Membrane Water Treatment, *Vol. 7*, *No. 1* (*2016*) *1-10*
DOI: http://dx.doi.org/10.12989/mwt.2016.7.1.001

Cleaning agents efficiency in cleaning of polymeric and ceramic membranes fouled by natural organic matter

Agnieszka Urbanowska* and Małgorzata Kabsch-Korbutowicz [a]

Department of Environmental Engineering, Institute of Environment Protection Engineering,
Wrocław University of Technology, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland

(*Received September 26, 2014, Revised October 22, 2015, Accepted November 13, 2015*)

Abstract. Ultrafiltration is known to be one of the most commonly applied techniques in water treatment. Membrane fouling is the main limiting factor in terms of process efficiency and restricting it to the manageable degree is crucial. Natural organic matter is often found to be a major foulant in surface waters. Among many known fouling prevention techniques, the membrane chemical cleaning is widely employed. This study focuses on evaluating the cleaning efficiency of polymeric and ceramic membranes with the use of various chemicals. The influence of cleaning agent type and its concentration, membrane material and its MWCO, and cleaning process duration on the recovery of membrane flux was analyzed. Results have shown that, regardless of membrane type and MWCO, the most effective cleaning agent was NaOH.

Keywords: ultrafiltration; polymeric membrane; ceramic membrane; natural organic matter; fouling; chemical cleaning

1. Introduction

Natural organic matter (NOM) removal from water is crucial due to their influence on human health and on water treatment process facilities. Beside intensive colour and disagreeable odour of NOM contaminated waters they adversely impact water treatment processes and distribution systems operation. NOM compounds easily interact with oxidants during disinfection thus creating undesirable by-products that provide nourishment for microbes present in distribution system (Ajmani *et al.* 2014, Filella 2014, Metsämuuronen *et al.* 2014). Problems related to NOM removal from water are being investigated since 1970s (Bond *et al.* 2014). At present, beside processes such as coagulation, active carbon adsorption, oxidation and ion exchange, pressure-driven membrane separation processes: nano- (NF), ultra- (UF) and microfiltration (MF) are applied. These processes allow to remove wide range of contaminants from water. Another advantage of membrane filtration is that it does not transform pollutants nor re-contaminate treated water. Significant membrane parameter in terms of practical application is permeate flux and its decline during operation (Yunos *et al.* 2014, Li and Kim 2014, Konieczny *et al.* 2009). This is a decisive factor when process economics (upkeep) is considered. Flux decline could be caused by, e.g., concentration polarization or fouling. Concentration polarization creates in membrane immediate

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∗Corresponding author, Ph.D., E-mail: agnieszka.urbanowska@pwr.edu.pl
[a] Professor

http://www.techno-press.org/?journal=mwt&subpage=5 ISSN: 2005-8624 (Print), 2092-7037 (Online)

proximity a thin layer of contaminant concentration higher than average in feed solution. From a membrane efficiency viewpoint, the most important is fouling phenomenon which is caused by accumulation of suspended solids, colloids and macromolecular compounds on the membrane surface and/or its pores. It leads to permanent and often irreversible change of membrane properties and thus, beside of flux decline, reducing its lifetime. Significant influence on membrane filtration process, including flux decline, has such factors as (Gao *et al*. 2011, Judd and Jefferson 2003, Zularisam *et al*. 2006):

- natural organic substances nature (e.g., polarity, aromaticity, hydrophilicity/hydrophobicity, particle size);
- solution and NOM properties (e.g., pH, ionic strength, temperature, etc. – they influence electrical charge, configuration and NOM chemical potential);
- membrane properties (e.g., pore diameter, material),
- operating condition of process (i.e., transmembrane pressure - TMP, membrane geometry) and NOM concentration;
- physicochemical interactions between NOM and membrane;
- feed solution pretreatment.

Natural organic matter could be divided to fractions: very hydrophobic (fulvic and humic acids), slightly hydrophobic (dicarboxylic acids) and hydrophilic (polysaccharides and alcohols), that vary in composition, molecular weight distribution and affect membrane fouling to varying degree (Matilainen *et al*. 2010, Metsämuuronen *et al*. 2014). Membrane fouling mechanism depends also on membrane type: in case of microfiltration it takes the form of pore blocking and filtration cake formation that, as a result, reduces membrane pores size and increases contaminant separation rate (He *et al*. 2014, Kim *et al*. 2006). Adsorption inside membrane pores occurs in case of ultrafiltration (Uyak *et al*. 2014). It causes membrane pore diameter reduction and upgrades, to some extent, separation rate.

Membrane blocking could be reduced or suppressed by fouling control techniques or by preventing its occurrence. The restoration of membrane permeability can be achieved by chemical cleaning (Yamamura *et al*. 2014a, b). Cleaning agent selection depends on nature of contaminants blocking the membrane and membrane properties. Most commonly chemicals used, individually or combined, for membrane cleaning are: weak and strong bases, acids, disinfectants, enzymes, detergents (alkaline or non-ionic) and complexing agents. Detergents suspend contaminants and desorb organic compounds while oxidants and enzymes react and “crumble” NOM particles accumulated on the membrane surface (Porcelli and Judd 2010).

The objective of this study was to assess selected cleaning agents efficiency in polymeric and ceramic membrane cleaning fouled with NOM. The influence of cleaning agent type and its concentration, membrane material and its MWCO, as well as cleaning process duration on the recovery of membrane flux was analysed.

2. Materials and methods

Following membrane types were used in this study:

- INSIDE CéRAM™ tubular ceramic membranes (TAMI Industries),
- flat sheet polymeric membranes (Microdyn Nadir).

Membrane properties could be found in Table 1.

Table 1 Membranes used in experiments

Membrane type		Material	Cut-off, kDa	Max. pressure, MPa	Max temp., °C	pH range	Effective filtration area, cm^2
Tubular ceramic, 1-channel							
CeramINSIDE 15 kDa	UF	$Al_2O_3 \cdot TiO_2$	15 kDa	< 9	150	0-14	40
CeramINSIDE 50 kDa			50 kDa				
Flat sheet organic							
PES 5	UF	Polyethersulfone (PES)	5 kDa	-	95	1-14	45.3
PES 10			10 kDa				
C 5		Regenerated cellulose (C)	5 kDa		55	1-11	
C 10			10 kDa				

Table 2 Water sample characteristics

Solution	UV 254 nm absorbance, cm^{-1}	Colour, [$g\ Pt \cdot m^{-3}$]	DOC, $g\ C \cdot m^{-3}$	Conductivity, [$\mu S \cdot cm^{-1}$]	pH	Temperature, °C
Model solution 1	1.97	283.7	34.1	705	5.8	21
Model solution 2	1.67	217.9	27.3	58	4.5	

2 model solutions were used to foul the membranes. Model solution 1 consisted of 0.5 g of humic acid (Sigma-Aldrich) diluted in 1 dm^3 of de-chlorinated tap water. Model solution 2 was taken from humic-acid rich stream flowing from a peat-bog in the Table mountains (Poland) (sampling point location: 50°27′29.97″ N; 16°23′16.87″ E). DOC concentration, UV absorbance at 254 nm, and colour intensity were the measures of organic matter concentration in examined solutions. The water sample characteristics are given in Table 2. In model solution 2 very hydrophobic acids and slightly hydrophobic acids fractions, characteristic for humic and fulvic acids, make up 54% of NOM content. 5% of NOM was found to be a charged hydrophilic compounds fraction and 41% was a neutral hydrophilic substances fraction, consisting of low molecular weight hydrophilic, neutral charge compounds. Fractionation of NOM present in water source used to prepare model solution 2 has been covered in previous papers (Urbanowska and Kabsch-Korbutowicz 2015).

As a membrane cleaning agents the following solutions were used:

- NaOH (0.0025 M; 0.01 M; 0.05 M[1]),
- HCl (pH 3, pH 4),
- citric acid (pH 3, pH 4),
- SDS (1 $g \cdot dm^{-3}$, 5 $g \cdot dm^{-3}$),
- distilled water.

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[1] 0.05 M NaOH solution (pH 12.4) exceeds C membrane recommended pH range (1-11)

Ceramic membrane cleaning experiments were conducted with the use of J.A.M. INOX PRODUKT laboratory installation (Fig. 1) consisting of a membrane module, 10 dm^3 feed tank, flux temperature control unit, and Grundfos pump. Membranes were hermetically sealed in a metal housing equipped with inlets and outlets.

A lab-scale Amicon 8400 (Millipore) set-up (Fig. 2) was used to evaluate polymeric flat sheet membrane cleaning effectiveness. Amicon ultrafiltration cell, suitable to work with flat membranes in a dead-end mode, has 400 cm^3 of maximum feed solution capacity and 76 mm of membrane diameter. In order to ensure equal distribution of contaminants in feed solution, the cell was placed on a magnetic stirrer.

The transmembrane pressure used in each experiment was 0.3 MPa. In cross-flow filtration experiments, cross-flow velocity equal to 1.9 m/s was maintained.

Each new membrane, before experiments, was conditioned by continuous filtration of distilled water until the constant permeate flux (J_0) was achieved. Than selected model solution was

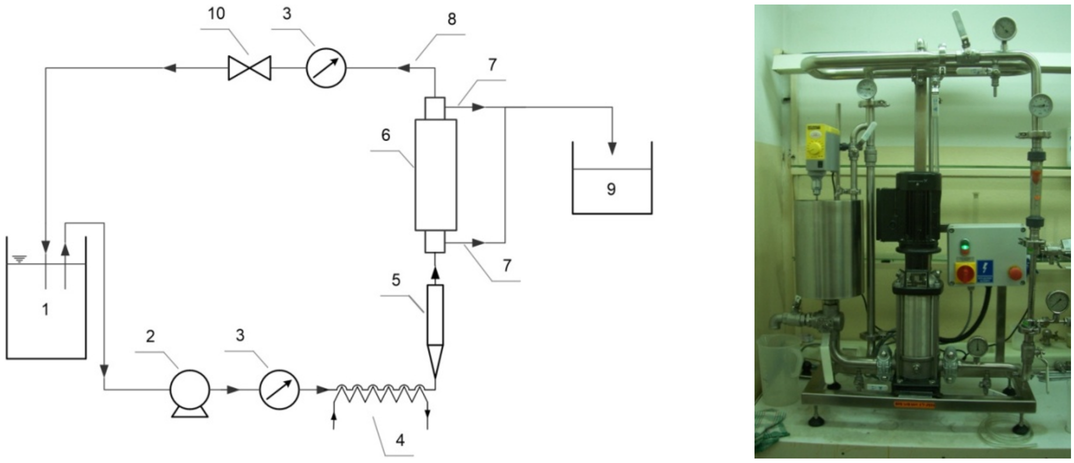


Fig. 1 J.A.M. INOX PRODUKT cross-flow membrane system (1 - feed tank, 2 - pump, 3 - pressure gauge, 4 - thermostat, 5 - flowmeter, 6 - membrane module, 7 - permeate, 8 - concentrate, 9 - permeate tank, 10 - valve)

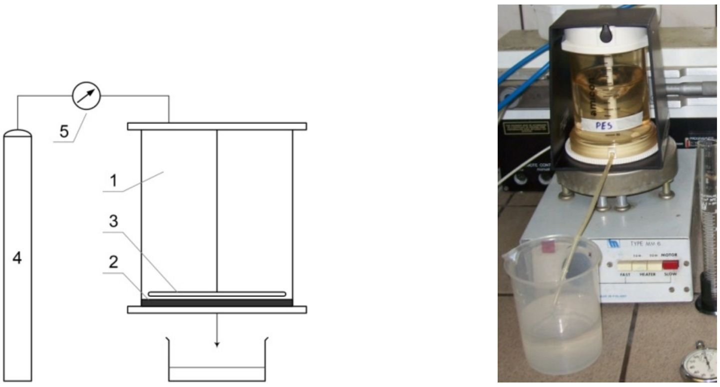


Fig. 2 Amicon 8400 dead-end ultrafiltration system (1 - ultrafiltration cell, 2 - membrane, 3 - stirrer, 4 - pressurized nitrogen cylinder, 5 - pressure valve)

continuously filtered through membrane in order to foul the membrane until no measurable permeate flux (J_f) change was observed (membrane was considered as fouled then). Fouled membrane cleaning was subsequently started by replacing the feed water with cleaning solution. Constant TMP 0.3 MPa was maintained during fouling and cleaning. Cleaning was continued until no permeate flux volume improvement could be observed or initial permeate flux (J_0) was achieved. Finally, 30 minutes of distilled water filtration was performed to test the final cleaning outcome.

Apart from analysis of permeate flux, total membrane resistance value was calculated (using Hagen-Poiseuille equation)

$$J = \frac{TMP}{\mu \cdot R} \tag{1}$$

where TMP – transmembrane pressure (Pa), μ – dynamic viscosity factor (Pa·s), R – total membrane resistance (m^{-1}).

Membrane susceptibility to fouling was determined upon value of relative membrane permeability calculated as a ratio of cleaning agent permeate flux (J) to membrane initial permeate flux (J_0). Cleaning effectiveness (η) was calculated as percent of flux recovery

$$\eta = \left(1 - \frac{J_0 - J}{J_0 - J_f}\right) \cdot 100\% \tag{2}$$

3. Results

Transport properties of membranes in terms of their total resistance (R) during entire process (conditioning, fouling with solution 1, cleaning with the use of 0.0025 M NaOH solution, final distilled water filtration) are presented in Fig. 3. When model solution 2 was used, similar curve shapes for each process parts were observed. Clean 50 kDa ceramic membrane was found to be most permeable ($R = 1.11 \cdot 10^{13}$ m^{-1}) while ceramic 15 kDa was on the opposite (over one order of magnitude more resistant - $1.66 \cdot 10^{14}$ m^{-1}). 50 kDa ceramic membrane was more prone to fouling than C 10 kDa and the latter was found to be least resistant when fouled ($2.77 \cdot 10^{13}$ m^{-1} vs. $1.70 \cdot 10^{13}$ m^{-1}). Although Fig. 3. presents only one fouling solution and single cleaning agent, the results are typical for all others: constant flux in conditioning, gradual increase in membrane resistance during fouling until quasi-constant state, sharp recovery of permeability in early minutes of cleaning then slowly reaching maximum level of recovery and steady flux in final rinsing with distilled water. Total membrane resistance before fouling and after cleaning for other membranes and cleaning agents can be found in Table 3.

Fouling experiments has clearly shown that ceramic membranes were visibly more prone to fouling than polymeric membranes. Moreover, C membranes tends to be significantly less prone to fouling than the membrane made of PES (Fig. 4.). Relative membrane permeability (J/J_0) values decreased to 0.32 - 0.37, 0.42 - 0.50 and 0.52 - 0.80, respectively for ceramic, PES and C membranes. No significant influence of feed solution type on membrane fouling could be noticed. Such uniform results for each solution are connected with feed water characteristics: analytical data has shown similar composition of model solutions. Moreover, rapid permeate flux decline was noticed during first 20 minutes of filtration. Subsequent filtration resulted in flux stabilization up to constant value reached at about 120 min of filtration.

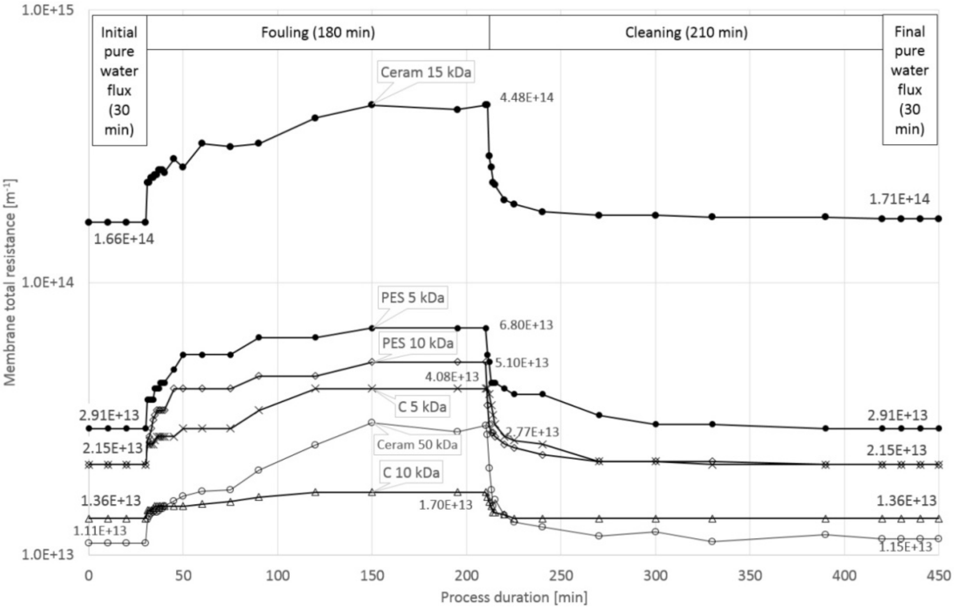
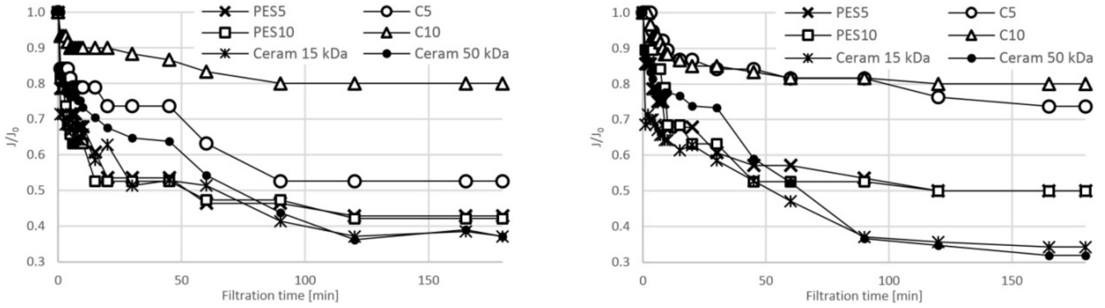


Fig. 3 Total membrane resistance for various membranes (membranes fouled with model solution 1 and cleaned by 0.0025 M NaOH)

Table 3 Total membrane resistance before fouling and after cleaning (membranes fouled with model solution 1)

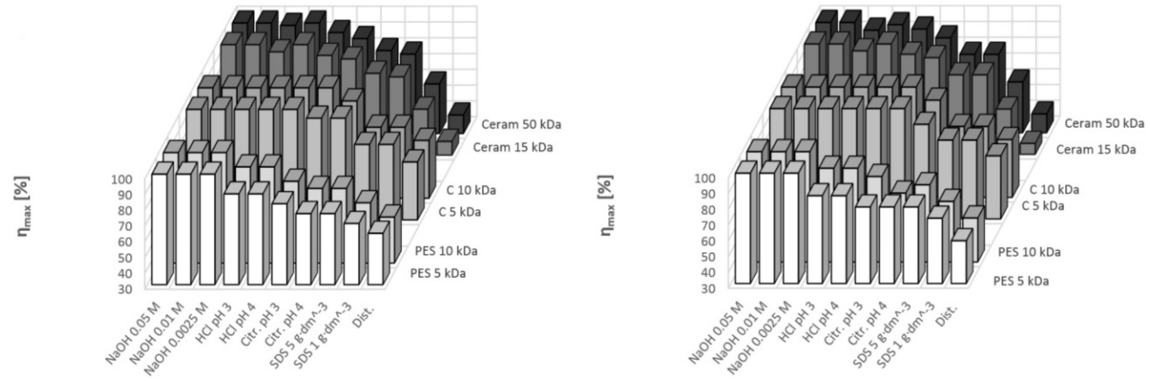
Membr.	Distilled water, clean membr.	After cleaning									
		NaOH			HCl		Citric acid		SDS		Distilled water
		0.05 M	0.01 M	0.0025 M	pH 3	pH 4	pH 3	pH 4	5 g·dm^{-3}	1 g·dm^{-3}	
PES 5	$2.91\cdot10^{13}$	$2.91\cdot10^{13}$	$2.91\cdot10^{13}$	$2.91\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$3.14\cdot10^{13}$	$3.14\cdot10^{13}$	$2.27\cdot10^{13}$	$2.27\cdot10^{13}$
PES 10	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$3.14\cdot10^{13}$	$3.14\cdot10^{13}$	$2.27\cdot10^{13}$	$2.27\cdot10^{13}$	$3.26\cdot10^{13}$	$3.40\cdot10^{13}$	$2.40\cdot10^{13}$
C 5	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$
C 10	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$2.15\cdot10^{13}$	$2.15\cdot10^{13}$	$1.36\cdot10^{13}$	$1.36\cdot10^{13}$	$2.21\cdot10^{13}$	$2.21\cdot10^{13}$	$1.36\cdot10^{13}$
Ceram 15 kDa	$1.66\cdot10^{14}$	$1.66\cdot10^{14}$	$1.66\cdot10^{14}$	$1.71\cdot10^{14}$	$1.69\cdot10^{14}$	$1.74\cdot10^{14}$	$1.76\cdot10^{14}$	$1.91\cdot10^{14}$	$1.91\cdot10^{14}$	$2.24\cdot10^{14}$	$2.71\cdot10^{14}$
Ceram 50 kDa	$1.11\cdot10^{13}$	$1.11\cdot10^{13}$	$1.11\cdot10^{13}$	$1.15\cdot10^{13}$	$1.12\cdot10^{13}$	$1.16\cdot10^{13}$	$1.18\cdot10^{13}$	$1.27\cdot10^{13}$	$1.27\cdot10^{13}$	$1.46\cdot10^{13}$	$1.75\cdot10^{13}$

Influence of cleaning agent type and its concentration on maximum cleaning efficiency ($\eta_{\max}$) of each membrane fouled with the use of examined solutions was determined in membrane cleaning experiments (Fig. 5). Obtained results allowed to arrange cleaning agents according to their ability to clean fouled membrane in the following order: NaOH > HCl > citric acid > SDS > distilled water for PES membrane, NaOH = HCl > citric acid > SDS > distilled water for C and ceramic membranes, which is in accordance with findings of other authors (Zondervan and Roffel 2007). Results clearly show that NaOH, regardless of its concentration, was the most effective



(a) (b)

Fig. 4 Relative membrane permeability for model solution 1 (a) and 2 (b) during membrane fouling

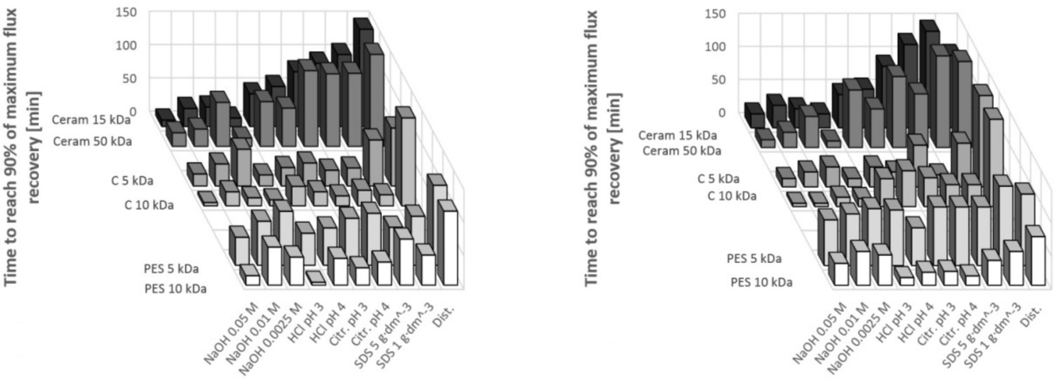


(a) (b)

Fig. 5 Maximum cleaning efficiency of cleaning solutions for membranes fouled with NOM using model solution 1 (a) and 2 (b)

cleaner, being able to fully restore initial flux. This effect was obtained regardless of membrane and feed solution type (except for ceramic 50 kDa membrane cleaned with 0.0025 M NaOH). It could be attributed to high amount of hydrophobic NOM compounds present in analysed solutions (Urbanowska and Kabsch-Korbutowicz 2015). Fouling by hydrophobic compounds has been found to be effectively removed by NaOH (Lee *et al*. 2001). Maximum cleaning efficiency (100%) was also noticed for HCl, but only when applied to C or ceramic membrane. In the case of PES membrane HCl was less effective (87 - 90%). Distilled water was found to be least effective (PES: 57 - 63%, C: 67 - 70%, ceramic: 38 - 43%). Influence of cleaning agent concentration on η_{max} was also observed. For example, application of citric acid solution with pH 3 instead of pH 4 or 5 $g \cdot dm^{-3}$ instead of 1 $g \cdot dm^{-3}$ SDS solution resulted in η_{max} improvement, e.g., from 73 to 84% and from 68 to 79% respectively (for PES 10 kDa and model solution 2).

In the experiments the kinetics of membranes cleaning process has been also analysed. Influence of cleaning process parameters on time necessary to reach at least 90% of maximum permeate flux recovery (0.9 η_{max}) is shown in Fig. 6. It could be derived that polymeric 10 kDa membranes tend to be clean faster than membranes with lower cut-off value or ceramic membranes. Also, ceramic membranes were found to be much less effectively cleaned by weak

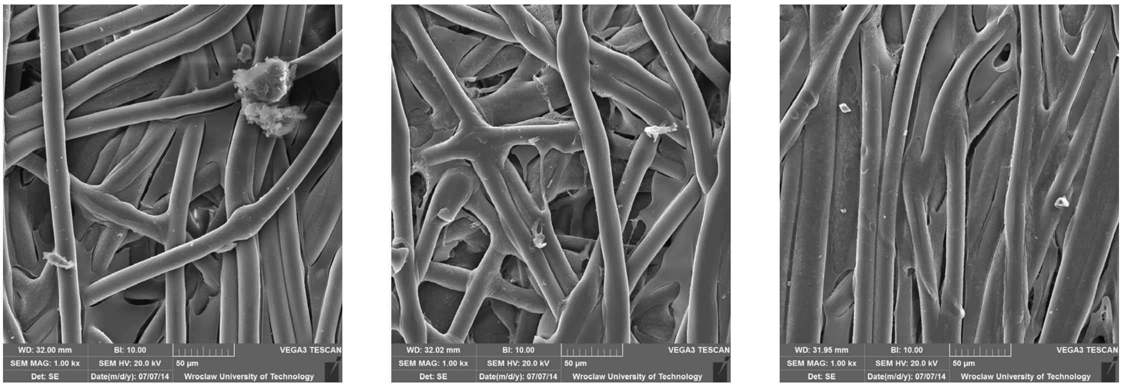


(a) (b)

Fig. 6 Cleaning process kinetics: time required to reach 90% of $\eta_{\max}$ for membranes fouled with NOM using model solution 1 (a) and 2 (b)

cleaners (citric acid and SDS) than polymeric membranes. HCl solution at pH 3 was found to be very fast cleaning agent for each 10 kDa polymeric membrane and each ceramic membrane (regardless of fouling solution properties). Distilled water was found to be slowest cleaning agent. Remarkable influence of cleaning agent concentration on cleaning performance was observed: higher agent concentration resulted in faster cleaning, which is in accordance with other reports (Bird and Barlett 2002, Porcelli and Judd 2010). Moreover, C and ceramic membranes were cleaned significantly faster by NaOH and HCl when compared to PES membranes.

Additionally, SEM images of new PES 10 kDa membrane surface, fouled by NOM and cleaned using 0.01 M NaOH were taken (Fig. 7). No significant visible amount of NOM contamination (e.g., cake layer) can be found, and it could be inferred that either SEM imaging conditions (vacuum) destroyed NOM foulants or standard fouling occurred. In case of standard fouling, NOM particles accumulate inside membrane pores thus limiting their diameter. Thus, probably, fouling was caused by pore blocking inside membrane, which is with accordance to expectations about ultrafiltration.



(a) (b) (c)

Fig. 7 SEM images of consecutively: new, fouled and cleaned PES 10 kDa membrane surface (magnitude 1000×)

4. Conclusions

One of the main factors limiting pressure-driven membrane processes application in water treatment is increasing permeate flux drop over time observed during water treatment system operation that is caused by membrane fouling. One of the techniques that aids in limiting this adverse phenomenon is chemical membrane cleaning with the use of strong and weak bases, acids, detergents etc. Research has shown that the most effective cleaning agent in terms of reclaiming the initial permeate flux of membranes fouled with natural organic matter is NaOH. It reached 100% membrane cleaning efficiency (for each tested membrane; 0.01 M or higher NaOH concentration) which could be attributed to feed solution properties (hydrophobic NOM compounds). Cleaning dynamics results has shown that polymeric membranes made of cellulose were cleaned faster than those made of polyethersulfone and ceramic material. Not without significance is membrane cut-off value: 10 kDa membranes were cleaned more rapidly than others. It is also worth noticing that cleaning agent concentration influenced process dynamics: more concentrated solution gave maximum initial flux reclaim earlier.

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