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Impact of pretreatment conditions and chemical ageing on ultrafiltration membrane performances. Diagnostic of a coagulation/adsorption/filtration process

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ABSTRACT

This study investigated the impact of water pretreatments (i.e. activated carbon, ferric chloride and polyelectrolyte organic polymer) and dynamic chemical ageing by chlorine on performances of PES/PVP hollow fiber membranes. For this, several filtration experiments were carried out on pristine membranes and on 5-year-old membranes sampled from a large drinking water treatment plant (DWTP membranes) exhibiting strong fouling event with no clear explanation. Autopsy performed on the DWTP membranes revealed the presence of a brown fouling layer consisting of organic matters, iron, flocculent polymer and activated carbon. Filtration tests showed the strong fouling sensitivity of the autopsied membranes compared to the pristine membranes. Further autopsy analyses and filtration experiments demonstrated the link between PVP degradation inside the membrane due to frequent chlorine backwashes and the increase in membrane fouling sensitivity.

1. Introduction

Ultrafiltration (UF) is an effective technology for drinking water production. This technology has proven a high efficiency to remove microorganisms, suspended particles, colloids and presents an economic and safe way to provide drinking water [1–4]. However UF technology widespread application is still limited by membrane fouling which induces higher production costs related to a larger consumption of chemical compounds (during pretreatment or membranes cleaning) and a loss of membrane performances (flux decline, membrane's mechanical resistance, etc.) [5,6]. Therefore, operating an UF process at industrial scale needs reliable pretreatments and chemical membrane cleaning procedures.

A pretreatment step is first design to mitigate fouling (i.e. coagulation, adsorption, oxidation) but it could also be used to improve the quality of the produced water (i.e: powdered activated carbon (PAC)/coagulation/UF) [7–11]. As reported in literature, coagulation/flocculation is one of the most successfully used pretreatment operations for membrane processes optimization. In contrast, the addition of PAC into such hybrid processes could be difficult to operate and contradictory effects on membrane fouling have been reported [12]. Some studies showed that pretreatment prior to UF induced an increase in membranes' permeability and decreased the need of chemical cleaning [13,14], while other studies have shown a negative effect especially on flux decline [15–17]. PAC was reported to negatively impact the filtration performances of hydrophobic membranes inducing stronger interaction with natural organic matter (NOM) [12,15].

Furthermore, in order to improve coagulation/flocculation processes, organic polyelectrolyte polymers have been intensively employed in water treatment for approximately four decades [18,19]. Those polymers increase size and strength of flocks and thus improve their settling ability [20–26]. The impact of those polymers on membrane performances is still unclear, but according to their molecular weight of several kDa they might be responsible of MF/UF membranes fouling [24,27]. However, only few works investigated the impact of those polymers on membrane fouling [28,27]. Wang et al. [28] showed that flocculent polymer in low concentration usually used in potable water plant (0.1 mg L^{-1}) induced a strong permeability decrease of MF membranes (0.2 μm) mostly due to pore blocking mechanism.

Comparatively to fouling mechanisms understanding or pretreatment optimization, only few studies have investigated the impact of chemical cleaning procedure on membrane performances [29,30]. Thus, as stated by Porcelli and Judd [30], the same level of understanding as for fouling phenomena has to be reached for membrane chemical cleaning mechanisms. Water backwashes (BW), classified as physical cleaning, are commonly

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used in order to limit membrane fouling but chemical cleaning methods are more efficient in restoring membrane permeability [31–34].

For example, caustic soda encourages organic matters dissolution and promotes the cleavage of polysaccharides and proteins into smaller sugar and amines [35,36]. Acidic cleanings are often employed to remove inorganic cationic species deposited on membranes [37]. Oxidants, such as sodium hypochlorite, are commonly used for reducing biological and NOM fouling [38]. Indeed, during oxidative treatment NOM functional groups are degraded mostly into carboxyl, ketonic compounds and NOM are hydrolyzed at high pH [39,40]. Therefore, oxidative membrane cleaning is often combined to caustic cleaning. However, oxidative cleaning could not be always used as they could degrade membrane materials or produce disinfection byproducts [41–45]. Specifically, it was usually observed that a degradation of membrane material induced a decrease of membranes' tensile properties, an increase in pure water permeability and a modification of membrane adsorption capability (hydrophilicity) consequently increasing the irreversible fouling [46–50]. Acceptable oxidant doses according to membrane materials are often prescribed by membranes suppliers based on limited information and optimization on production site. Furthermore, in all reported studies membranes were exposed to high dose of chlorine compared to field conditions and contact between oxidant and membrane were often performed in static conditions by soaking pristine membranes. In contrast, during UF operation at industrial scale, chemical cleaning sequences are performed on fouled membrane in dynamic backwash mode with low chlorine concentration (e.g. around 15 mg Cl_2 L^{-1}).

Thus, additional data on the impact of chemical cleaning efficiency with realistic conditions (i.e. low chlorine concentration, fouled membrane and dynamic cleaning) are still needed to better understand membranes cleaning efficiency.

In order to provide a relevant diagnostic on the UF performances, all influencing parameters (operating conditions, cleaning, water constituents) have to be studied. Hence, the aim of this study was to improve knowledge on the impact of pretreatments and chemical cleaning on PES/PVP ultrafiltration membrane's performances. In a first part of the study, membranes from a DWTP (after 5 years of water production) were autopsied in order to identify main foulants and to evaluate the membrane ageing. The sampled UF plant exhibited strong membranes permeability decrease with no clear link with the feed's water quality. The autopsy results help to demonstrate if the sampled DWTP membranes were fouled or not. In a second part, autopsy results were used to select experimental conditions for lab-scale filtrations. Filtration tests and accelerated chemical ageing were performed on both pristine membranes and/or on 5-years-old DWTP membranes in order to elucidate the specific role of chemical ageing and fouling on the UF membranes' performances.

2. Material and methods

2.1. Description of the DWTP

The investigated DWTP has a treatment capacity of 150,000 m^3day^{-1} from groundwater resources (L'Haÿ-les-roses, France). The treatment chain combined a pretreatment step with UF separation in order to eliminate potential pesticide traces, turbidity and microbial contamination. The raw water was pretreated by coagulation with 6 mg L^{-1} $FeCl_3$ (technical grade 41% $FeCl_3$ solution from UNIVAR, France), and flocculation in presence of 0.14 mg L^{-1} AN905 organic polyelectrolyte polymer (SNF, France). Powder activated carbon (DACARB, France) was also added at 3.5 mg L^{-1} during the coagulation step. The treated water was then separated from the sludge in a lamellar settling tank. After the settling tank, a microcoagulation step performed with about 0.75 mg L^{-1} $FeCl_3$ and a 130 μm pore size filter protected the UF modules against fine particles that were not removed in the settling tank.

The TOC values and the turbidity of the raw and pretreated waters varied only between 0.3 and 0.4 mg L^{-1} and 0.3–0.5 NFU, respectively. No significant changes were observed during pretreatments. Dissolved ferric iron after microcoagulation was < 10 μg L^{-1}. This large UF plant exhibits important decrease in membrane permeability during the production with no clear link with the feed's water quality. These extreme decreases of permeability oblige membrane operators to perform numerous backwashes and cleaning in place (involving acidic, caustic soda and chlorine cleaning) consequently increasing operating costs and decreasing process efficiency.

2.2. Membrane characteristics and membrane autopsy procedure

The studied membranes were polyethersulfone/polyvinylpyrrolidone (PES/PVP) UF hollow fiber (HF–PES/PVP) membranes with nominal MWCO of 150 kDa. These fibers exhibited inner and outer diameters of 0.8 and 1.3 mm, respectively and were used in inside-out flow mode. The membrane autopsy and the filtration experiments were performed with virgin membranes used as reference and with membranes collected from an industrial module (around 46 m² filtration surface area) used in the DWTP for 5 years. All autopsied fibers were chosen randomly to avoid any influence of a potential degradation/fouling profile inside the module. These membranes were called DWTP membranes. During this 5-year period, the module was periodically backwashed every 6 h with 15 mgCl_2 L^{-1} chlorine solution at pH 8.5 and was also cleaned every 12 days with 32 mM caustic soda solution followed with 15 mM sulfuric acid solution for 8 and 13 min, respectively. Specific cleaning using 15 mM sulfuric acid solution during 13 min was also performed when transmembrane pressure was too high (approximately 0.8–0.9 bar). The DWTP membranes were stored at 4 °C in a 0.077 M sodium bisulfite solution before autopsy and filtration tests. Sodium sulfite is commonly used to protect membrane against microbial growth and preliminary tests showed that sodium bisulfite had no impact on pure water membranes' permeability.

First, 20 full length DWTP fibers were opened lengthwise by using a scalpel and were immersed in ultrasound bath for 5 min to remove the deposit layer. The suspension was then freeze-dried to collect the deposit. The extract was weighed and analytical results were expressed in mg of dry matter per m^2 of hollow fiber.

Secondly, 5 fibers (4 cm length) were chosen randomly and were mineralized in a mixture consisting of 1 mL HNO_3 (69%) and 2 mL H_2O_2 (30%). After heating under reflux at 105 °C during 2 h (Heater block CR-4200, WTW France), the total volume was adjusted to 10 ml with HNO_3 (69%). This mineralization procedure was performed in triplicate on the DWTP fibers. Blank controls were performed on virgin fibers. The HNO_3 solution was analyzed by using an Inductively Coupled Plasma with Optical Emission Spectrometry (ICP–OES, Perkin Elmer, France) Optima 4300 DW for metal quantification. Thermal Differential Analysis and Thermal Gravimetric Analysis (TDA/TGA) were conducted on 5.57 mg of dried extract by using a Thermal Analysis Q600. The virgin membrane, the polymer and the dry deposit were also analyzed by using pyrolysis gas chromatography mass spectrometry (Py-GC/MS) according to the protocol described in Christy et al. [51]. The inner surface of the virgin and DWTP membranes was observed with a scanning electron microscope (SEM) JEOL JSM 5600LV. Attenuated Total Reflectance – Fourier Transformed Infra-Red Spectroscopy (ATR–FTIR) was performed with a Thermo Nicolet 6700 ATR–FTIR.