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In-line coagulation prior to ceramic microfiltration for surface water treatment—minimisation of flocculation pre-treatment

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ABSTRACT

In-line coagulation/flocculation with subsequent low pressure ceramic membrane filtration has emerged during the last years as a treatment alternative for surface waters with high natural organic matter (NOM) content and low turbidity. In such a hybrid process, the requirements on the flocculation step may significantly differ, if compared to treatment schemes where for example rapid filters are used instead of a membrane. Thus, process performance, expressed as DOC and colour removal, membrane fouling and residual metal concentration, was investigated in dependence on the coagulant dosage, flocculation time and shear, while all other coagulation conditions were kept constant. Minimum flocculation requirements were established. A synthetic surface water (DOC 6.8 mg C l^{-1}, colour 55 mg Pt l^{-1}) was treated by rapid inline coagulation with Polyaluminium chloride (PACl), at Al-dosages of 2.6 and 4.4 mg l^{-1} and a coagulation pH of 6, followed by inline flocculation at varying conditions (G-values: 4–300 1 s^{-1}, retention times: 10–240 s), and final membrane filtration at 250 l m^{-2} h^{-1}. While the DOC removal only depended on the coagulant dose and not on the flocculation conditions, flocculation times of at least 60 s were necessary in order to stabilise the irreversible fouling rate below 1 mbar h^{-1}. In general, the process performance was improved by increasing the coagulant dosage. The findings of this study were confirmed by the evaluation of experimental design and described by linear regression modelling.

Keywords: NOM removal; Colour removal; Ceramic membranes; Microfiltration; Coagulation; Flocculation; Surface water

1. Introduction

Ceramic low pressure membranes coupled with a coagulation/flocculation pre-treatment is an emerging full scale treatment alternative for drinking water production from surface waters containing high loads of organic matter and colour [1]. In the past, direct filtration of Natural Organic Matter (NOM) by nanofiltration (NF) membranes has been successfully used, however a number of disadvantages have been identified; high irreversible fouling, high operating pressures at low fluxes, permeability loss over time and high chemical demand [2]. With ceramic microfiltration (MF) these can be avoided to a large extent. Low pressure membranes can operate more energy efficiently, where higher investment costs for ceramic membranes can be offset by operating with significantly higher fluxes [3].

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Surface waters in the northern region of Europe are typically characterised by a high content of NOM, resulting in high colour, very low turbidity, low alkalinity and low hardness, due to the natural conditions [4]. Although the main part of NOM is not harmful, some fractions like algogenic matter can cause colour, taste and odour problems or are even toxic like the algae toxin microcystin. Special fractions of NOM in the drinking water can potentially lead to bacterial regrowth in the distribution system. Removal of NOM also reduces the load of following treatment steps and facilitates elimination of important trace compounds such as pesticides found in the NOM. Furthermore, these substances increase the necessary amount of disinfectants and are recognized as precursors for disinfection by-product formation, such as THMs which can be carcinogenic. The Norwegian Institute of Public Health has subsequently provided limiting values and recommendations in the national drinking water guidelines. The removal of NOM is therefore one of the major concerns and makes an advanced drinking water treatment necessary. Furthermore, there is a growing concern on the increase of NOM in natural water sources, where recent studies have shown that the concentration of NOM in surface water has increased in the past and might further increase during the next decades, caused by progressing climate change issues or changed precipitation patterns [5,6].

Pre-treatment needs are assumed to differ quite significantly for membrane filtration, compared to conventional processes (i.e. rapid filtration). However, how the membrane exactly responds to different pre-treatment, such as varying flocculation conditions (flocculation time, *G*-value, coagulant dose), how this may impact the process and how much flocculation actually is necessary, has not been studied in detail so far. Thus, pilot studies have been conducted, in order to address the issue. Process performance, expressed as DOC and colour removal, membrane fouling and residual metal concentration, was investigated in dependence on the coagulant dosage, flocculation time and shear, while all other coagulation conditions were kept constant. Minimum flocculation requirements were established.

2. Methods

2.1. Raw water

The raw water used in this study was prepared using a NOM concentrate from a full scale ion exchange treatment plant, which was mixed with tap water to make up an analogue water with a turbidity of around 1 NTU, a colour of 55 ± 1.78 mg Pt l^{-1} at pH 7 (corresponding to an absorbance of 2.25 ± 0.12 m^{-1} at a wavelength of 436 nm), a UV_{254}-absorbance of 28.0 ± 1.1 m^{-1} and a DOC concentration of 6.8 ± 0.2 mg l^{-1}. Analogue feed water ensures that the same experimental conditions apply for all experiments conducted. Previous studies have shown that this method can be successfully used and simulates real conditions quite well [3,7].

The organic matter concentrate used in this study can be characterized as highly hydrophobic and humic acid like. As already shown in Meyn and Leiknes, a fluorescence excitation emission matrix (FEEM) of the raw water showed a very distinct peak in the humic acid like region [3]. The organic matter can be further characterized by a relatively high SUVA of 4.5 m^{-1} l mg^{-1} C, indicating a high aromatic carbon content [8]. After blending the concentrate with tap water the FEEM shows another dominant peak in the fulvic acid like region (Fig. 1(b)). Fractionation analysis revealed that the dominant fraction (64%) of the raw water composition is the very hydrophobic acid (VHA) fraction. The VHA fraction is predominantly composed of higher molecular weight humic acids. Slightly hydrophobic acid (SHA) represents fulvic acid like components [9]. The results of the organic matter fractionation are shown in Fig. 1(a). Further comparison of the analogue raw water used in this study with natural water, obtained from a lake near Trondheim, Norway, showed no significant differences. It can be therefore concluded, that the results obtained in this study can be transferred to natural Norwegian water sources and are representative for Norwegian conditions. Specifics of the fractionation technique have been described elsewhere [10].

2.2. Pilot plant configuration

Experiments were conducted with a membrane filtration pilot plant using an inline coagulation/flocculation pre-treatment configuration, as shown in Fig. 2. Prior to the membrane filtration unit, a static mixer ensured intensive mixing of coagulant into the already pH-adjusted raw water, followed by a slow mixing pipe flocculation step. After that, the coagulated water is filtered by the membrane unit. The pilot plant was equipped with three identical and independent process trains.

In this study multi-channel ceramic membranes, operated in dead-end, inside-out mode with a nominal pore size of 0.1 μm were investigated. Each membrane module is 1 m long with 55 channels giving an effective surface area of 0.43 m^2. The membrane modules are mounted vertically with feed water pumped in an up-flow direction. The plant was operated in constant flux mode, maintaining a flux of 250 l m^{-2} h^{-1} (Table 1). Regular cleaning was performed each hour by an initial backwash with pressurized permeate and then, after

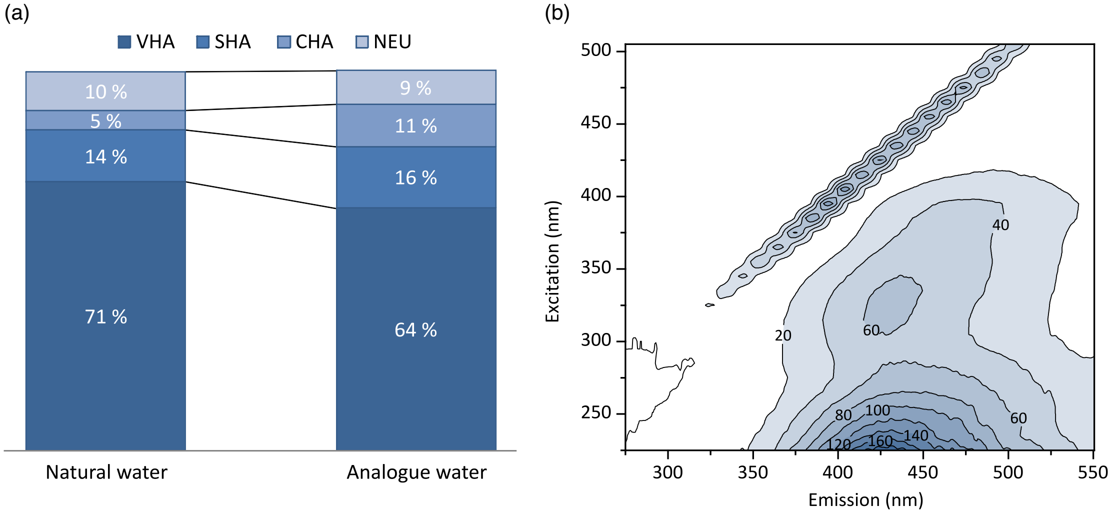


Fig. 1. Raw water characterization. (a) Composition of natural Norwegian lake water and the analogue raw water used in this study. (b) Fluorescence excitation emission matrix of the raw water.

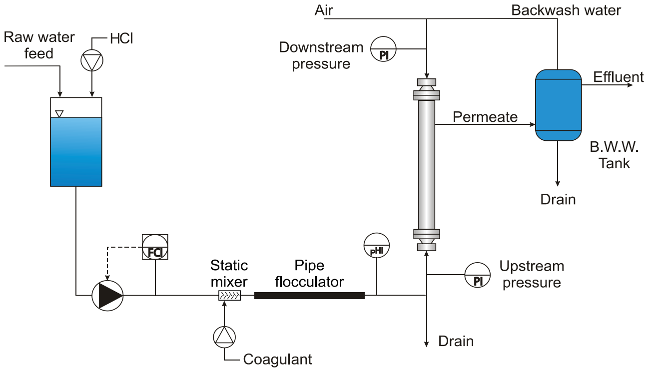


Fig. 2. Exemplary flow diagram of one train of the membrane filtration pilot plant.

Table 1
Membrane operating conditions and module specification

Membrane type	Ceramic MF
Module length/ diameter	1 m/0.03 m
Channels per module	55
Channel diameter	2.5 mm
Module area/ nominal pore size	0.43 m^2/0.1 µm
Operational flux/ filtration velocity	250 l m^{-2} h^{-1}/6 m d^{-1}
Regular cleaning intervals/procedure	1 h/backwash and air blow

some seconds, by a simultaneous air blown into the feed channels. A pressurized tank was used for the backwash. The backwash pressure expands from initially 5 bar to about 2 bar at the end of the regular cleaning. The pressure of the air blow is likewise 2 bar. In total the regular cleaning cycle lasts about 10 s. The obtained sludge was discharged to the sewer system. After each experiment the membrane modules were cleaned intensively by soaking alternating in citric acid solution (w = 1%) and sodium hypochlorite solution (c = 3000 ppm).

The process performance was assessed as a function of coagulant dosage, the flocculation G-value and flocculation time. The DOC and colour removal, irreversible and reversible fouling and residual aluminium concentration in the permeate were measured for evaluation of the process performance. Coagulant doses 2.6 and 4.4 mg Al l^{-1} were chosen, corresponding to about 0.4 and 0.65 mg Al mg^{-1} of DOC. It has been shown that for raw waters with a pH of 6 and high DOC not much NOM removal is achievable with doses significantly less than 2.6 mg Al l^{-1}, and where membrane fouling increases drastically, as stated in Meyn and Leiknes [3] and confirmed by unpublished results. The G-values 4, 31, 98 and 300 s^{-1} were investigated. These values were chosen on the rationale that with a G-value of 4 s^{-1} on the lower end and with 300 s^{-1} on the upper end, the range covers extreme conditions with almost no to relatively turbulent mixing. Previous experiments have shown that ceramic microfiltration coupled only with rapid mixing pre-treatment and without any flocculation, removes the same amount of DOC and colour as an extensive classical two-stage coagulation/flocculation pre-treatment [3]. The irreversible fouling on the other hand was quite severe, indicating the need for further

Table 2
Overview of the full factorial experimental design and the containing variables

Role	Name	Values			
Design variables	Coagulant dose [mg Al l^{-1}]	2.6	4.4		
	G-value [s]	4	31	98	300
	Flocculation time [s]	10	60	240	
Response variables	DOC-removal [%]	Measured during experiments			
	Colour removal [%]				
	Residual aluminum [μg Al l^{-1}]				
	Irreversible fouling [mbar h^{-1}]				
	Reversible fouling [mbar h^{-1}]				

optimization of the process. Therefore, the three flocculation times were investigated (10, 60 and 240 s) to evaluate if there is a minimal necessary flocculation time, and to assess if a relatively long flocculation time of 240 s still has a beneficial effect compared to shorter times. Table 2 gives an overview of the flocculation conditions and the experimental design.

Polyaluminium chloride (PAX-18) supplied by Kemira Chemicals was used as coagulant. Coagulation pH was set to 6, which has shown to be optimal for removal of NOM with an aluminium based coagulant as stated in Vik et al. [11] for conventional water treatment and in Meyn and Leiknes [3] for coagulation/flocculation coupled with microfiltration. At pH 6 it is further expected that high residual Al concentrations in the permeate can be avoided. Each condition was tested for 48 h or until the TMP reached 2 bar. The *G*-value in the static mixer was 8000 s^{-1}. For adjustment of the various flocculation conditions tested, the pipe flocculator was constructed from tubes with different lengths and diameters as shown in Table 3.

Table 3
Pipe flocculator dimensions, length and diameter, used in this study

G-value [s]		4	31	98	300
Tubing diameter [mm]		38	19	13	10
		Tube length [m]			
Flocculation time [s]	10	0.26	1.06	2.23	3.80
	60	1.58	6.34	13.40	22.81
	240	6.33	25.36	53.60	91.24

2.3. Experimental design

A full factorial 2 × 3 × 4 experimental design with two repetitions was chosen for this study. Such a design contains all possible combinations of factors and their interactions. It was proven in previous experiments that different process trains or membrane modules do not have a significant effect on the experimental results. In total, 48 experiments were carried out.

The experimental design was analyzed with help of multiple linear regression (MLR), minimizing the sum of squared residuals. Such a full linear first-order model for three independent parameters and all their interactions has the general form:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_6 x_2 x_3 + \beta_7 x_1 x_2 x_3 + \in \quad (1)$$

A linear second-order model, including also quadratic effects, was also considered. Such a model expresses a curvilinear relationship between a response variable and the design variables. The achievable fit and the model prediction of our real observations would have been better than with a linear first-order model. However, due to the strongly parabolic shape of such a regression the ability to actually interpolate between the investigated data points would have been very limited, since, that is negative response values could occur. Hence, a linear first-order model was chosen.

Before the analysis, the design variables were negatively checked for potential multicollinearity, which would have affected the regression statistical relevant and thus should be avoided. In order to find the optimal model for each response a full model was analysed, including the three main effects and all their interactions. The full model was then used to identify and remove outliers and to check if a reasonable regression was possible and if significant factors were present in the model. An outlier was identified by having a standardized residual greater than 2.5. The regression was considered to be reasonable, if in a hypothesis test the hypothesis H_0, that all coefficients in the model are equal to zero, was rejected at a 0.05 α-level. In this test H_0 was compared with a second hypothesis H_1, stating that at least one of the coefficients in the model is unequal to zero. The rejection of H_0 does not automatically mean that H_1 must be true, but it represents strong evidence that this is the case.

An alternating stepwise regression was then performed, in order to simplify the models and to identify significant coefficients. This method is described in detail elsewhere [12]. The probability for integrating or removing a parameter into the model was set to $\alpha = 0.05$. For the resulting models an analysis of variance (ANOVA) was performed and the models were checked for assumption violations. It was confirmed by residual analysis, showing that the errors are independently and normally distributed with zero mean and a constant variance σ^2. The Anderson–Darling test was chosen for proving normality. If the *p*-value for the Anderson–Darling test was lower than the chosen significance level 0.05, it was concluded that the data do not follow the specified distribution. The adjusted and predicted R^2 values of the models were calculated and compared.

As a last step, the obtained regression models were used for process optimization. All response variables were paired with a desirability function. Favourable size ranges of the responses were rated with a high desirability value, low desirability values were assigned to unwanted ranges. For the responses DOC and colour removal, a desirability function for maximization was selected. The other responses residual aluminium, irreversible and reversible fouling, minimizing desirability functions were chosen. The residual aluminium concentration was further restricted by the limiting value of 150 μm Al l^{-1}. Finally, the regression models were used for maximising the overall desirability to find the process optimum. All statistical analyses were conducted with the software packages Minitab® 15 and JMP® Statistical Discovery Software 8. A more detailed description of experimental design and result analysis can be found elsewhere [12].

2.4. Experimental analysis

The membrane performance was monitored by logging the transmembrane pressure (TMP) development for constant flux operation. Samples were taken before the coagulation and after the membrane filtration twice a day during different stages in the process cycles. Turbidity measurements (90° scattered light method, Turbidimeter 2100N, Hach) and the residual metal concentration (measured by High Resolution ICP-MS at the Institute for Chemistry at NTNU) in the permeate were analysed for each sample. The removal of organic matter was monitored by measuring colour, UV-absorption at 254 and 436 nm (Spectrophotometer U-3000, Hitachi) and DOC (Laboratory analyser: Dohrmann Apollo 9000, Teledyne-Tekmar; Online spectrometric probe: Spectro::lyser™, s::can Meßtechnik GmbH, Vienna, Austria).

In this study measurements were conducted to distinguish between reversible and irreversible fouling. By definition, reversible fouling represents material that can be removed by regular cleaning procedures without using chemicals whereas irreversible fouling has to be removed by enhanced chemical cleaning. This is usually done when a defined level of the system permeability is undercut.

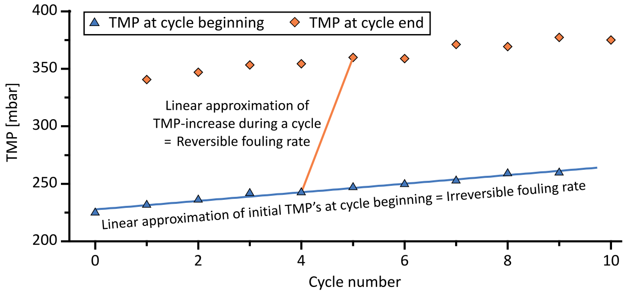


Fig. 3. Exemplary calculation of reversible and irreversible fouling rate.

In the conducted experiments the TMP was measured for each cycle before and after a backwash. For calculation of the irreversible fouling rate, the data points of the TMP at the beginning of a cycle, directly after a backwash, were linear approximated as shown in Fig. 3, and the slope of the regression curve calculated. The reversible fouling rate was calculated by linear approximating the TMP increase within a cycle and calculating the slope. In order to obtain the reversible fouling rate for one particular experiment, the results from all filtration cycles were averaged.

2.5. Flock size and charge measurements

Jar tests were performed by applying rapid mixing at 400 rpm for 1 min, followed by slow mixing at 40 rpm for 60 min. Acid for pH adjustment was dosed before the experiments, coagulant right before the rapid mixing started. Flock growth was monitored with a Photometric Dispersion Analyser 2000 (PDA 2000, Rank Brothers LTD, Cambridge, UK). The PDA measures the mean transmitted light intensity (dc value) and the root means square (rms) value of the fluctuating component. The ratio (rms/dc), in this study called flocculation index, provides a sensitive index of particle aggregation [13]. Zeta potential was measured with a Zetasizer Nano ZS (Malvern Instruments Ltd, Worcestershire, UK) at the beginning and end of the jar tests.

3. Results and discussion

3.1. NOM removal

The removal of DOC and colour, expressed as VIS_{436}, depended only on the amount of dosed coagulant, since the pH-value was stable and set to 6 for all experiments. Flocculation time and *G*-value did not influence the amount of organic matter removed at all.

Depending on the coagulant dose, the average DOC removal varied between 55.5% with an Al-dosage of 2.6 mg l^{-1} and 70.4%, achieved by dosing 4.4 mg Al l^{-1} (Table 4).

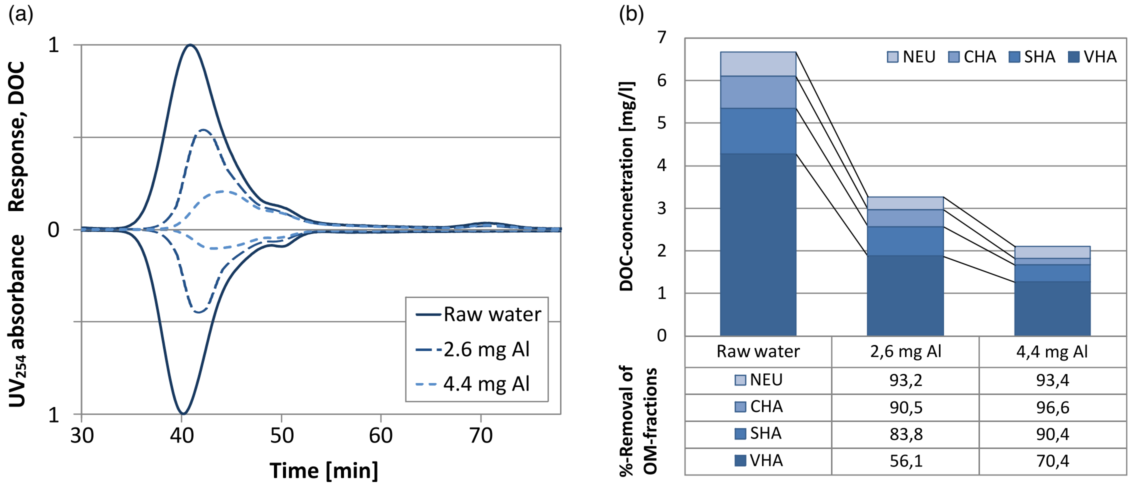
Table 4
Averaged DOC, UV absorbance and colour removal in dependence on coagulant dosage

Parameter	% – Removal at coagulant dosage:	
	2.6 mg Al l^{-1}	4.4 mg Al l^{-1}
DOC	55.5 ± 1.1	70.4 ± 0.7
UV_{254}	71.2 ± 1.2	87.7 ± 1.0
VIS_{436}	84.6 ± 0.9	91.7 ± 0.9

This corresponds to residual DOC concentrations of 3 and 2 mg l^{-1} respectively, with a raw water DOC of 6.8 mg l^{-1}. These removal rates are about 10%–15% lower than previously observed in Meyn and Leiknes for a comparable setup where a similar raw water and coagulant doses were used but with a 30% lower DOC concentration of 5.2 mg l^{-1} [3]. These results were therefore obtained with a significantly lower DOC/Al ratio. However, the study further used a classical two-stage tank-coagulation and flocculation pre-treatment configuration instead of an inline process, but with an otherwise similar setup. The different removal rates cannot be assumed caused by the modification in the process configuration, since the results presented in this study show that variation of the flocculation parameters did not influence the DOC removal, even at an extended flocculation time of 240 s. The different DOC removal rates found in the two comparative studies are therefore caused only by the altered DOC/Al ratio. This conclusion corresponds well with preliminary results also published in Meyn and Leiknes, where a setup with tank pre-treatment was compared directly with a simplified inline setup, using iron chloride as coagulant [3]. No significant difference in DOC removal was observed. DOC removal was reported to vary as a function of coagulation pH, with optimal removal using PACl as coagulant being at pH-values 5.5–6. Thus it can be concluded that the DOC removal for the processes combination presented in this study, provided that similar raw water is treated, only depends on the parameters pH-value and the coagulant dose.

The removal of UV absorbance and colour followed a similar pattern to that observed for DOC removal, but was generally on a higher level. Average removal of UV absorbance was around 71% for a coagulant dose of 2.6 mg Al l^{-1} and 88% for 4.4 mg Al l^{-1}, respectively (Table 4). Average colour removal was around 85% for a coagulant dose of 2.6 mg Al l^{-1} and 92% for 4.4 mg Al l^{-1} respectively. As already described and explained for DOC reduction, the removal of UV absorbance and colour only depend on the coagulant dose and not on flocculation time or *G*-value.

The higher UV absorbance and colour removal compared to DOC can be explained by a favoured removal of a DOC portion, which can be characterized as a very hydrophobic high molecular weight fraction with high aromatic carbon content. This fraction generally expresses high colour and UV absorption. This preferential removal is reflected by the reduction of the specific UV absorbance from 5.4 $m^{-1} \cdot l\ mg^{-1}$ C in the raw water to 2.8 $m^{-1} \cdot l\ mg^{-1}$ C at an aluminium dosage of 2.6 mg l^{-1} and 1.7 $m^{-1} \cdot l\ mg^{-1}$ C for 4.4 mg Al l^{-1}. LC-OCD analysis of the raw water and permeate confirms this observation. As can be seen in Fig. 4(a)), the larger molecular weight fraction showing the highest UV absorption is preferentially removed. Fig. 4(b) shows that the absolute removal is greatest for the VHA fraction, the neutrals seem to accumulate in the permeate, even at higher coagulant dose. The favoured removal



	Raw water	2,6 mg Al	4,4 mg Al
NEU		93,2	93,4
CHA		90,5	96,6
SHA		83,8	90,4
VHA		56,1	70,4

Fig. 4. NOM characterization from raw water and permeate in dependence on coagulant dosage (a) LC-OCD analysis (b) Resin fractionation.

of colour and UV absorbance over DOC corresponds well with findings of other studies, that is Owen et al. [14]. Vik et al. showed that raw waters containing more low molecular weight NOM species are more difficult to treat in terms of DOC removal than water sources with higher molecular weight NOM [11]. This is generally the case where higher molecular weight humic acid species are easier to remove than the low molecular weight fulvic acid species.

To investigate possible coagulation pathways and for further characterization of the coagulation/flocculation system, a series of jar tests was performed, where raw water was coagulated at different coagulant doses and zeta potential and flock growth as a function of flocculation time were measured. As shown in Fig. 5a, the zeta potential in the raw water has a negative value of −18.8 mV at an aluminium dose of 2.6 mg l^{-1}, whereas at 4.4 mg l^{-1} it is already positive, at around 10 mV. Zero zeta potential can be observed at a dose of around 3.5 mg Al l^{-1}. At this dose the biggest flocks were formed in the jar test and flock formation was fastest, as summarized in Fig. 5(b). Floc growth was monitored for 60 min at coagulant doses between 2.5 and 5.0 mg Al l^{-1}, in 0.5 mg intervals. The surface graph shown in Fig. 5(b) was created by interpolating those data. However, the higher coagulant dose of 4.4 mg Al l^{-1} showed a superior organic matter removal compared to 2.6 mg Al l^{-1} and from the zeta potential measurements and jar tests one can assume that better removals may be observed at higher coagulant dosages, despite the more positive zeta potential.

Previous studies have shown that charge neutralization is the dominant coagulation mechanism only for low organic matter concentrations around a pH-value of 6. Shin et al. stated for example a DOC concentration of 2.7 mg l^{-1} in the raw water as the upper limit [15]. If the concentration is below this value, only a very narrow window for charge neutralization exists in terms of coagulant dose and pH-value, since charge reversal occurs if the coagulant is overdosed. At higher DOC concentrations no restabilization by charge reversal was observed and the window for optimal organic matter removal was wider. Charge reversal still occurs at higher coagulant dosages, as can be seen in Fig. 5a, but is compensated by formation of aluminium hydroxides, followed by adsorption of NOM and/or Al–NOM complexes on $Al(OH)_3(s)$ with a continuous transition to precipitate enmeshment as the dosage is incrementally increased. Edwards and Amirtharajah [16] and Vik et al. [11] showed similar results. A further increase of coagulant could lead to a higher organic matter removal since for example more of the low molecular weight fraction can be coagulated, but the removal efficiency decreases due to an increasing consumption of coagulant per removed mg of DOC ratio. Reaction rates for $Al(OH)_3(s)$ formation are lower than for destabilization reactions forming Al–NOM complexes, but they are high enough to ensure fast particle formation even at very short flocculation times. Results from testing a static mixer directly in front of the membrane module without a defined flocculation stage showed similar DOC and colour removal levels compared to the flocculation options tested in this study. It can be therefore concluded that in the pH and

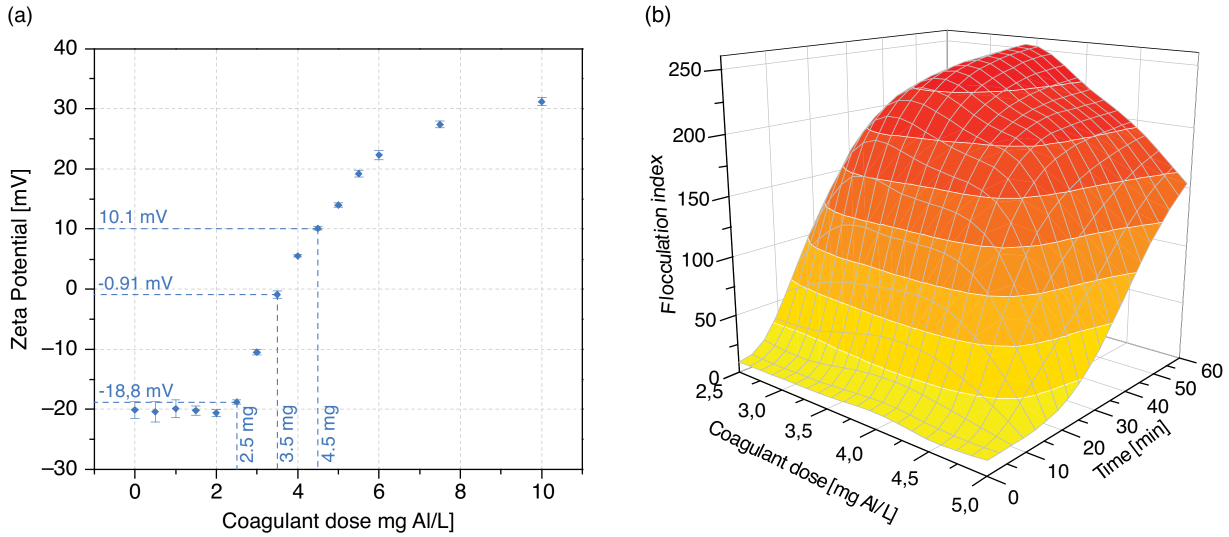


Fig. 5. Interaction between surface charge and jar test flock growth controlled by coagulant dose at pH 6. (a) Zeta potential in the coagulated raw water in dependence on the coagulant dose. (b) Jar test floc growth in dependence on coagulant dose and flocculation time.

Al dose range investigated particles are always formed that can be efficiently retained by the membrane, independent of the flocculation conditions. The hollow channels as found in the membrane employed can work as a pipe flocculator themselves and therefore support a further floc development. Due to the flow pattern in the channels a dense columnar cake layer is promoted at the dead-end points, but cake layer formation is alleviated on the rest of the membrane surface [17].

3.2. Residual Al concentration

The residual aluminium concentrations measured depended on all three process variables as shown in Fig. 6. In general it decreased with increasing coagulant dose. For the 2.6 mg Al l^{-1} dose, the residual concentration was higher than the limiting value in the drinking water guidelines (150 µg Al l^{-1}) in all cases except three experimental conditions. At a dose of 4.4 mg Al l^{-1} the residual Al level was generally lower with only four experimental conditions exceeding the limiting value. As already discussed in the previous section, at a higher coagulant dose more organic matter is removed, indicating that the interaction of aluminium species with themselves and with the organic matter is more efficient. It is most likely not only $Al(OH)_3(s)$ that is better retained at a higher dosages, since the organic matter removal increased drastically at the same time.

Increasing *G*-value had also a decreasing effect on the residual metal concentration with a restriction at a *G*-value of 300 s^{-1} and flocculation times of 60 s and higher, where the residual Al concentration increases again. It can be generally stated that better mixing leads to lower metal concentrations, most likely due to increased contact and collision frequencies at higher turbulence. At a higher *G*-value smaller but more flocs are formed, increasing the total floc surface area and collision frequency, and therefore the chance that particles will interact and agglomerate. The results also indicate there may be an upper limit for the mixing intensity since the residual Al increased again at a *G*-value of 300 s^{-1}. At a too high mixing intensities floc growth is possibly suppressed, with possible floc breakage, and therefore more Al is found in the permeate.

A longer flocculation time reduced the residual Al concentration, especially at a dosage of 4.4 mg Al l^{-1}. The more time the flocculation may proceed the less metal is found in the permeate. Interestingly, this has practically no effect on the organic matter removal, which depends on the coagulant dose only, as stated earlier. The reactions binding the organic molecules appear to be finished after a few seconds or even milliseconds, with the particles formed quickly reaching a state where they are efficiently retained by the membrane.

3.3. Membrane fouling

High irreversible fouling in the range of 5–25 mbar h^{-1} was observed at 10 s flocculation time. For longer times the fouling was generally found to have a low average value of 1.6 mbar h^{-1}, independent from the other two varied parameters, *G*-value and coagulant dose (Fig. 7). The lowest fouling rate of 0.8 mbar h^{-1} was found at an Al dose of 4.4 mg l^{-1}, a *G*-value of 31 s^{-1} and 60 s flocculation time. However, at 10 s flocculation time a higher *G*-value led to significantly reduced irreversible fouling. An exception must be made for a *G*-value of 4 s^1, where fouling was also lower. The coagulant dose had only a

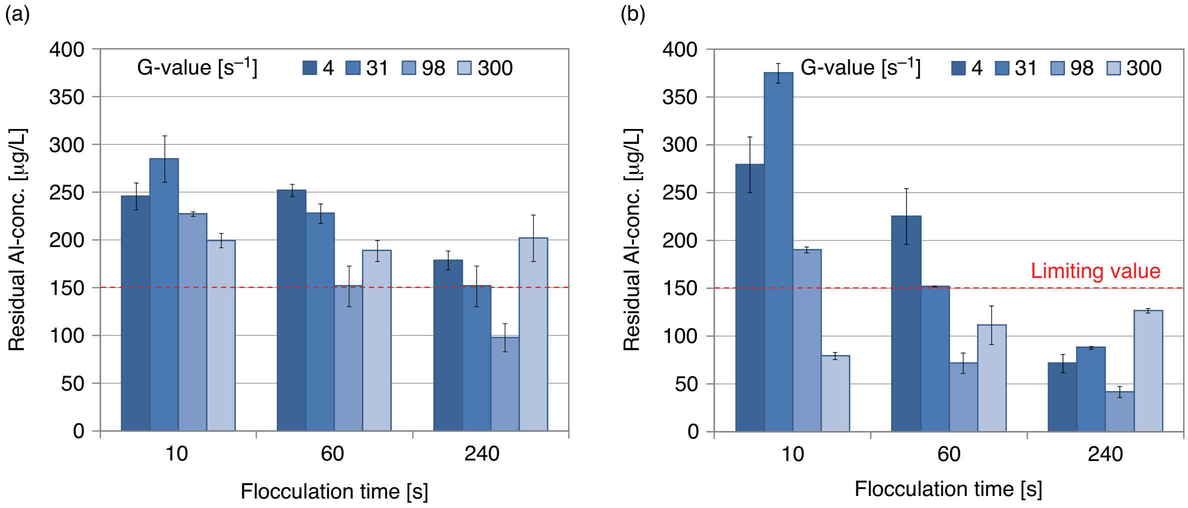


Fig. 6. Residual metal concentration dependence on flocculation time, *G*-value and aluminium dosage. (a) Coagulant dose 2.6 mg Al l^{-1}. (b) Coagulant dose 4.4 mg Al l^{-1}.

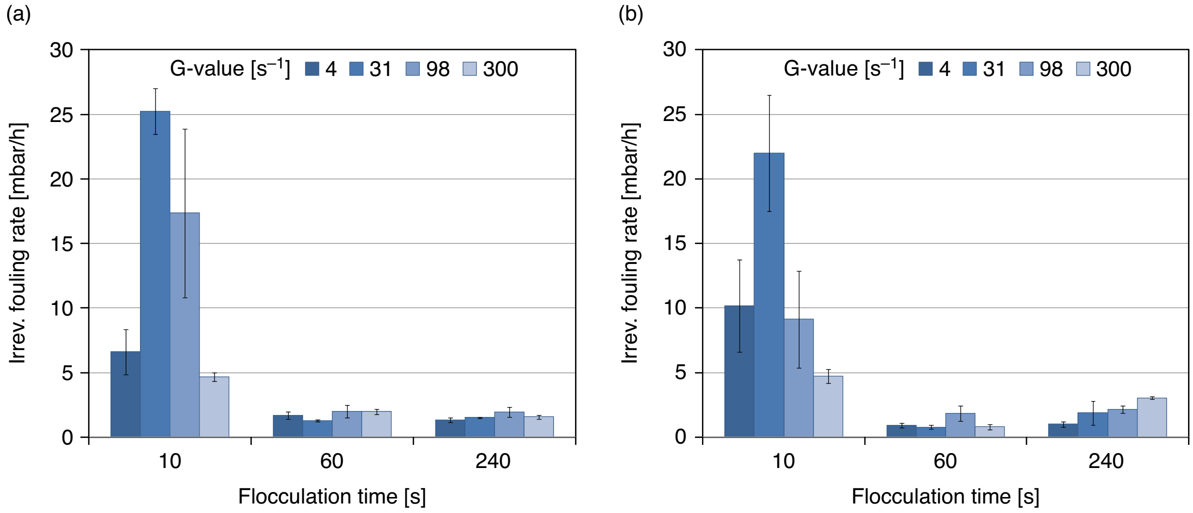


Fig. 7. Irreversible fouling in dependence on flocculation time, *G*-value and aluminium dosage. (a) Coagulant dose 2.6 mg Al l^{-1}. (b) Coagulant dose 4.4 mg Al l^{-1}.

minor influence on the irreversible fouling. The differences in irreversible fouling at flocculation times of 60 and 240 s are very small and more experiments with different times are necessary to validate and to identify if the observed trends are consistent.

From the results obtained it can be concluded that after a minimum flocculation time of 60 s the irreversible fouling was generally at a low level, independently from the other two varied flocculation parameters. As discussed for the residual metal concentration, these findings indicate that the flocculation reactions and particle aggregation are not completed after short flocculation times, even though the organic matter removal is not affected by this particle formation process. This fact can be visualized by in situ measurements of floc size as a function of the flocculation conditions directly before the membrane. Results are shown in Fig. 8. It can be clearly seen that the floc size is bigger at higher coagulant dose and higher flocculation times, but much lower compared to observations in the jar tests performed (Fig. 5(b)). The size maximum at a 4.4 mg Al l^{-1} dose, 240 s flocculation time and a *G*-value of 98 s^{-1} is possibly an indication that a further increase of mixing intensity up to 300 s^{-1} leads to a suppressed floc growth and possible floc breakage which may further explain the increased residual metal concentrations at this *G*-value.

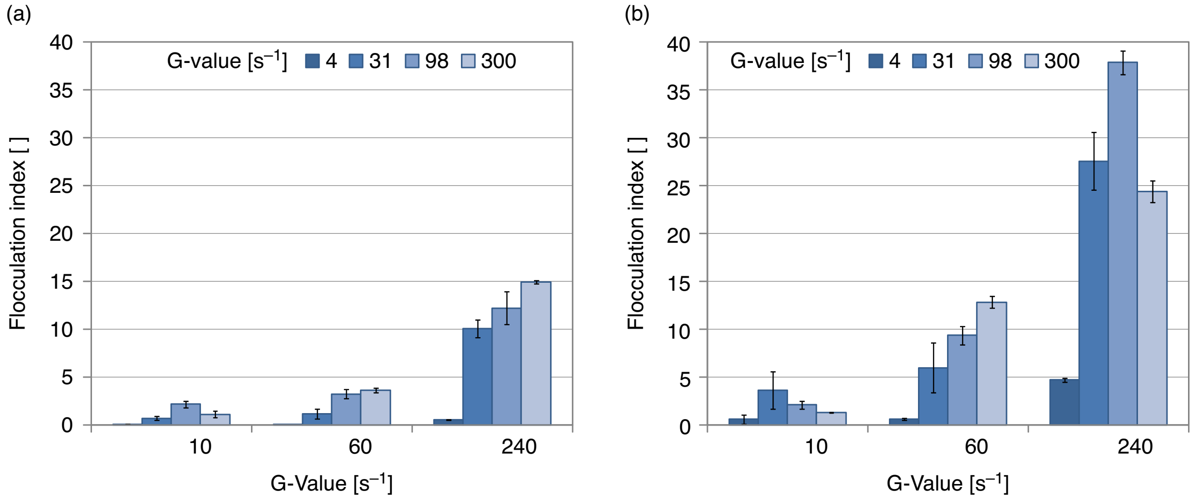


Fig. 8. Flocculation index dependence on flocculation time, *G*-value and aluminium dosage. (a) Coagulant dose 2.6 mg Al l^{-1}. (b) Coagulant dose 4.4 mg Al l^{-1}.

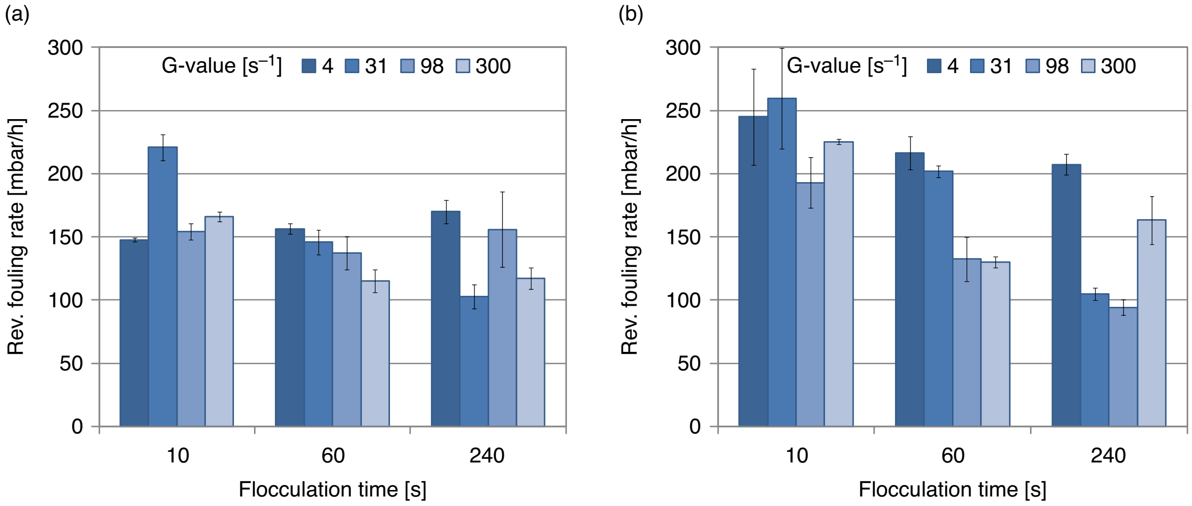


Fig. 9. Reversible fouling rate dependence on flocculation time, *G*-value and aluminium dosage. (a) Coagulant dose 2.6 mg Al l^{-1}. (b) Coagulant dose 4.4 mg Al l^{-1}.

However, measurements for a flocculation time of 10 s in particular are close to the detection limit of the analytical technique. According to the manufacturer the limits of particle size are roughly 0.5–100 µm. In general it can be concluded that after reaching a certain floc size level irreversible fouling was generally low, and where additional increase in floc size does not appear to further reduce the irreversible fouling.

All investigated flocculation parameters had a strong influence on the reversible fouling as shown in Fig. 9. Increased coagulant dosage elevated the reversible fouling, probably due to the increased organic matter removal and formation of particulate material thereby increasing solids load on the membrane. Increased mixing intensity or flocculation time generally decreased the reversible fouling, most likely due to a progressed aggregate formation, which then leads to a lower hydraulic resistance.

3.4. Design analysis

By stepwise regression the flocculation parameters and their interactions having a significant influence on the process response parameters were identified. Table 5 shows the obtained regression coefficients for each response and the quality of the obtained model.

In general the models showed a good correlation, however some responses were less explainable by the applied predictors. The residual metal variation in the permeate was only explained by 70% from the model, the reversible fouling even less by 50%. Here obviously other parameters not investigated in this study play a role. For the irreversible fouling also a poor correlation was found due to a nonlinear relationship. Therefore the linear regression was split for two different flocculation intervals, one from 10 to 60 s and the second from 60 to 240 s. This was assumed to be reasonable since in Fig. 7 it can be seen that the fouling dramatically decreases after an increase of flocculation time from 10 to 60 s, and stays on a low level after a further increase to 240 s. The two new models obtained showed very good correlation, explaining 96% and 80% of the variance respectively. However, it should be stated that a couple of outliers had to be removed, especially at a flocculation time of 10 s, in order to be able to get a model following the requirement of a normal distribution of the model residuals. This is can be explained by the severe fouling occurrence in some experiments. Once the membranes reach a certain level of fouling no stable operation is no longer possible and the further performance decrease from that point is rather random and does not follow any ordered pattern.

The major trends discussed were confirmed and quantified as shown in Fig. 10. It is apparent that all organic matter removal parameters are only influenced by the coagulant dose and not by the flocculation setup. The residual metal concentration decreased with increase of all three prediction parameters, but was influenced most by the interaction of dose and flocculation time followed by the *G*-value and coagulant dose. The reversible fouling behaviour was dominated by the coagulant dose and the interaction of dose and flocculation time. The irreversible fouling was influenced most by the flocculation time and the *G*-value at times lower or equal to 60 s. At higher flocculation times no direct influence of this parameter was found. Interaction terms

Table 5

Results of multiple linear regression: partial models with coefficients and quality parameters

Response	Constant	Predictors							No. of samples	No. of excluded outliers	R^2 (adj) [%]	R^2 (pred) [%]	Usefullness of model (*p*-value)	Normality test of residuals (*p*-value)
		Coagulant dose (A)	*G*-value (B)	Flocc. time (C)	AB	AC	BC	ABC						
DOC removal	33,969	8296							48	0	98.1	98.0	0.000	0.245
VIS_{436} removal	74,342	3958							48	0	95.0	94.7	0.000	0.908
UV_{254} removal	47,405	9168							48	0	98.1	97.9	0.000	0.078
Residual Al	3,41,247	−28,299	−0.312			−0.128	−0.001		48	3	69.7	66.3	0.000	0.076
Irreversible 10, 60	1733		−0.040	−0.245		−0.006	−0.001		16	7	96.3	91.5	0.000	0.064
Fouling at 60, 240	2091	−0.258	0.010		−0.003		-8E-05	3E-05	32	3	80.1	73.5	0.000	0.088
Flocc. time [s]: 10, 60, 240	3209			−0.007					48	8	14.8	8.1	0.008	0.203
Reversible fouling	76,553	37,630		0.649	−0.041	−0.260	−0.002	−0.001	47	2	49.6	40.6	0.000	0.199

are dominating, where changes of one prediction parameter cause in how other prediction parameters influence the responses. At a low *G*-value the flocculation time has almost no effect on the irreversible fouling, but has a strong negative effect once the *G*-value increases. At flocculation times of 60 s the *G*-value has no influence on the irreversible fouling. At higher flocculation times an increasing *G*-value leads to increasing irreversible fouling. This behaviour is represented in Fig. 10(b)) by the bar of the BC-interaction.

For process evaluation and optimization five different scenarios were assumed and investigated: (1) Maximising the NOM removal, (2) minimisation of residual metal concentration, (3) minimisation of irreversible fouling, (4) combined maximisation of NOM removal and minimisation of residual metal and fouling, (5) same as (4), but balancing treatment efforts with treatment needs and practical limitations.

- Scenario (1): Coagulant dose is the only parameter of interest. The other parameters do not influence the organic matter removal at all. Higher coagulant dose leads to increased removal, which is with 70.5% highest at a dose of 4.4 mg Al l^{-1}. However, depending on the other settings high fouling and residual metal in the permeate are possible to occur.
- Scenario (2): The interaction of coagulant with flocculation time has the biggest influence on the residual metal concentration, followed by *G*-value and flocculation time (Fig. 10(d)). They are further inversely proportional to the residual metal. At a coagulant dose of 4.4 mg Al l^{-1} and a flocculation time of 240 s the residual Al content is within a range of 82.0–93.5 μg Al l^{-1}. At these conditions however, an increase of the *G*-value has an increasing effect on the residual metal concentration due to the BC-interaction. Therefore the residual metal concentration is minimized at a *G*-value of 4 s^{-1}.
- Scenario (3): For minimisation of the irreversible fouling, the flocculation time should be equal to or higher than 60 s. In that time range higher coagulant dose reduces irreversible fouling, as can be derived from Fig. 10(b). However, due to the additionally dominant interaction terms fouling can be minimised by choosing a shorter flocculation time of 60 s, where the irreversible fouling is in the range of 0.96–1.03 mbar h^{-1}, at a coagulant dose of 4.4 mg Al l^{-1}. The *G*-value does not play a role at these conditions. The irreversible fouling stays in the stated range also at higher flocculation times, but only if the *G*-value is kept on a low level, otherwise the fouling increases significantly again.
- Scenario (4): High coagulant dose of 4.4 mg Al l^{-1} and high flocculation time of 240 s maximise the organic matter removal (70.5%) and decrease the residual

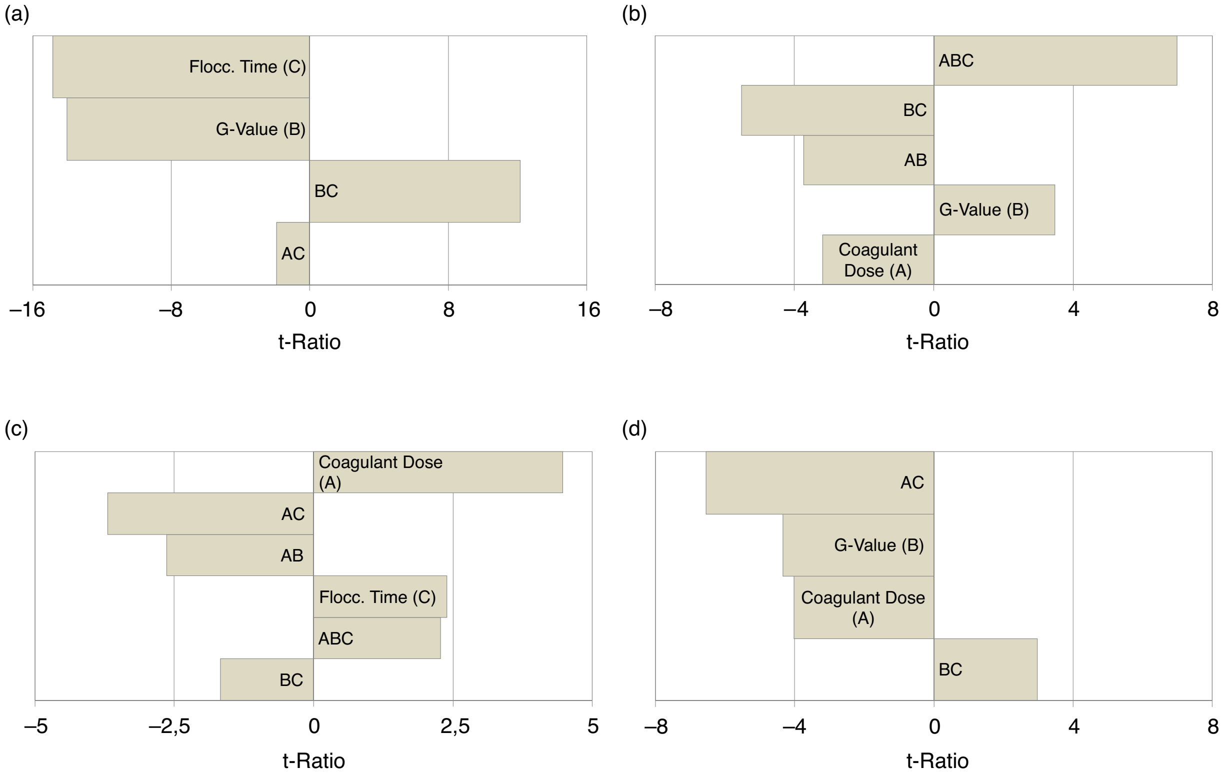


Fig. 10. Standardized effects of predictor variables and their interactions on different process performance parameters. (a) Irreversible fouling, at 10–60 s flocc. time. (b) Irreversible fouling, at 60–240 s flocc. time. (c) Reversible fouling. (d) Residual Al concentration.

metal concentration (82.0 mg Al l^{-1}). At these conditions the *G*-value has to be low at 4 s^{-1} to suppress irreversible fouling, leading to an irreversible fouling rate of 0.98 mbar h^{-1}. Furthermore, these conditions are beneficial for reduced reversible fouling, since a low *G*-value and higher coagulant dose have a decreasing effect under the stated conditions, resulting in a reversible fouling of 124 mbar h^{-1}. The pipe flocculator designed for these conditions would have a diameter of 38 mm and length of 6.33 m and is not suited for practical use, since it consumes a lot of space and diminishes the advantages of inline flocculation.

- Scenario (5): As can be seen from the results of scenario (4) further optimisation is necessary, including practical considerations. A flocculation time of 240 s and a *G*-value of 4 s^{-1} maximise the space needed for the pipe flocculator. Depending on the raw water quality it might not be necessary to achieve maximum organic matter removal at 4.4 mg Al l^{-1}, as long as disinfection precursors and colour are efficiently removed. However, the results presented in this study show that a high coagulant dose maximizes the organic matter removal but reduces residual metal and irreversible fouling at the same time and a dose 4.4 mg Al l^{-1} therefore maximises the overall desirability. The minimization of the residual metal concentration is achieved at cost of a more extensive treatment by increased time, dose and pipe diameter, but it only has to be below the limiting value. The results discussed earlier show that a flocculation time of 60 s is high enough to prevent extensive fouling, but also to keep the residual Al concentration down and further reduce the pipe flocculator size. 60 s were therefore chosen as being optimal. Finally a *G*-value had to be selected high enough to press the residual metal concentration below 150 µg l^{-1}, which was the case at 150 s^{-1}. The residual metal concentration could be further decreased by a higher *G*-value. This would lead to a diameter decrease and therefore length increase of the pipe flocculator, which is not desirable. Fig. 11 summarises the process performance as a result of the optimised flocculation parameters according to scenario 5. At a coagulant dose of 4.4 mg Al l^{-1}, a *G*-value of 150 s^{-1} and a flocculation time of 60 s the DOC removal would be at 70.5%, the residual metal concentration at 149 µg l^{-1}, the membrane would irreversibly foul with a rate of 1 bar h^{-1} and the reversible fouling would be at 197 mbar h^{-1}. The pipe flocculator would have a tube length of 3.8 m with a diameter of 12.3 cm, provided for a flux of 250 l m^{-2} h^{-1}.

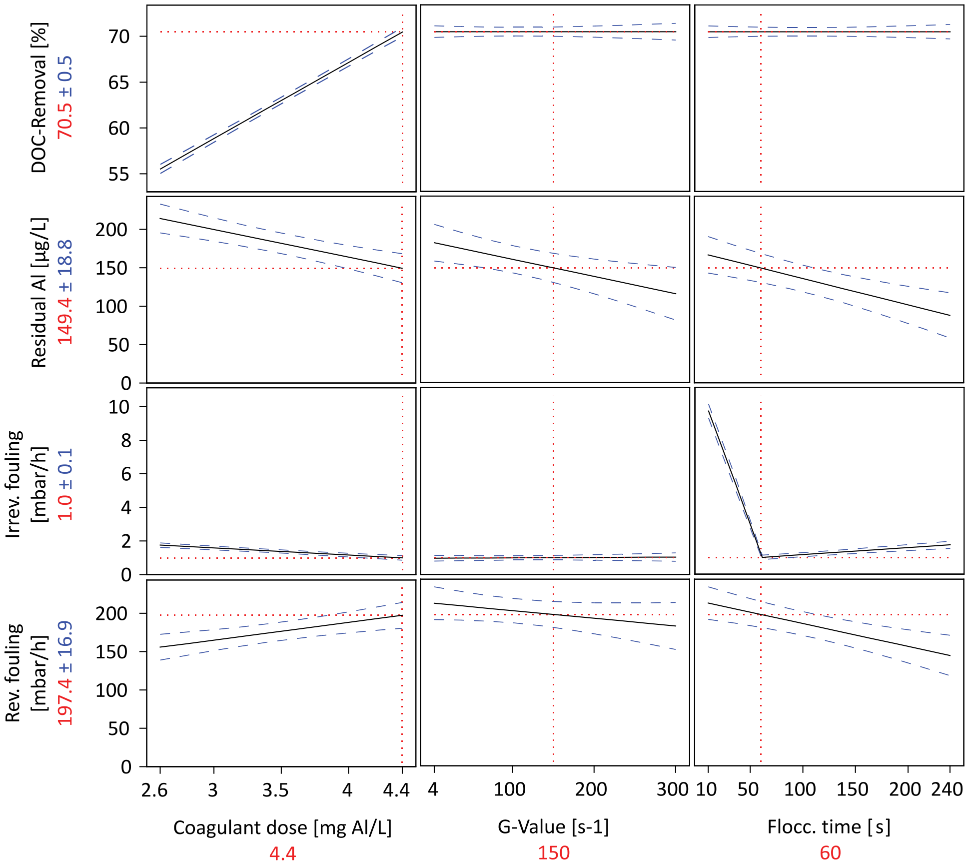


Fig. 11. Optimized flocculation parameters according to scenario 5 and their effect on the process performance, colour code: black continuous—modelling results; blue dashed—95% confidence interval; red dotted—optimized conditions.

4. Conclusions

Inline coagulation/flocculation coupled with ceramic microfiltration is a promising treatment alternative for low turbidity waters with a high organic matter content. Depending on the adjusted flocculation conditions, this hybrid process efficiently removed organic matter up to 70% and colour up to 90%. Low irreversible fouling of below 1 mbar h^{-1} was achieved at the same time, operating at a high flux of 250 l m^{-2} h^{-1}. Furthermore, it is possible to push the residual aluminium concentration below the limiting value of 150 mg l^{-1}. However, if the flocculation process is not optimized high membrane fouling and residual metal concentrations are likely to be the consequence.

The organic matter removal turned out to be very robust, by only depending on the applied coagulant dose and not at the other varied flocculation conditions at all. In contrast, membrane fouling and residual metal were quite sensitive to changes of all flocculation parameters. Generally it can be stated that there is a minimum flocculation time needed for the prevention of irreversible membrane fouling. In this study, this was found to be at 60 s. However, the true minimum flocculation time can be lower, since no times between 10 and 60 s were tested. This should be investigated further, since a reduction of flocculation time would lead to shorter pipe flocculators and less space consumption. In addition longer flocculation times help to reduce the residual metal concentration and the reversible fouling. Nonetheless, it is not desirable in practise to extend the flocculation time across a reasonable amount, since the result would be expensive and space consuming flocculator units. Therefore it has been attempted to balance actual treatment needs with treatment efforts.

Since the organic matter removal did not depend on the flocculation setup and only the coagulant dose, it is assumed that the reactions binding the organic molecules are finished after a few seconds or even milliseconds, leading to an efficient retention of organic matter by the membrane already after only 10 s of flocculation, even at conditions with almost no mixing in the flocculation stage. If additional flocculation time is provided the removal does not change, suggesting that the rest of the time is just used for particle shaping for fouling minimization. Since the residual metal concentration decreases as well with longer flocculation times it is assumed that charge neutralization and sweep flocculation occur in parallel. Charge neutralisation and bridging very fast creates microflocs, which can then be retained by the membrane. If longer flocculation time is provided $Al(OH)_3(s)$ can form and sweep flocculation occurs, resulting in bigger flocs which can be detected by the PDA. These processes are supported by the flow pattern in the membrane channels, which act as a pipe flocculator themselves. As long as the particles entering the membrane have a characteristic that they do not block the membrane pores or stick to the surface, the flow pattern in the channels will allow further flocculation and deposit the particles at the end of the channels near the dead end points.

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