulant matter was overall stable in nature but increased in quantity between 2005 and 2006.

3.2. *Changes of the foulant deposit during storage*

After a storage time of 4 weeks, some heterogeneity between the spectra corresponding to different areas of the membrane samples was observed (Fig. 1). This heterogeneity remained after a storage duration of 8 weeks. The appearance of heterogeneity in the disposition of the foulant deposit on the membrane surface may result from decrease of foulant matter quantity in different areas of the membrane associated with storage.

The IR signal near 700 cm^{-1} was used (as the membrane reference) to calculate ratio corresponding to relative IR signals of biomass (amide I/membrane signal, amide II/membrane signal and band at 1080 cm^{-1}/membrane signal). The means ± standard deviations of the relative IR signals corresponding to the five spectra of membrane cuttings stored for 0, 4 and 8 weeks are presented in Table 1.

All the relative IR signals of membrane biofoulants were significantly decreased after a storage duration of 4 weeks ($P < 0.05$). The decreases of amide I and polysaccharides IR signals observed after 8 weeks of storage were weak and not significant ($P > 0.05$). Regarding membrane permeability of the fouled flat sheets, a slight increase was found after the first 4 weeks period of storage (Fig. 2). Then, this parameter remained stable. It could be hypothesized that a minor part of the fouling deposit may be released from the membrane surface at the end of the first four weeks of storage. In our system of storage in static bath, the fouling deposit release is not thought to be induced by physical forces such as movement of fluids bathing [12]. Biofilm stability is determined by two mutually exclusive processes: attachment of cells to and detachment from the biofilm matrix. Different reports have shown that active detachment in microbial biofilms

Table 1
Effect of storage and cleaning on relative IR signals of membrane biofoulants

Storage length (weeks)	Cleaning	Relative IR biofilm signals		
		Amide I	Amide II	Polysaccharides
0	–	6.8 ± 1.60	4.18 ± 0.97	16.68 ± 4.39
	+	2.34 ± 1.37	1.36 ± 0.75	5.07 ± 2.47
4	–	4.32 ± 2.37	2.47 ± 1.33	9.62 ± 5.75
	+	2.58 ± 1.89	1.59 ± 1.05	5.35 ± 4.18
8	–	4.15 ± 2.35	2.47 ± 1.51	9.39 ± 5.96
	+	4.03 ± 1.96	2.43 ± 1.10	9.42 ± 5.26

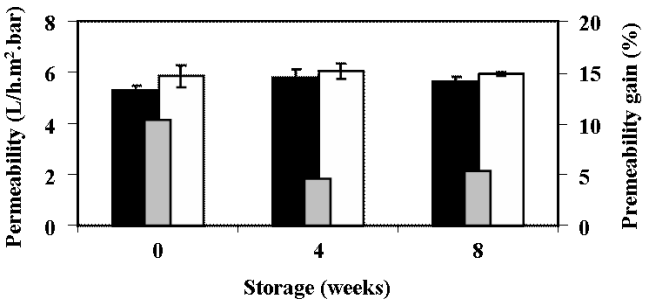

Fig. 2. Membrane permeability measurements. Black boxes: permeability before cleaning. White boxes: permeability after cleaning. Grey boxes: permeability gain.

is related to changes in nutrient supply [13,14]. Since we stored the fouled membranes in distilled water, we produced a nutrient stress that could constitute an induction signal for active biofilm detachment.

3.3. Chemical cleaning tests

After chemical cleaning, several modifications of the foulant matter were observed (Table 1). ATR-FTIR spectra of the membranes cleaned immediately after sampling were modified in an heterogeneous way. The relative signals corresponding to proteins, polysaccharides and nucleic acids decreased significantly after cleaning ($P < 0.05$), indicating the release of biofoulants. Some heterogeneity appeared among signals corresponding to the broad complex region from 900 to 1200 cm^{-1}, and some peaks corresponding to the membrane appeared near 1150 and 1250 cm^{-1}. The signals corresponding to the biofouling deposit of the membrane samples stored for 4 weeks also decreased significantly after cleaning for amide I, amide II and polysaccharides signals ($P < 0.05$). A slight and not significant decrease of the amide I IR band was also observed after cleaning of the membrane cuttings stored for 8 weeks and no modification was observed among the signals corresponding to polysaccharides and nucleic acids. Thus, the biofouling deposit modifications that occurred during storage were associated with a degree of resistance to chemical cleaning after 8 weeks. Increases in permeability of 10, 5, and 5% were obtained after cleaning of the fouled flat sheets not stored, stored for 4 or 8 weeks, respectively. Although chemical cleaning helped to restore hydraulic properties, it seemed to have a very limited impact on the deposit composition. This has been previously observed with an industrial chemical cleaning process used in the plant of Méry sur Oise [2]. However, it should be specified that recovering 10% of the initial permeability after in vitro cleaning is weaker than the permeability gains usually obtained after an industrial cleaning process. The partial restoration of membrane filtration performances observed in the present study can be associated with foulants release and membrane modifications. We only looked at foulants removal but did not check for membrane modifications after cleaning. Cleaning has been shown to modify the surface properties of NF membranes [4,15]. These modifications associated with zeta potential changes conduct to permeability increase of virgin membranes [15]. Alkaline cleaning with chelatants have been shown to be the most efficient cleaning both in term of flux recovery and foulant removal on NF255 nanofiltration membranes in a pilot plant study [4]. Acidic cleanings have been shown to make the membranes less permeable and are thought to repair the membrane ion retention characteristics, even if they remove fouling material from the membrane [4]. Since the cleaning procedure used in our study is a succession of alkaline and acidic treatments with antagonistic effects in term of flux recovery, it was difficult to predict the resultant effect of cleaning onto foulants release and membrane performance restoration. The partial restoration of membrane filtration performances observed after cleaning of membranes stored 8 weeks without any significant biofouling deposit removal could be explained either by a direct effect of cleaning agents onto the membrane (membrane modification) or by release of some inorganic foulants that do not give any IR signal by ATR-FTIR analysis.

4. Conclusion

In conclusion, flux water measurements combined with ATR-FTIR analysis is efficient to evaluate the ageing of the foulant deposit during storage of NF membranes extracted from a drinking water plant. The storage of fouled NF membrane cuts in distilled water at 4°C conducts to alterations of the biofouling deposit but is compatible with cleaning efficiency tests after a storage period of 4 weeks at the most. Our study was done with relatively short membrane samples coming from one module compared to the large membrane surface area of 8 inches-spiral wound modules and to the 9,120 NF200 B-400 membrane elements of the Méry-sur-Oise plant. To evaluate the efficiency of a new cleaning procedure, it would be necessary to test several membrane cuts coming from different areas of several modules. Nevertheless, our results clearly demonstrate that the approach based on the use after storage of fouled membrane samples cut from industrial modules can be applied to test new cleaning chemicals.

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