

University of Groningen

Evaluation of different cleaning agents used for cleaning ultra filtration membranes fouled by surface water

Zondervan, Edwin; Roffel, Brian

Published in:
Journal of Membrane Science

DOI:
[10.1016/j.memsci.2007.06.041](https://doi.org/10.1016/j.memsci.2007.06.041)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2007

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Zondervan, E., & Roffel, B. (2007). Evaluation of different cleaning agents used for cleaning ultra filtration membranes fouled by surface water. *Journal of Membrane Science*, 304(1-2), 40-49.
<https://doi.org/10.1016/j.memsci.2007.06.041>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Evaluation of different cleaning agents used for cleaning ultra filtration membranes fouled by surface water

Edwin Zondervan*, Brian Roffel

Department of Chemical Engineering, Research Institute for Technology & Management, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 20 April 2007; received in revised form 25 May 2007; accepted 19 June 2007
Available online 23 June 2007

Abstract

This paper reviews the published literature on potential membrane fouling components, available cleaning agents and possible interactions between cleaning agents and fouling components. It also lists the cleaning models available in the literature, and evaluates the advantages and disadvantages of these models. Based on this outcome, a new cleaning model is proposed to capture cleaning dynamics for 10 different cleaning agents, varying from acidic, alkali and oxidizing to sequestering agents and detergents that were used to clean dead-end ultra filtration membranes fouled by surface water. The model is effectively fitted to the experimental data of the different cleanings. Two criteria are subsequently introduced to quantify the overall cleaning effect of a cleaning agent in terms of cleaning rate and cleaning effectiveness. For membranes fouled by surface water with high organic content it was found that caustic-and oxidizing cleaning agents give the best overall cleaning results.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Ultra filtration; Surface water; Chemical cleaning; Modeling

1. Introduction

Membrane ultra filtration is increasingly used as a total or intermediate surface water purification technique. In the last 15 years, production of polymeric membrane fibers as well as ceramic membranes became economically attractive. Membrane performance, however, is influenced by fouling. In addition to hydraulic cleaning, chemical cleaning in which cleaning agents are used is a common way to remove foulants. Although chemical cleaning is a useful way to restore membrane performance, membrane cleaning procedures are often based on rules of thumb and are usually conservative.

This paper presents a brief literature review on potential fouling components, cleaning agents and possible interactions between fouling components and cleaning agents. It also addresses the modeling efforts reported in the literature. From a practical viewpoint, a component-balance-based model will be used in the further evaluation of different cleaning agents. The model is fitted to the data collected for the dif-

ferent cleaning agents, and subsequently the instant cleaning rate and overall cleaning effectiveness can be calculated. The cleaning rate and effectiveness form good evaluation criteria for the selection of a proper cleaning agent. The proposed model and selection criteria are suitable to evaluate different cleaning agents. However, it should be noted that some cleaning procedures are more sensitive to measurement errors than others. For modeling data, the response from turbidity measurements and pH measurements is collected. In some cases, the turbidity response was found to be small, compared to the measurement noise, resulting in considerable modeling errors.

For Twente canal water (characterized as water with reasonable amount of organic content, DOC = 9 mg/l, TOC = 9.5 mg/l), caustic and oxidative cleaning procedures are most effective. Also commercial blends can be used to clean the membrane. Commercial blends often contain detergents. It was found that detergents should be used in low concentrations (around 0.05–0.1%), otherwise negative effects occur, such as TMP increase, instead of a decrease.

The main objective of this research is to evaluate the cleaning model for different cleaning agents and to develop criteria to value the overall effect of a cleaning agent.

* Corresponding author. Tel.: +31 53 428 7309.
E-mail address: e.zondervan@rug.nl (E. Zondervan).

2. Theory

2.1. Fouling components

Surface water is known to contain three potential membrane fouling categories, namely microbial content (bacteria, viruses, etc.) [7], organic content (natural organic matter) [8–13] and inorganic content (minerals) [14,16–18]. Sometimes a fourth category is added, namely: colloidal content (e.g. clay). The physicochemical mechanisms of fouling components attaching to the membrane surface are complex and poorly understood. Physical adsorption, electro-static charge and bridge-formation are fouling mechanisms frequently reported in the literature. An overview of the research conducted in the field of membrane chemical cleaning in relation to membrane fouling is presented in Table 1. The plus and minus sign in the fouling section of the table indicate if a certain type of fouling was present (+) or absent (–). The symbols in the chemical cleaning agents part of the table mean: (+) tests were performed with this type of cleaning agent, (–) no tests were performed with this cleaning agent, (0) this type of cleaning agent found to be most effective and (*) no information available. Table 1 gives an overview of what kind of foulants were found on membrane surfaces and which cleaning agents were accordingly found to be most effective removing the foulant. It shows that for surface water and waste water the feed is a complex mixture of the three basic fouling categories. Organic fouling has been reported in many publications, in addition to that, was found that caustic cleaning procedures are often most effective.

2.2. Cleaning agents

Cleaning agents are substances that can be used to effectively remove matter that is not an integral part of the membrane surface. Chemical cleaning effectiveness depends on the cleaning flow, the concentration of the cleaning agent and/or the cleaning temperature. In principle six basic cleaning agent categories can be distinguished [14](see Table 2). In addition to the basic categories, many commercial blends are available. Commodity agents (such as sodium hydroxide or hydrochloric acid) are generally less expensive than the commercial blends, however, blends can be dosed in lower concentrations.

2.3. Interactions between fouling components and cleaning agents

Weis et al. [17] believes that a cleaning agent can affect fouling materials present on a membrane surface in three ways: (i) foulants may be removed, (ii) morphology of foulants may be changed (swelling, compaction) and/or (iii) surface chemistry of the deposit may be altered, such that the hydrophobicity or charge is modified. The cleaning agents may react chemically or physically with the foulant, to weaken the cohesion forces between the foulants themselves and the adhesion between the foulants and the membrane surface. The possible reactions between foulant and cleaning agent are: hydrolysis, peptization, saponification, solubilisation, dispersion (suspension) and

chelation [14], as presented in Table 3. It is further noted that biocides (cleaning agents used to treat microbial fouling) are grouped under ‘Disinfectants’. For a more extended discussion on chemical cleaning in relation to treatment of biofouling, the reader is referred to Ref. [15].

In addition to positive effects between cleaning agent and foulant, also negative effects might occur if an inappropriate cleaning agent is chosen, membrane performance could even be adversely affected. Suppliers of cleaning agents advise in which fouling case, which cleaning agent should be used (cleaning solutions are generally applied within the range of 0.5–1.5%). In Table 4 an overview of preferred cleaning solution in relation to membrane fouling is presented.

According to Mohammadi [19], the best choice of cleaning agent selection is based on a knowledge of the feed and the foulant composition and is in most cases performed by trial and error. Other decision criteria are based on the safety, the stability, the price and the waste treatment of the cleaning agent. Especially the impact of the cleaning agent on the environment and the membrane are important factors in the selection of a cleaning agent according to Maartens et al. [5].

2.4. Modeling of membrane chemical cleaning

2.4.1. Model by Bird and Bartlett

Bird and Bartlett [1] developed a model to predict the change in flux during caustic cleaning of a flat plate cross flow micro filtration membrane fouled by whey proteins. Starting with Darcy’s equation, which relates the flux J to the total resistance R_t as:

$$J = \frac{\Delta P}{\mu R_t} \quad (1)$$

where ΔP is the trans-membrane pressure and μ is the viscosity. The total resistance is modeled by a resistance in series approach:

$$R_t = R_m + R_c + R_p + R_{cp} \quad (2)$$

where R_m is the membrane resistance, R_c is the hydraulic resistance as a result of fouling at the membrane surface, R_p the resistance as a result of in-pore fouling and R_{cp} is the so-called resistance as a result of concentration polarization. In Bird and Bartlett’s model the resistance as a result of concentration polarization disappears on the release of TMP and the membrane resistance is a material property. The resistance decrease during caustic cleaning at the membrane surface is modeled by a second order decrease, according to:

$$\frac{dR_c}{dt} = -k_c R_c^2 \quad (3)$$

And the in-pore resistance is correlated to the effective pore diameter by Carman–Kozeny’s equation:

$$R_p = \frac{36\tau(1-\varepsilon)^2 l}{\varepsilon^3 d_c^2} \quad (4)$$

where τ is the tortuosity, ε the porosity and l is the length of the pore. The effective pore diameter d_c is based on the diameter of the particle that is blocking the pore. During caustic cleaning the

Table 1
Research performed in relation to fouling and chemical cleaning of membranes

Researcher	Application	Membrane type	Organic fouling	Inorganic fouling	Microbial fouling	Acidic cleaning	Caustic cleaning	Detergent cleaning	Sequestering cleaning	Oxidative cleaning	Enzymatic cleaning	Blend cleaning
Li et al. [2]	Gluth. Ferm. Broth	UF/PS	+	–	+	+	0	0	–	+	+	+
Madaeni and Mansourpanah [3]	Boiler water	RO/PA	–	+	–	+	0	0	0	+	–	+
Maartens et al. [5]	Paper effluent	UF/PES	+	–	–	–	+	+	–	+	+	0
Mohammadi et al. [6]	Waste water	RO/PA	–	–	–	–	0	0	0	–	–	–
Lee et al. [19]	Surface water	UF/PES	+	–	–	+	0	+	–	–	–	–
Liikanen et al. [20]	Surface water	NF/PPA	+	+	+	+	0	+	0	+	–	+
Mohammadi [21]	Waste water	UF/PS	+	+	–	+	0	0	+	+	–	–
Madaeni et al. [22]	WPC	RO/PA	+	+	+	0	–	+	+	+	+	+
Zhu and Nystrom [23]	BSA/LYS	UF/PES	+	–	–	+	0	+	–	+	–	–
Munoz et al. [24]	BSA/WPC	UF/PS	+	–	–	–	0	+	–	–	0	–
Bartlett [25]	WPC	MF/CER	+	–	–	0	–	–	–	–	–	+
Pavlova [26]	Waste water	UF/PAN	+	+	+	–	0	–	–	0	–	–
Sungpet et al. [27]	Textile effluent	NF/*	–	+	–	0	+	–	–	–	–	–
Mo and Huanga [28]	Raw water	MF/PE	+	+	+	0	0	–	–	–	–	–
Veza and Rodriguez-Gonzalez [29]	Waste water	RO/*	–	+	–	–	0	–	–	0	–	–
Chen et al. [30]	Waste water	UF/PES	–	–	–	+	+	–	–	–	–	0
Gwon et al. [31]	Ground water	UF/PA	+	+	–	0	0	–	–	–	–	–
Weis [32]	Sulphite liquor	UF/PES	+	+	–	–	0	–	–	–	–	+
Lim and Bai [33]	Waste water	MF/PVDF	+	+	+	0	0	–	–	0	–	–

(+) present/tested; (–) not present/tested; (0) best tested; (*) no information available.

Table 2
Basic cleaning agent categories and examples

Caustic	Acidic	Sequestering/complexing	Detergent/surfactant	Enzymatic	Oxidizing/disinfectant	Blend
NaOH	HCl	EDTA	Alkyl sulphate	Alpha-CT	NaClO	4Aquadclean (Aquacare)
KOH	HNO ₃		SDS	CP-T	H ₂ O ₂	Divos (Diverseylever)
NH ₄ OH	H ₂ SO ₄		CTAB	Peroxidase	KMnO ₄	Triclean (triton)
	H ₃ PO ₄					Ultrasil/Aquadclean (Ecolab)
	Oxalic					
	Citric					

Table 3
Possible interactions between cleaning agents and foulants

	Caustic	Acidic	Sequestering	Oxidizing/disinfection	Detergent/surfactant	Enzymatic
Organic	Hydrolysis	Hydrolysis/saponification	Dispersion	Oxidizing	Chelation	Peptization
Inorganic	Solubilization/chelation	Solubilization/chelation	Dispersion	Oxidizing	Chelation	–
Microbial	–	–	–	Disinfecting	–	Peptization

particle size is decreasing which means that the effective pore diameter is increasing. Bird and Bartlett propose the following swelling–compaction relationship:

$$d_e = \left(d_0 - 2 \left(\frac{\delta}{k_1 t + \delta} \right) (k_2 t + \delta) \right) \quad (5)$$

where d_0 is the initial pore diameter and k_1 , k_2 and δ are fit parameters. Although the model proposed by Bird and Bartlett may elucidate some physical insight into the cleaning process, the model is not very suitable for process optimization. The model contains too many parameters, such as porosity, tortuosity, particle diameters, rate constants, etc., that cannot easily be determined by means of experiments. In addition, the model does not incorporate adjustable control variables such as flow, concentration or temperature.

2.4.2. The Li model

Li et al. [2] modeled the chemical cleaning of dead-end ultra filtration membranes fouled by fermentation broth of glutamic acid by a simple kinetic model, assuming that the flux will increase during cleaning according to a first order equation:

$$\frac{dJ}{dt} = kJ \quad (6)$$

where k is a rate constant related to temperature according to the Arrhenius equation:

$$k = k_0 \exp \left(\frac{-E_A}{RT} \right) \quad (7)$$

The advantage of the Li model is that it is simple, the protocol to determine the model parameters is straight forward and it has only two model parameters. It includes a variable to control the cleaning process (temperature) and the Arrhenius term implies cleaning is a kinetic process. However, the experimental verification of the model was not done extensively. In addition, the first-order Li model may not be able to capture cleaning behavior well, if operational setting of the cleaning process change, and dynamics become more complex.

2.4.3. Model by Zondervan

The model proposed by Zondervan et al. [34] was tested on the caustic cleaning of dead-end ultra filtration membranes fouled by surface water and is based on two component balances:

$$\frac{dx_W}{dt} = -k'J(x_W - x_{W,\infty}) + r_W'' \quad (8)$$

$$\frac{dx_C}{dt} = k'J(x_{C,\text{in}} - x_C) + n_C r_W'' \quad (9)$$

where x_W is the fouling state and x_C is the cleaning agent state. J is the normalized cleaning flux and $x_{C,\text{in}}$ is the cleaning agent concentration at the inlet of the membrane. k' is the flushing rate

Table 4
Preferred cleaning

	Proteins	Glucanes	Pigments	Minerals	Hydrophobes	Starch	Tanins	Pectin	Fat
Alkaline	0	–	–	–	–	0	0	0	0
Acidic	0	–	0	+	–	–	–	–	–
Surfactants	0	0	+	–	+	0	–	0	+
Soil dispersers	0	0	+	0	0	0	0	0	0
Complexing agents	0	0	+	+	0	0	0	0	0
Enzymes	+	+	–	–	–	+	–	+	+
Oxidizers	+	+	–	–	0	+	+	+	0

(+) positive cleaning effect; (–) negative cleaning effect; (0) positive, neither negative effect. Reference: Ecolab Membrane Cleaning Congress 2005, Dusseldorf.

constant, $x_{W,\infty}$ is the fouling state at infinite cleaning time and n_C is a pseudo-stoichiometric constant. r_W'' is the cleaning rate, defined as:

$$r_W'' = -k'' x_C (x_W - x_{W,\infty}) \quad (10)$$

where k'' is a cleaning rate parameter which may be dependent on the cleaning temperature.

The fouling state is defined in terms of trans-membrane pressure:

$$x_W(t) = \frac{\Delta P(t)}{\Delta P_0} \quad (11)$$

where ΔP_0 is the trans-membrane pressure at the beginning of the cleaning and $\Delta P(t)$ is the trans-membrane pressure during cleaning. As trans-membrane pressure during cleaning cannot directly be measured, cleaning dynamics are captured by turbidity measurements. The cleaning concentrate is collected at the membrane outlet, and turbidity is subsequently measured. The following relationship between the trans-membrane pressure during cleaning and the measured turbidity is suggested:

$$\Delta P(t) = 1 - \varepsilon_\infty \frac{\int_0^t E dt}{\int_0^{t_e} E dt} \quad (12)$$

E is the turbidity measured at the outlet of the membrane unit and t_e is the duration of the chemical cleaning procedure. The integral of the turbidity reflects the amount of irreversible fouling that has been removed. The integral is normalized to one and scaled by means of the trans-membrane pressure-based cleaning effectiveness:

$$\varepsilon_\infty = \frac{\Delta P_0 - \Delta P_\infty}{\Delta P_0 - \Delta P_m} \quad (13)$$

where $\Delta P_\infty \approx \Delta P(t_e)$ and ΔP_m is the trans-membrane pressure of a clean membrane determined at a specified clean water flux. The cleaning effectiveness is the ratio of the decrease in trans-membrane pressure during a chemical cleaning procedure and the increase in trans-membrane pressure during a production cycle.

The cleaning state can be determined by means of pH measurements and is defined according to:

$$x_C(t) = \frac{10^{-\text{pH}(t)}}{10^{-\text{pH}^*}} \quad (14)$$

where $\text{pH}(t)$ is the pH measured at the outlet of the membrane unit and pH^* is a reference pH.

To characterize the effect of a cleaning agent we introduce two important evaluation criteria, the instant cleaning rate, defined as:

$$r_i = \left. \frac{dx_W}{dt} \right|_{t=0} \quad (15)$$

And the overall cleaning effectiveness, η :

$$\eta = \frac{x_W(0) - x_W(t_e)}{x_W(0) - x_{W,\infty}} \quad (16)$$

where $x_W(0)$ is the fouling state at the beginning of the cleaning and $x_W(t_e)$ is the fouling state at the end of the cleaning process.

The model by Zondervan is simple, has three model parameters, namely k' , k'' and n_C , that can be determined by a straightforward experimental protocol (based on pH and turbidity measurements). The model also includes control variables as cleaning flow and cleaning agent concentration. Even temperature may be incorporated, by determining the relationship between temperature and the cleaning rate constant. The model structure is based on component balances and is suitable for process optimization. From the model two intuitive criteria can be derived easily for quantification of the overall cleaning effect.

3. Materials and methods

3.1. Experimental setup

Fouling and subsequent cleaning experiments were performed with a laboratory scale dead-end ultra filtration unit. The setup consisted of a 1 in. ultra filtration membrane module (100 fibers of 30 cm in a module housing with diameter = 1 in.), a filtration and a backwash pump, flow meters to monitor fluxes, thermometers to record temperature and correct trans-membrane pressure. Pressure meters to determine trans-membrane pressure. In this setup, trans-membrane pressure can only be measured during filtration. During a cleaning experiment, concentrate is collected in fractions, at the permeate outlet, and from these fractions pH and turbidity (E) are determined. A simplified diagram of the setup is shown in Fig. 1.

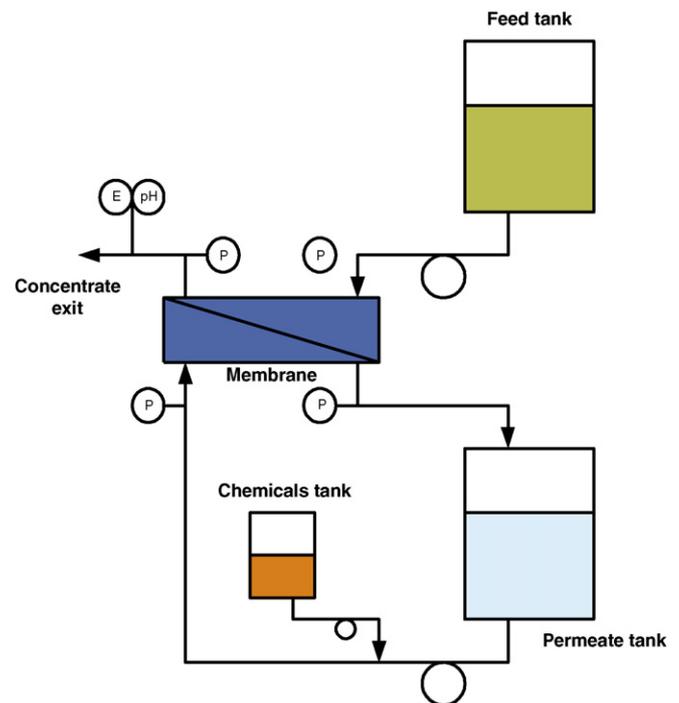


Fig. 1. Simplified scheme of the experimental setup. During a fouling experiment, surface water is pumped from the feed tank through the membrane and is collected in the permeate tank. During a backwash, permeate water is flushed in opposite direction through the membrane and is drained from the system at the concentrate outlet. During chemical cleaning, chemicals are flushed through the membrane and drained at the concentrate outlet.

Table 5
Twente canal water quality parameters

pH	7.70
Conductivity (mS/m)	56.0
Turbidity (FNU)	13.5
UV254 (l/m)	21.3
NO ₂ (mg/l)	0.00
NO ₃ (mg/l)	5.70
Cl (mg/l)	11.0
NH ₄ (mg/l)	0.10
<i>o</i> -PO ₄ (mg/l)	0.10
Si (mg/l)	1.60
SO ₄ (mg/l)	38.3
Al (μg/l)	90.0
Ca (mg/l)	48.4
Mg (mg/l)	6.70
Fe (mg/l)	0.80
TOC (mg/l)	9.40
DOC (mg/l)	8.80

Twente canal surface water is used to foul the UF membranes. In Table 5 water quality parameters are summarized.

No flocculant is added to the surface water. The water has an average pH of 7.5, an average conductivity of 580 μS/cm, an average O₂ concentration of 8–10 mg/l and an average turbidity of 2–20 FNU. The average water temperature was approximately 15°C. Twente canal water is known for its high organic content (DOC/TOC values around 10 mg/l). Surface water is stored in a 201 feed tank, which is refreshed every 5 h. Ten different cleaning agents were used to clean the fouled membrane. The membrane used in the experiments is a Norit-Xiga FSU hollow fiber ultra filtration module with a membrane surface of $A_m = 0.07 \text{ m}^2$.

3.2. Experimental procedure

The experimental protocol followed for fouling and cleaning of the membrane is shown in Fig. 2. First a filtration procedure with a flux of 100 l/(h m²) is performed until the temperature corrected trans-membrane pressure of the membrane has increased from $P_m = 350 \text{ mbar}$ to approximately 500 mbar. Subsequently a backwash procedure is executed, in which a volume of 500 ml permeate is flushed back with a backwash flux of 150 l/(h m²). Next, a second filtration procedure

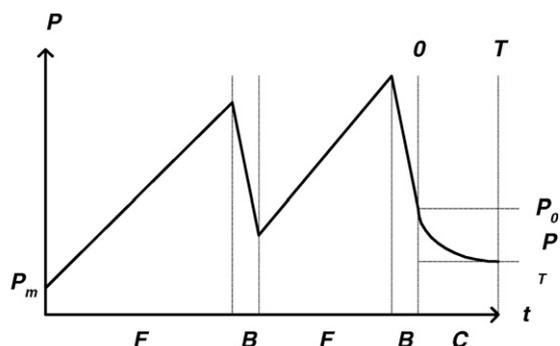


Fig. 2. Experimental procedure following (1) filtration (F), (2) backwash (B), (3) filtration (F), (4) backwash (B) and (5) flushing with chemicals (C).

is started with a flux of 100 l/(h m²), until a temperature corrected trans-membrane pressure of approximately 550 mbar is reached. This filtration is followed by a backwash procedure in which a volume of 500 ml permeate is flushed back with a backwash flux of 150 l/(h m²). Then a volume 1000 ml of the selected cleaning agent is flushed back through the membrane with a flux of 150 l/(h m²) at a concentration of 0.05 mol/l. (For the commercial blends, the instructions for cleaning solution preparation were applied.) At the permeate outlet, the concentrate is collected and pH and turbidity are measured. After the chemical cleaning, remaining chemicals are flushed out of the system with an additional backwash of 500 ml performed at a flux of 150 l/(h m²). Trans-membrane pressure is measured before and after the chemical cleaning procedure by a short filtration at a flux of 100 l/(h m²) with clean water. The processed cleaning agent volume can be converted to time t (min) by $t = V/(A_m J)$, where $A_m = 0.07 \text{ m}^2$ and $J = 150 \text{ l/(h m}^2) = 2500 \text{ ml/(min m}^2)$. The system has a dead time of $\tau_d = 1.14 \text{ min}$ which corresponds to a dead volume of approximately $V_d = 200 \text{ ml}$.

Trans-membrane pressure and turbidity measurements are used to monitor the fouling state, while the pH is used as an indicator for the cleaning agent state. In Zondervan et al. [34] the proposed relationship between the model variables (x_w and x_c) and the measurable variables (trans-membrane pressure, pH and turbidity) is explained in more detail.

Table 6
Estimated model parameters and fits for different cleaning agents

Agent	Type	k'	k''	n_c	%Fit (x_w)	%Fit (x_c)
Hydrochloric acid	Acidic	2.3	0.0	0.0	75.8	87.3
Sulphuric acid	Acidic	3.1	3.3	2.8	75.4	88.7
Citric acid	Acidic	2.6	0.0	0.0	64.3	91.2
4AquaClean Fer 12	Caustic/detergent/sequestering	1.4	0.0	0.0	91.5	85.9
P3 Ultrasil 70	Acidic/detergent	2.7	0.0	0.0	86.5	90.4
Kleen MTC 411	Acidic/detergent	1.7	0.0	0.0	50.8	85.9
P3 AquaClean Sal	Caustic/detergent/sequestering	2.0	0.0	8.0	68.1	87.4
P3 Ultrasil 115	Caustic/detergent/sequestering	2.4	7.6	0.5	76.3	80.7
Sodium hypochlorite	Caustic/oxidizing	2.0	5.9	0.0	88.8	91.9
Hydrogen peroxide	Oxidizing	0.9	0.0	0.1	60.3	85.2

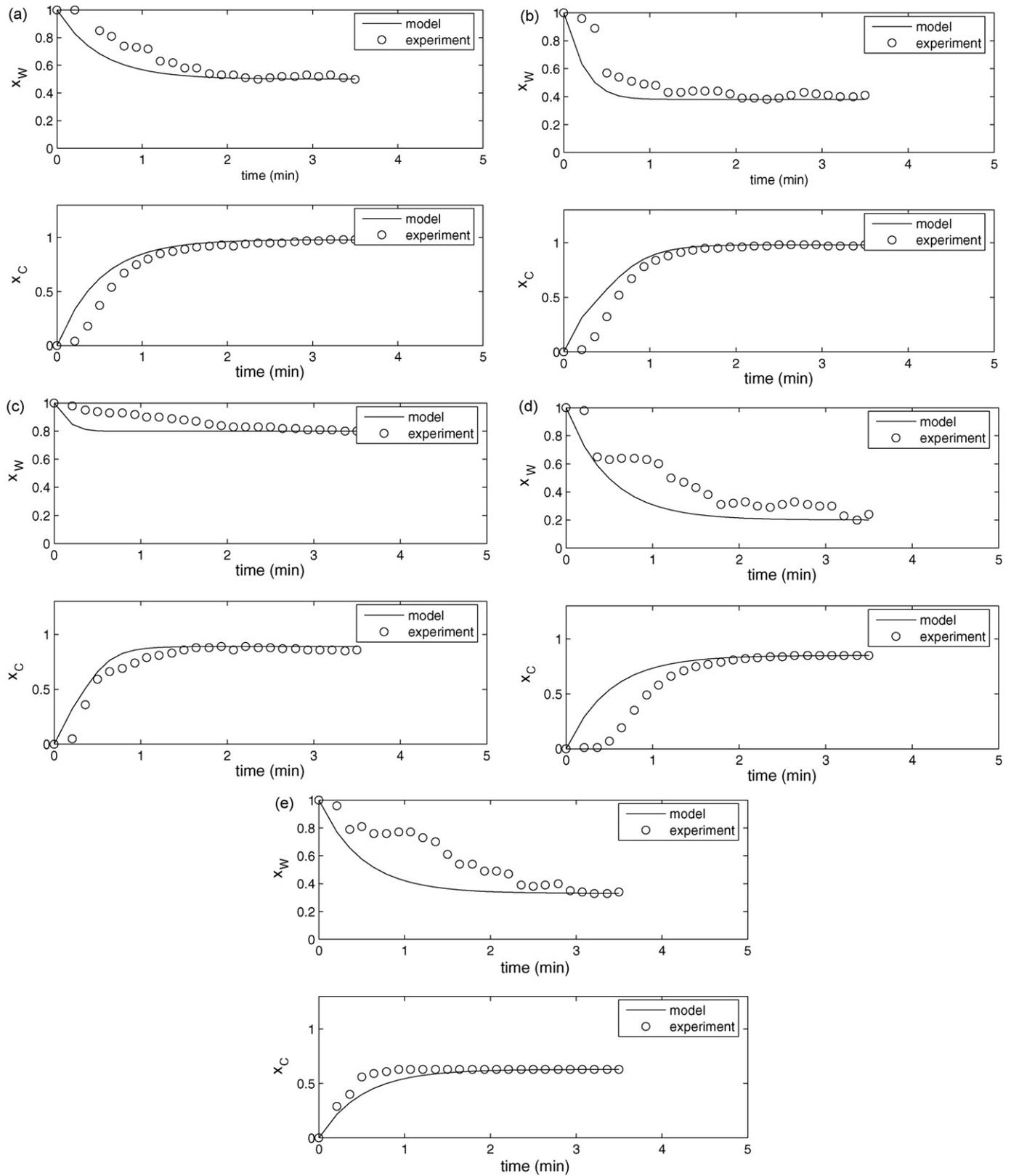


Fig. 3. Modeling and experimental results for different cleaning agents; the upper figures are the fouling states and the lower figures are the cleaning agent states. From left to right: hydrochloric acid (a), sulphuric acid (b), citric acid (c), 4AquaClean Fer 12 (iminodisuccinic salt) and P3 AquaClean Sal (e).

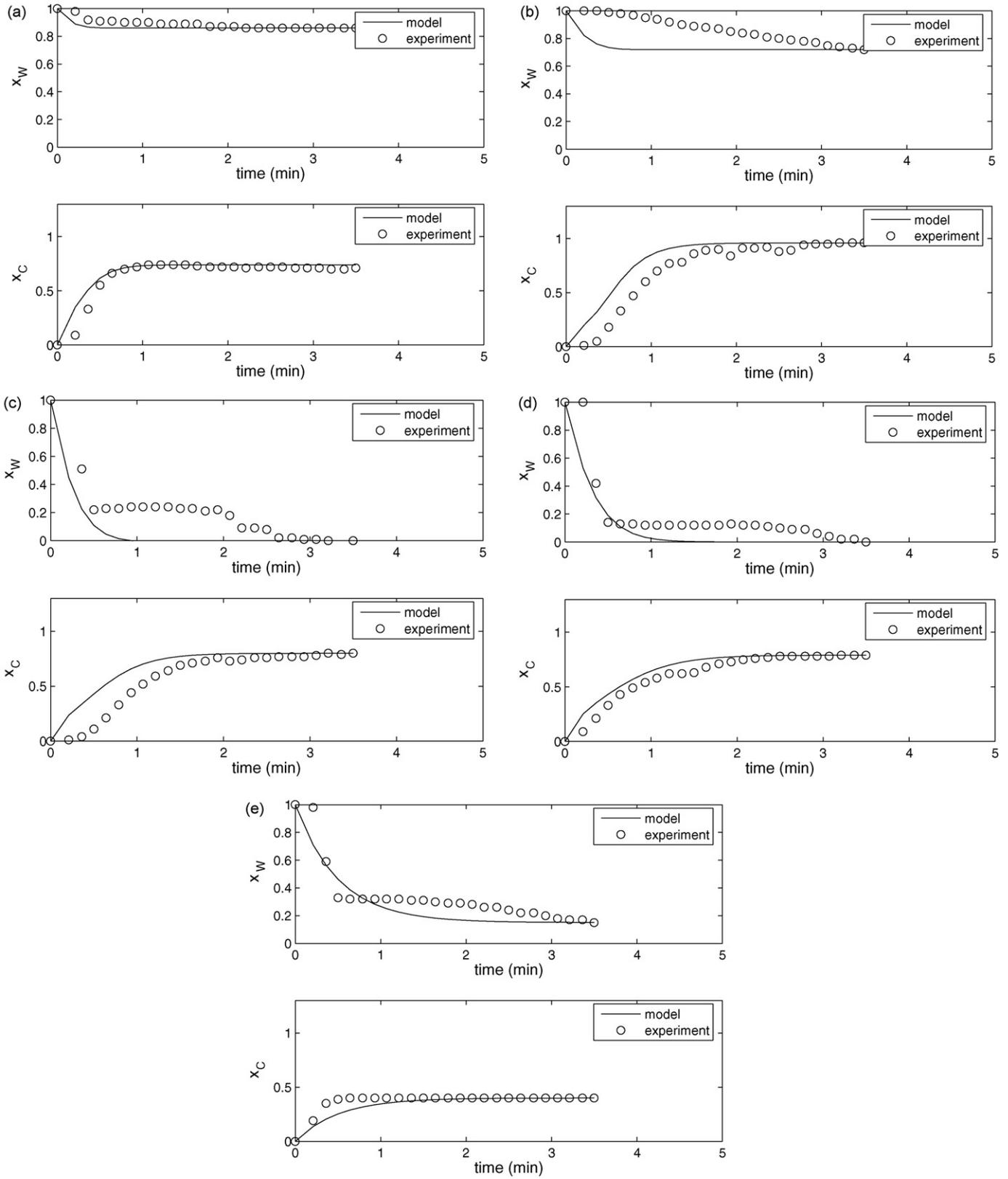


Fig. 4. Modeling and experimental results for different cleaning agents; the upper figures are the fouling states and the lower figures are the cleaning agent states. From left to right: P3 Ultrasil 70 (phosphoric acid) (a), Kleen MTC 411 (sodium borate) (b), P3 Ultrasil 115 (potassium hydroxide) (c), sodium hypochlorite (d) and hydrogen peroxide (e).

4. Results and discussion

4.1. Modeling results for different cleaning agents

Ten different cleaning agents were evaluated, covering the overall range of available cleaning agents. In Table 6 an overview of the tested cleaning agent is presented. Also the estimated model parameters and the fits are listed in Table 6. It is noted that n_C is evaluated as a fit parameter and does not have physical relevance.

The experimental data and estimated models are graphically represented in Figs. 3 and 4, showing the fouling state x_W (upper row) and cleaning agent x_C (lower row) state as a function of time. In general the cleaning model fit is 70% or more. In some cases, however, the model fit is not adequate, especially for citric acid (64%), hydrogen peroxide (60.3%) and Kleen MTC (51%). In these cases, the measurement signal (turbidity) was small compared to the measurement noise, leading to increased error. It is also noted that concentrations of cleaning agents containing detergents (such as the Ultrasil products) should be kept minimal. Overdosing with detergents leads to an increase in membrane resistance instead of a decrease. The pores may be covered with a film of detergent, resulting in an increased resistance. However, the loss of performance is not permanent, and the membrane resistance may be restored by extensive rinsing with clean water. Lower dosings (in the range of 0.05–0.1%) were tried until the desired cleaning effects took place.

In Figs. 5 and 6 the instant cleaning rate and overall cleaning effectiveness are calculated for the different cleaning agents, according to Eqs. (15) and (16). A reference cleaning with sodium hydroxide was performed to correct for changes in water quality. In general, caustic and oxidizing agents were found to have higher instant cleaning rates and overall cleaning effectiveness. This is in good agreement with the fact that the surface water is characterized as containing higher concentrations of organic content.

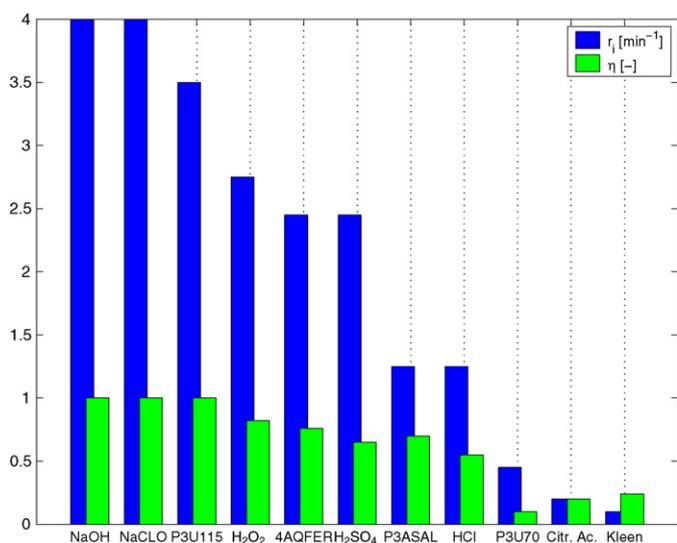


Fig. 5. Instant overall cleaning rate and overall cleaning effectiveness for different cleaning agents.

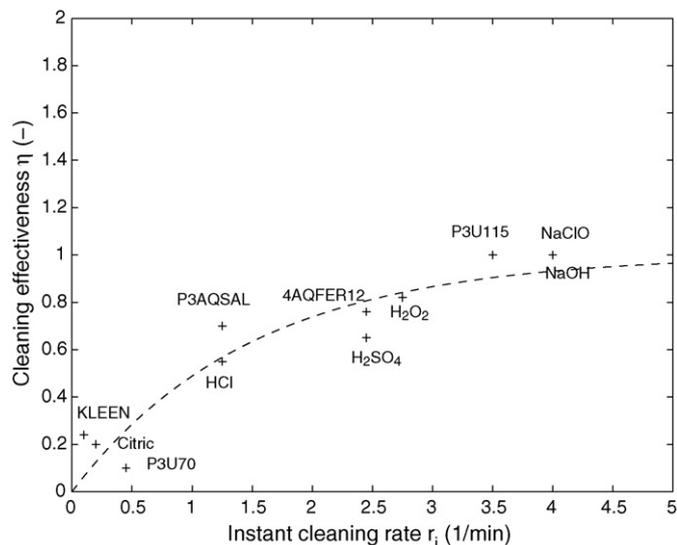


Fig. 6. Instant cleaning rate vs. overall cleaning effectiveness for different cleaning agents.

In Fig. 6 overall cleaning effectiveness is plotted versus the instant cleaning rate for the different cleaning agents. The figure shows that faster cleaning may yield higher cleaning effectiveness.

5. Conclusions

The cleaning model and experimental protocol proposed by Zondervan et al. can be effectively used to capture cleaning dynamics for a considerable number of cleaning agents. For two cleaning agents the model fit was less adequate due to sensitivity to measurement error. Data was collected from turbidity and pH measurements. The response for the turbidity measurements was in some cases small, compared to the measurement noise, leading to this error. By introduction of the instant cleaning rate r_i and the overall cleaning effectiveness η , the overall effect of a cleaning agent can be effectively quantified. For membranes fouled by Twente canal surface water (characterized as water with high organic content) it can be concluded that caustic and oxidizing cleaning agents are the most effective.

Acknowledgements

The financial support of NWO/STW, Aquacare Europe, Hatendoer-Water, Norit Membrane Technology and Vitens Laboratory & Process technology is gratefully acknowledged.

Nomenclature

List of symbols

A_m	membrane surface (m^2)
d_0	initial pore diameter (mm)
d_e	effective pore diameter (mm)
E_A	activation energy (J/mol)

J	cleaning flux
k	rate constant (1/min)
k_0	Arrhenius constant (1/min)
$k_{1,2}$	swelling/compaction rate constant (1/min)
k'	flushing rate constant (1/min)
k''	cleaning rate constant (1/min)
l	pore length (mm)
n_C	pseudo stoichiometric constant
ΔP	trans-membrane pressure (mbar)
r_i	instant cleaning rate (1/min)
r''	cleaning rate (1/min)
R	gas constant (J/(mol K))
R_c	resistance as result of surface fouling (1/m)
R_{CP}	resistance as result of concentration polarization (1/m)
R_m	membrane resistance (1/m)
R_p	resistance as result of in-pore fouling (1/m)
R_t	total resistance (1/m)
t	time (min)
T	temperature (K)
V	volume (m ³)
x_C	cleaning agent state
$x_{C,in}$	cleaning agent state at the inlet
x_W	irreversible fouling state
$x_{W,\infty}$	irreversible fouling state at infinite cleaning time

Greek symbols

δ	swelling/compaction parameter (mm)
ε	porosity
η	cleaning effectiveness
μ	viscosity (Pa s)
τ	tortuosity
τ_d	dead time (min)

References

- [1] M.R. Bird, M. Bartlett, Measuring and modelling flux recovery during the chemical cleaning of MF membranes for the processing of whey protein concentrate, *J. Food Eng.* 53 (2) (2002) 143.
- [2] X. Li, Chemical cleaning of PS ultrafilters fouled by the fermentation broth of glutamic acid, *Sep. Purif. Technol.* 42 (2) (2005) 181.
- [3] S.S. Madaeni, Y. Mansourpanah, Chemical cleaning of reverse osmosis membranes fouled by whey, *Desalination* 161 (1) (2004) 13.
- [5] A. Maartens, UF of pulp and paper effluent: membrane fouling prevention and cleaning, *J. Membr. Sci.* 209 (2002) 81–92.
- [6] T. Mohammadi, S.S. Madaeni, M.K. Moghadam, Investigation of membrane fouling, *Desalination* 153 (1–3) (2003) 155.
- [7] J.S. Vrouwenvelder, D. van der Kooij, Diagnosis, prediction and prevention of biofouling of NF and RO membranes, *Desalination* 139 (1–3) (2001) 65.
- [8] S.-H. Yoon, Effect of calcium ion on the fouling of nanofilter by humic acid in drinking water production, *Water Res.* 32 (1998) 2180–2186.
- [9] C.-W. Li, Y.-S. Chen, Fouling of UF membrane by humic substance: effects of molecular weight and powder-activated carbon (PAC) pre-treatment, *Desalination* 170 (1) (2004) 59.
- [10] W. Yuan, A. Kocic, A.L. Zydney, Analysis of humic acid fouling during microfiltration using a pore blockage-cake filtration model, *J. Membr. Sci.* 198 (1) (2002) 51.
- [11] W. Yuan, A.L. Zydney, Humic acid fouling during microfiltration, *J. Membr. Sci.* 157 (1) (1999) 1.
- [12] A. Maartens, P. Swart, E.P. Jacobs, Feed-water pretreatment: methods to reduce membrane fouling by natural organic matter, *J. Membr. Sci.* 163 (1) (1999) 51.
- [13] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, *J. Membr. Sci.* 132 (2) (1997) 159.
- [14] T. Gun, Membrane cleaning, *Desalination* 71 (1989) 325–335.
- [15] C. Whittaker, H. Ridgway, B.H. Olson, Evaluation of cleaning strategies for removal of biofilms from reverse-osmosis membranes, *Appl. Environ. Microbiol.* 48 (3) (1984) 395.
- [16] S.L. Kim, Study on feed pretreatment for membrane filtration of secondary effluent, *Sep. Purif. Technol.* 29 (2002) 171–179.
- [17] A. Weis, M.R. Bird, M. Nystrom, The chemical cleaning of polymeric UF membranes fouled with spent sulphite liquor over multiple operational cycles, *J. Membr. Sci.* 216 (1–2) (2003) 67.
- [18] Kulkarni, Flux enhancement by hydrophilization of thin film composite reverse osmosis membranes, *J. Membr. Sci.* 114 (1996) 39–50.
- [19] H. Lee, Cleaning strategies for flux recovery of an ultrafiltration membrane fouled by natural organic matter, *Water Res.* 35 (14) (2001) 3301.
- [20] R. Liikanen, J. Yli-Kuivila, R. Laukkanen, Efficiency of various chemical cleanings for nanofiltration membrane fouled by conventionally-treated surface water, *J. Membr. Sci.* 195 (2) (2002) 265.
- [21] T. Mohammadi, Chemical cleaning of a polyamide membrane, *Desalination* 139 (1–3) (2001) 381.
- [22] S. Siavash Madaeni, T. Mohammadi, M. Kazemi Moghadam, Chemical cleaning of reverse osmosis membranes, *Desalination* 134 (1–3) (2001) 77.
- [23] H. Zhu, M. Nystrom, Cleaning results characterized by flux, streaming potential and FTIR measurements, *Colloids Surf. A: Physicochem. Eng. Aspects* 138 (2–3) (1998) 309.
- [24] M.J. Munoz-Aguado, D.E. Wiley, A.G. Fane, Enzymatic and detergent cleaning of a polysulfone ultrafiltration membrane fouled with BSA and whey, *J. Membr. Sci.* 117 (1–2) (1996) 175.
- [25] M. Bartlett, M.R. Bird, J.A. Howell, An experimental study for the development of a qualitative membrane cleaning model, *J. Membr. Sci.* 105 (1–2) (1995) 147–157.
- [26] S. Pavlova, Study on the cleaning of new ultrafiltration spiral-wound modules to prevent membrane fouling (including biological fouling), *Desalination* 172 (3) (2005) 267.
- [27] A. Sungpet, R. Jiratananon, P. Luangsowan, Treatment of effluents from textile-rinsing operations by thermally stable nanofiltration membranes, *Desalination* 160 (1) (2004) 75.
- [28] L. Mo, X. Huang, Fouling characteristics and cleaning strategies in a coagulation–microfiltration combination process for water purification, *Desalination* 159 (1) (2003) 1.
- [29] J.M. Veza, J.J. Rodriguez-Gonzalez, Second use for old reverse osmosis membranes: wastewater treatment, *Desalination* 157 (1–3) (2003) 65.
- [30] J.P. Chen, S.L. Kim, Y.P. Ting, Optimization of membrane physical and chemical cleaning by a statistically designed approach, *J. Membr. Sci.* 219 (1–2) (2003) 27.
- [31] E.-M. Gwon, Fouling characteristics of NF and RO operated for removal of dissolved matter from groundwater, *Water Res.* 37 (12) (2003) 2989.
- [32] W. Andreas, The chemical cleaning of polymeric UF membranes fouled with spent sulphite liquor over multiple operation cycles, *J. Membr. Sci.* 216 (2003) 67–79.
- [33] A.L. Lim, R. Bai, Membrane fouling and cleaning in microfiltration of activated sludge wastewater, *J. Membr. Sci.* 216 (1–2) (2003) 279.
- [34] E. Zondervan, B.H.L. Betlem, B. Roffel, Development of a dynamic model for cleaning an ultra filtration membrane fouled by surface water, *J. Membr. Sci.* 289 (2007) 1–2.