

## Research Paper

# Retention of humic acid by ultrafiltration with polyaluminium coagulant

Vitaly Gitis, André Lerch and Rolf Gimbel

### ABSTRACT

The chemical and technological aspects for the retention of humic acid (HA) by combining coagulation and ultrafiltration (UF) are discussed in this paper. Coagulation was performed with polyaluminium chloride (PACl) in three operating modes: *in-line* 30 s coagulation, coagulation with 25 min flocculation, and coagulation/flocculation with 3 h sedimentation. UF capillaries with a molecular weight cut-off (MWCO) of about 200 kDa, made of polyethersulfone (PES), were operated in inside-out mode with constant positive pressure. The applied experimental scheme posed additional demands to the HA-PACl flocs, limiting their size and density. The optimal floc was achieved at low  $[Al_T]/DOC$  mass-to-mass ratio of 0.4. The obtained flocs were big enough to provide sufficient retention of HA by UF, small enough to minimize clogging, and with moderate density to minimize fouling. The optimal floc provided a highest 70% HA retention with minimal fouling. Combining coagulation with flocculation we were able to achieve an accumulation of 5 mg HA per capillary not compromising the duration of the filter run. Alteration of pH and Al dose to achieve ultimate 'charge neutralization' or 'sweep coagulation' yielded virtually similar results in terms of HA retention.

**Key words** | fouling, humic acid, mass-to-mass stoichiometry, natural organic matter, ultrafiltration membranes

### INTRODUCTION

The water treatment industry currently faces a challenge of supplying microbiologically safe water under increased public awareness that chemical disinfection might have negative side effects. It is preferable to reduce the concentration of pathogenic microorganisms in the source water by a 'physical' method to make the chemical disinfection a 'polishing' stage. Among the most promising technologies based on physical principles are membrane processes, providing a virtually absolute barrier to any pathogenic microorganism. Among various membrane processes, ultrafiltration (UF) is a technology which combines extremely high pathogen-retaining abilities with reasonable costs. One of the main bottlenecks in further implementation of that technique is the irreversible fouling

effects caused by natural organic matter (NOM). As well as being a proven foulant, NOM includes precursor compounds that form health-compromising by-products when chemical disinfection is used. It is therefore preferable to neutralize and retain NOM by UF membranes rather than to vary membrane surface to minimize NOM fouling. This paper discusses various operational aspects of achieving enhanced NOM removal with minimal fouling.

In general, the term NOM is attributed to any organics which result from a breakdown of animal and plant material in the environment. These organic substances are present in all surface waters and in many groundwaters. They can be leached from soil, diffused from wetland sediments, and released by plankton and bacteria. With progress in

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instrumental analysis each detectable organic molecule in a NOM sample has been classified by molecular weight into: a light section of small hydrophilic acids, proteins and amino acids; a medium group of fulvic and humic polymers; and a group of high molecular weight organic polymers such as humines, polypeptides and carbohydrates (Crompton 2000). The current study was centred on the retention of humic acid (HA) for three main reasons: 1) HA is present in most source waters and can be high in some (Rebhun & Lurie 1993); 2) its hydrophobicity and negative charge causes rapid, severe 30–40% fouling (Kabsch-Korbutowicz *et al.* 1999; Howe & Clark 2002; Jung & Kang 2003); and 3) HA is a proven source of carcinogenic compounds in drinking water disinfected by chlorination (Alawi *et al.* 1994).

A UF-based technology for the removal of HA from source water includes the collection of HA into flocs that can be retained by the membrane and later removed during backwash (Bottero 1992). The application is accountable for three improvements: 1) enhanced retention of HA; 2) increased lifetime of membrane modules; and 3) lower operational expenses with moderate trans membrane pressure (TMP) build-up (Crozes *et al.* 1995; Taylor & Wiesner 1999; Lerch *et al.* 2003). The success of this treatment is influenced by membrane properties (Laine *et al.* 1989; Jucker & Clark 1994; Elimelech *et al.* 1997), characteristics of the raw water (Jucker & Clark 1994; Hong & Elimelech 1997; Braghetta *et al.* 1998; Kulovaara *et al.* 1999; Lee *et al.* 2000; Howe & Clark 2002) and NOM chemistry (Schaefer *et al.* 2000; Ariza *et al.* 2001).

The collection of HA into flocs is realized by a pre-treatment of the raw water with addition of coagulants. For many years, coagulation was achieved with addition of aluminium sulfate (alum,  $\text{Al}_2(\text{SO}_4)_3 \times 14.3 \text{ H}_2\text{O}$ ). Added to water, the salt rapidly dissociates into sulfate ions and  $\text{Al}^{3+}$ , when the latter is able to form a series of monomeric aluminium hydroxide species in equilibrium with an  $\text{Al}(\text{OH})_{3(s)}$  precipitate (Amirtharajah & Mills 1982). Later, the formation of alumohydroxo-humic flocs was performed also with sodium aluminate and polyaluminium chloride (PACl). PACl, examined in the study, is a coagulant that consists of pre-formed aluminium hydroxide species produced by the addition of base to concentrated aluminium chloride solution (Dempsey *et al.* 1984). With a general formula of  $\text{Al}_n(\text{OH})_m\text{Cl}_{3n-m}$  the exact composition of

hydrolysis products depends on the developed protocol which is usually a proprietary of the manufacturer. The protocol includes concentration of the stock  $\text{AlCl}_3$  solution, degree of neutralization, type of base, temperature, pressure and mixing technique.

Few attempts were made to classify the important aqua-Al species (Hayden & Rubin 1974; Dempsey *et al.* 1984; Hundt & O'Melia 1988; Van Benschoten & Edzwald 1990; Edzwald & Van Benschoten 1990; Pernitsky & Edzwald 2003). It was generally agreed that the total Al in water ( $\text{Al}_T$ ) can be adequately described by combinations of two monomers and polymer, i.e.  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ , in equilibrium with  $\text{Al}(\text{OH})_{3(s)}$  precipitates. The presence and relative fraction of each species was highly affected by the basicity number  $r = [\text{OH}]/[\text{Al}]$  and by pH. For high basicity numbers, in order of 2 and above, the important products were polynuclear  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  in equilibrium with  $\text{Al}(\text{OH})_4^-$  ion and  $\text{Al}(\text{OH})_{3(s)}$  precipitate (Pernitsky & Edzwald 2003). For low (0.4 ~ 1) and medium (1.1 ~ 1.5) basicity PACl the soluble aluminium was presented by a combination of monomers  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_4^-$  and polymer  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ . Regarding the  $\text{Al}(\text{OH})_{3(s)}$ , for low and medium basicity PACl the researchers found no filterable precipitate until a pH of 6 ~ 6.5. That view was also shared by Hundt & O'Melia (1988) who assumed the presence of monomers and small polymers between pH 5 and pH 6.6, and domination of  $\text{Al}(\text{OH})_{3(s)}$  beyond pH 6.6.

The possible mechanisms of interaction between NOM and PACl include adsorption of NOM onto the surface of floc particles regardless of their charge (so-called 'sweep coagulation'), and the complexation/precipitation of NOM with positively charged coagulant species (so-called 'charge neutralization') (Amirtharajah & Mills 1982; Van Benschoten & Edzwald 1990). The 'sweep coagulation' zone corresponds to the  $\text{Al}_T$ -pH conditions that are necessary for the formation of  $\text{Al}(\text{OH})_{3(s)}$  precipitate. The term 'charge neutralization' was attributed to a  $\text{Al}_T$ -pH zone where precipitation of  $\text{Al}(\text{OH})_{3(s)}$  is unlikely and where the formation of large polymers is uncertain or unexpected. The 'charge neutralization' zone suggests the presence of specific chemical reactions between positively charged coagulants and negatively charged carboxylic and phenolic end groups on the organic rim of HA. The opposite scenario of 'charge neutralization' suggests shielding the negatively

charged sites on the molecular rim in the Stern layer of the electrical double layer. It implies that, for the pH level below pH 6.6, the primary coagulation mechanism of NOM by PACl will be charge neutralization in a way of formation of  $-\text{COO}^- \text{Al}(\text{OH})_2^+$  and  $-\text{COO}^- \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  flocs. For pH 6.6 and higher the coagulation will occur via the dual mechanism of charge neutralization and sweep coagulation. It was argued above that the dual mechanism brings enhanced retention, since for standard treatment processes 'poorly separable or non-separable' flocs (Rebhun & Lurie 1993) will adsorb or interact with the  $\text{Al}(\text{OH})_{3(s)}$  'sweep flocs' and become amenable to separation.

The research was performed in order to optimize UF water treatment with capillaries operated in inside-out mode. The investigated scheme posed some unique limitations to the size of formed flocs as big flocs might clog the capillary and result in less than optimal filtration. The formation of big flocs was never realized as a concern for two other membrane configurations, flat sheet and spiral wound. On the contrary, it was assumed that the contribution of voluminous flocs with higher porosity to TMP is minor (Li & Elimelech 2004). Small dense flocs accounted for the formation of dense 'cake layers' on the membrane surface and for severe fouling. For capillaries with inside-out flow, the formation of lighter voluminous flocs with bigger dimensions might result in early clogging of the membrane capillaries. Therefore, favourable HA retention posed three main demands on the floc size and density: 1) the floc should be big enough to provide sufficient retention of HA by UF; 2) the floc should be small enough to minimize clogging; 3) the floc should have moderate density to minimize TMP increase. The attempt to achieve favourable retention was made by altering four parameters: operating mode, pH, concentration of HA and concentration of PACl. Favourable HA retention was assessed by a high degree of HA removal and minimal TMP increase.

## MATERIALS AND METHODS

### Membrane and apparatus

The membrane set was made on site from five polyethersulfone (PES) capillaries glued on both ends into 2 cm length

plastic tubes. Each experiment was performed with a new set of capillaries. The far end (from the pump) of the capillaries was blocked so the filtration occurred in a dead-end mode. The new capillaries were provided by X-Flow B.V. (Enschede, The Netherlands) and were of the type used by the company in CAPFIL UFC M5 membrane modules. The capillaries were 1 m in length and 0.7 mm in inner hydraulic diameter, providing 22 cm<sup>2</sup> membrane area per capillary. The molecular weight cut-off (MWCO) was 200 kDa, measured on dextrans. Each framed set was adjusted for horizontality and washed for 2 h with ultra pure deionized (DI) water (MilliQ quality) under 1 bar (10<sup>5</sup> Pa) pressure to rinse out the glycerin, used as coating agent for the storage of the capillaries before use. The filtration direction was inside-out with positive pressure supplied by a progressive cavity pump (PCP, MD 003-12, Seepex, Bottrop, Germany). After 2 h, the DI water in the feed tank was replaced by destabilized HA suspension. The flux was adjusted to 80 l (m<sup>2</sup>h)<sup>-1</sup>. Figure 1 presents a schematic of the bench-scale coagulation-UF module, designed and fabricated for the research.

Samples of permeate were collected into glass beakers placed on semi-analytical balances BA2100S (Sartorius AG, Göttingen, Germany). The collection was performed with three inter-touching funnels mounted just below the capillary set. The funnels are labelled in Figure 1 as Begin, Middle and End funnel by their relative distance from the feed pump. The balances were connected to a PC and tared at the beginning of each experiment. Frequent readings of permeate weight differences were performed on the collected data with DOS-based software. The setup allows the collection of all permeate between glued ends to assess the kinetics of HA retention with mass balance calculations.

### Experimental schedule

The feed suspension was prepared on site by dosing soil-based HA (sodium salt, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) to the City of Mülheim a.d. Ruhr tap water. The typical characteristics of the tap water, as analysed by the IWW Rheinisch-Westfälisches Institut für Wasser Beratungs- und Entwicklungsgesellschaft mbH (Mülheim a.d. Ruhr, Germany), are presented in Table 1.

The addition of 1 and 7 mg l<sup>-1</sup> HA was performed by taking appropriate volumes from a stock solution of

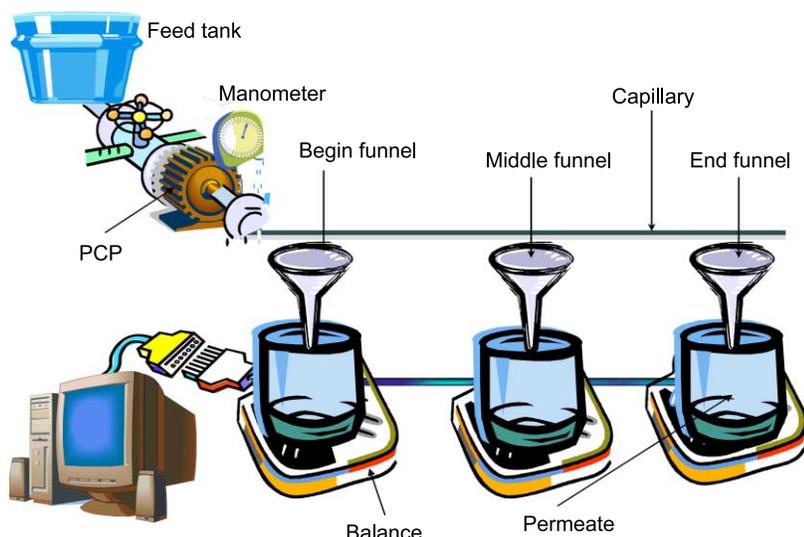


Figure 1 | Coagulation–flocculation–UF membrane unit set-up.

100 mg l<sup>-1</sup> HA, achieving a feed suspension in a typical range for raw surface water (Thurman 1985). The coagulant used was PACl (Sachtoklar<sup>®</sup> 39, Sachtleben Chemie GmbH, Duisburg, Germany), with 8.9 Mass-% Al<sup>3+</sup>, 21 Mass-% Cl<sup>-</sup>, basicity of 40 ± 2% and density of 1370 kg m<sup>-3</sup> at room temperature. The PACl was directly dosed into the feed suspension as described above. The added PACl volumes were 22.1 µl and 0.11 ml PACl per 11 of initial suspension, corresponding to 2.7 mg l<sup>-1</sup> and 13.5 mg l<sup>-1</sup> Al<sub>T</sub>, respectively. Concentrations of Al<sub>T</sub> were measured with ICP/MS Elan-500 (Perkin Elmer SCIEX, Wellesley,

Massachusetts) equipped with a Perkin Elmer AS 91 auto sampler. For pH correction, 0.1N HCl (Sigma-Aldrich) or 0.1N NaOH (Riedel-de Haen, Seelze, Germany) was introduced drop-wise. The correction was performed immediately after PACl dosing into the feed suspension, to the target levels of pH 5.25 and pH 6.75. pH levels were measured and recorded with pH196 pH meter (WTW, Weilheim i. OB, Germany). The set of experimental variables is presented in Table 2.

The examined coagulation/flocculation/sedimentation operating modes included: ‘contact’ membrane setup with 30 s rapid mixing at  $G$  values of 1,800 s<sup>-1</sup> using an Ultra Turrax T25 stirrer (Janke&Kunkel GMBH@Co., Staufen, Germany), followed by immediate filtration; ‘direct’ scheme with addition of 25 min batch flocculation in the feed tank by a conventional blade stirrer RE162 (Janke&Kunkel) at  $G$  value of 40 s<sup>-1</sup>; and a ‘conventional’ scheme where the flocculated suspension was allowed to stay for an additional

Table 1 | Characteristics of the tap water (Mülheim a.d. Ruhr) used in this study

Parameters	Range
Turbidity, NTU	< 0.1
pH	7.7–7.9
Temperature, °C	20–22
DOC, mg l <sup>-1</sup>	0.52
UV <sub>254</sub> absorbance, AIU	0.38
Conductivity, µS cm <sup>-1</sup>	616
Total alkalinity (as CaCO <sub>3</sub> ), mg l <sup>-1</sup>	144.6
Total hardness (as CaCO <sub>3</sub> ), mg l <sup>-1</sup>	57.8

Table 2 | Suspension composites

	Low	High
Coagulant dosage [mmol (Al <sup>3+</sup> ) l <sup>-1</sup> ]	0.1	0.5
pH	5.25	6.75
HA concentration [mg l <sup>-1</sup> of DOC]	1	7

3 hours in a laboratory beaker under a magnetic stirrer at 150 rpm conditions. The graphical representation of all six stages is depicted in Figure 2.

All experiments were performed for 360 min, sufficient time for filtration of 1 l of the feed suspension per capillary. Water flux, which is defined as the filtrate flow per unit of membrane filtration area per time interval, was calculated as:

$$J_T = Q/A = \frac{\Delta m}{\rho \pi D L \Delta t'} \quad (1)$$

where  $D$  = inner diameter of the capillary ( $0.7 \times 10^{-3}$  m);  $L$  = length of capillary segment (0.32 m);  $\Delta m$  = permeate weight differences (g);  $\Delta t'$  = frequency reading interval ( $8.3 \times 10^{-3}$  h);  $\rho$  = density of permeate ( $\text{g l}^{-1}$ ). The flux was normalized to a standard temperature of 20°C using the following empiric relationship (US EPA 2003):

$$J_{20} = J_T \left[ 1.784 - (0.0575 \cdot T) + (0.0011 \cdot T^2) - (10^{-5} \cdot T^3) \right] \quad (2)$$

Where  $J_{20}$  is a normalized flux at 20°C and  $J_T$  = actual flux at temperature  $T$ . The permeability was calculated as a ratio of the normalized flux  $J_{20}$  to TMP

$$M = J_{20}/TMP \quad (3)$$

where TMP was recorded from a pressure transducer DP205 (Mecotec, Meerbuch, Germany) connected to the inlet of the capillary set. The relative permeability curves were drawn in dimensionless form by dividing the obtained values by the

initial permeability of virgin membranes filtering DI water

$$M/M_0 = \frac{J_{20}/TMP}{(J_{20}/TMP)_{\text{virgin}}} \quad (4)$$

The initial permeability values were obtained for each membrane segment separately before each experiment. Accepted permeability curves had been smoothed by non-linear regression of second order prior to analysis.

### HA extraction and analysis

Soil-based HA was extracted as follows: 1 g of HA was dissolved in 20 ml of 1 N NaOH, diluted in 1 l of DI water and stirred for 2 h. Then the pH was adjusted to pH 5.5, the volume was adjusted to 2 l, and the solution was left overnight under continuous stirring. The obtained slurry was filtered through Whatman GF-A followed by 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE) flat membranes (Costar, Cambridge, Massachusetts). The obtained stock was kept in a refrigerator at 4°C.

The quantification of HA in solution was performed by a combustion-infrared method, measuring dissolved organic carbon (DOC) with a total organic carbon analyser Shimadzu A5500 (Shimadzu Corp., Kyoto, Japan). Ultra-violet and visible spectra of the HA sample (UV and VIS, respectively) were recorded using a Lambda 2 Spectral-photometer (Perkin Elmer Analytical Instruments, Shelton, Connecticut). The intensities of the spectra at 254 nm for UV and at 436 nm for VIS were recorded in absolute intensity units (AIU) and used as a surrogate quantitative measurement of HA. Carboxylic and phenolic acidities of HA sample in the DI water were determined by rapid titration using a potentiometric acid/base titration technique (Reckhow *et al.* 1990). The titration was performed by a potentiometric automatic titrator in the pH range from 11 to 3 with 0.1M HCl. All glassware used was treated with 'piranha solution' made of 30% hydrogen peroxide and 70% concentrated sulphuric acid. Based on previous results (Newcombe & Drikas 1997) pH 3 was deemed as the level of full protonation of HA, and pH 11 as the level of full deprotonation. A Bruker Minispec (Bruker Optics Inc., Rheinstetten, Germany) spectrometer at a frequency of 65 MHz was used to analyse the carbon functional groups. Chemical shift ranges were adopted from Ricca & Severini

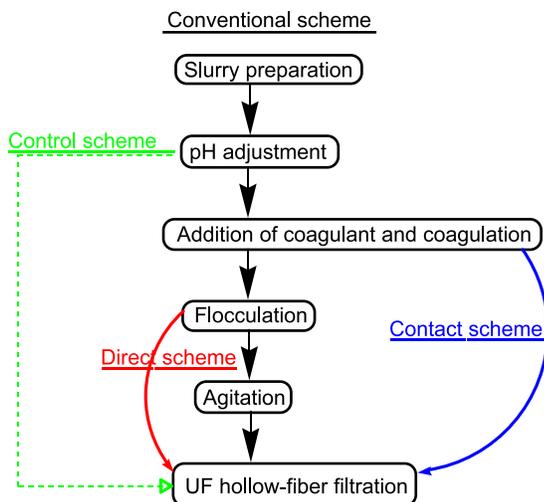


Figure 2 | Schematic of the bench-scale coagulation-UF system.

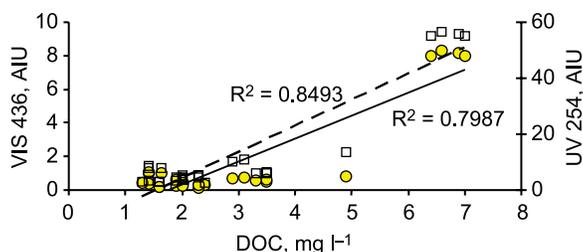
(1993) to indicate the aromatic content in the peak areas between 102 and 175 mg l<sup>-1</sup>. Aliphatic carbon was considered to compose the remainder of the <sup>13</sup>C-NMR (Nuclear Magnetic Resonance) spectrum.

## RESULTS

The <sup>13</sup>C-NMR data indicated that a typical HA sample contained 40% aromatic and 60% aliphatic carbon fractions. The potentiometric titration data showed two inflection points at pH 8.0 and pH 4.9 corresponding to phenolic (-OH) and carboxylic (-COOH) acidic groups, respectively. The carboxylic acidity (as expressed in milliequivalents per g of DOC) was 4.4 ± 0.3 meq g<sup>-1</sup> while the phenolic acidity was 2.2 ± 0.5 meq g<sup>-1</sup>. The obtained values were similar to the total acidity values reported by Reckhow et al. (1990) for aquatic humic and fulvic acids. The soil-based acidities of HA were usually higher, in the order of 8 ~ 13 meq g<sup>-1</sup> (Narkis & Rebhun 1977; Newcombe & Drikas 1997; Kaiser 1998). The somewhat lower values obtained in the current study were attributed to the double extraction performed by Sigma-Aldrich and after that on site.

The attempts to simplify the quantification of the HA by measuring UV 254 and VIS 436 values were performed with UF of HA solutions containing 1 to 7 mg l<sup>-1</sup> DOC. The calibration was performed with and without PACl addition. Figure 3 depicts UV 254 and VIS 436 values plotted against HA concentrations measured in mg l<sup>-1</sup> of DOC.

The parallel determination exhibited poor accuracy with Pearson's R<sup>2</sup> coefficients in a range 0.8 ~ 0.85 for a wavelength range of 250 to 450 nm. The poor correlation was explained by differences in retention of aromatic and



**Figure 3** | Correlation between DOC, UV (indicated as squares) and VIS (indicated as circles) results for the HA sample. Here DOC = dissolved organic carbon; UV 254 and VIS 436 = the intensity of ultraviolet and visible spectra at 254 and 436 nm wavelengths, respectively.

aliphatic fractions of HA, as has been reported before (Edzwald et al. 1985). The higher degree of removal of more hydrophobic aromatic fraction resulted in constant values of UV 254 and VIS 436 at low HA level. The further HA quantification was based on direct DOC measurements only. The degree of removal was expressed as HA removal ratio *R.R.*

$$R.R. = 1 - \left( \frac{C_p}{C_f} \right) \quad (5)$$

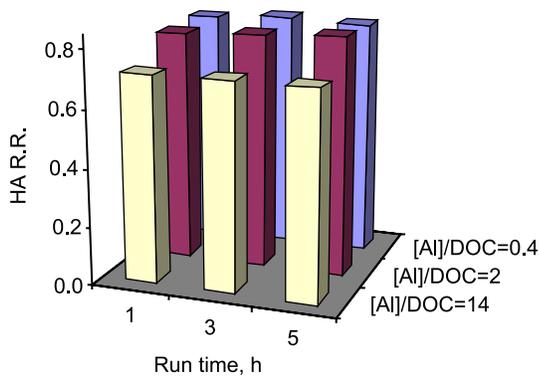
where  $C_p$  and  $C_f$  are permeate and feed concentrations in mg of HA, respectively. Degree of removal was calculated for 4 [Al<sub>T</sub>]/DOC mass-to-mass ratios of 0.38, 1.9, 2.7 and 13.5. The ratios were rounded off to 0.4, 2, 3 and 14 using the following calculation as exemplarily shown here for 0.5 mmol [Al<sub>T</sub>] and 7 mg l<sup>-1</sup> DOC:

$$\frac{0.5 \cdot 10^{-3} [M]Al}{7 [mg/L] DOC} \times \frac{27 [mg]Al}{10^{-3} [M]Al} = 1.92 \approx 2 \quad (6)$$

In the calculations, it was assumed that there is no additional contribution to HA from the background DOC concentration of 0.52 mg l<sup>-1</sup>. The assumption was based on the treatment chain of the city of Mülheim a.d. Ruhr tap water that includes addition of lime milk, PACl and NaOH (Lerch et al. 2003). It was unreasonable to assume that the second PACl introduction would be more efficient for the DOC residuals. Experiments performed with raw water without any pre-treatment with PACl resulted in virtually no retention of HA by the capillaries. Consequently, HA *R.R.* was calculated considering a 0.52 mg l<sup>-1</sup> DOC background in permeate. Figure 4 presents HA *R.R.* values at three run times during the run at pH 5.25.

The conventional filtration scheme was investigated. The presented data is for [Al<sub>T</sub>]/DOC levels of 0.4, 2 and 14. The intuitive assumption that *R.R.* will remain constant throughout the run was proved to be correct. A slightly lower removal of HA was depicted with [Al<sub>T</sub>]/DOC ratio of 14. This was attributed to the low available concentration of the Al(OH)<sup>2+</sup> fraction. It was assumed that the Al(OH)<sup>2+</sup> fraction responsible for charge neutralization partially reacted with a polynuclear Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub><sup>7+</sup> before reaching non-neutralized HA ligands.

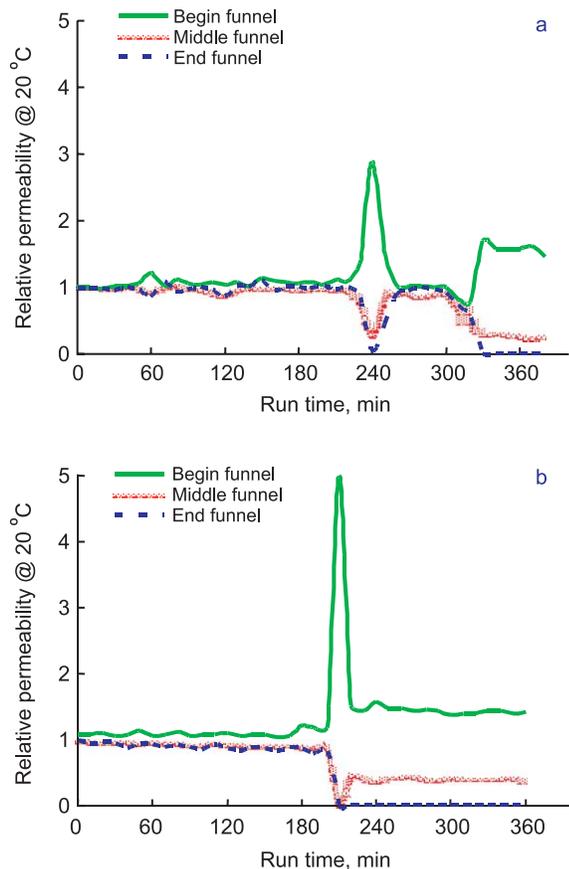
Figure 5 depicts relative permeability curves vs. run time. The presented plots were obtained during preliminary studies performed on single capillaries with conventional operation



**Figure 4** | HA removal ratio (R.R.) as a function of run time for different  $[Al]_T/DOC$  ratios at pH 5.25; conventional operating mode.

mode, to verify the previously described possibility of clogging the capillaries with flocs of big dimensions.

The reported curves were obtained at pH 5.25 with addition of  $13.5 \text{ mg l}^{-1}$   $[Al]$  for high HA content of  $7 \text{ mg l}^{-1}$

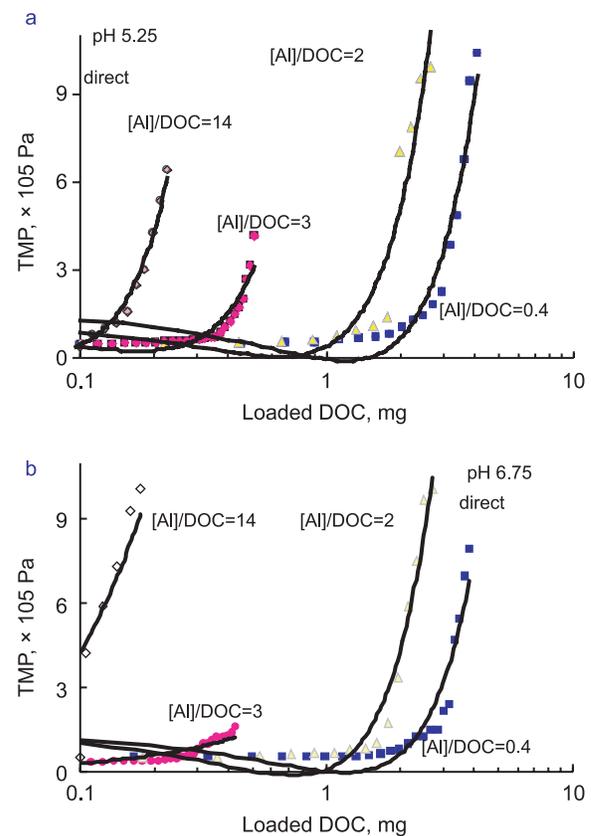


**Figure 5** | Relative permeability of UF membrane as a function of run time at pH 5.25,  $[Al]_T/DOC$  ratio of 2; conventional operating mode.

HA, i.e. with  $[Al]_T/DOC$  mass-to-mass ratio of 2. As expected, 3 h sedimentation resulted in the formation of bigger flocs, affecting membrane relative permeability and resulting in the earlier clogging of the capillaries. The big flocs cause an immediate (Figure 5b) or delayed (Figure 5a) blocking of parts of the capillary. Clogging of parts of the capillary increased the TMP drop over the total capillary and caused separation of fluxes, i.e. an increased flux at those parts of the capillary that remained open. The clogging was also easily detectable in terms of total HA accumulation assessed through mass balance calculations.

Figure 6 depicts the development of TMP plotted vs. removed HA measured in DOC values. The data was plotted on the semi-logarithmic scale for all four  $[Al]_T/DOC$  ratios and two pH levels of pH 5.25 (Figure 6a) and pH 6.75 (Figure 6b).

For both low and high pH levels the bigger  $[Al]_T/DOC$  ratio sharpened TMP increase. The low  $[Al]_T/DOC$  ratio of



**Figure 6** | TMP as a function of removed HA for various  $[Al]_T/DOC$  ratios and different pH values; direct operating mode.

0.4 allowed prolonged filtration cycles with accumulated HA removal of 4 ~ 5 mg per capillary. The highest  $[Al_T]/DOC$  ratio of 14 caused a steep rise of TMP up to 10 bars ( $10^6$  Pa) during the first hour of filtration, and the cumulative HA removal was below 0.2 mg. The possible explanation of such effects could be the presence of bigger flocs which might pose an inside barrier as described previously in Figure 5.

The influence of the  $[Al_T]/DOC$  ratio on relative permeability  $M/M_0$  (Equation 4) for the begin funnel is depicted in Figure 7. The contact (Figure 7a and b), direct (Figure 7c and d) and conventional (Figure 7e and f) operation modes were plotted vs. loaded HA for both pH values of pH 5.25 and pH 6.75. As observed, the degree of decrease in relative permeability was directly linked to the  $[Al_T]/DOC$  ratio. A lower  $[Al_T]/DOC$  ratio of 0.4 resulted in higher values of accumulated HA up to 5 mg per capillary, using the direct operation mode. Higher  $[Al_T]/DOC$  ratios caused a more significant decrease of relative permeability vs. time. As a result, levels of HA accumulated per capillary decreased down to values of 0.3–0.4 mg HA for  $[Al_T]/DOC$  ratio of 14. That was attributed to the formation of additional Al flocs of big dimensions. The exceptional conventional set-up at pH 5.25 (Figure 7e) was distinguished earlier in the experiment by the observable settling of flocs inside the pump and distribution pipes before reaching the capillary set. The settling resulted in a stable relative permeability, that constantly increased to levels greater than 1 as the dead-end of the set became clogged. This effect is similar to the results obtained in experiments performed on single capillaries as shown in Figure 5, where the capillaries also start to get clogged first at the dead-end.

Figure 8 shows the relative removal of HA as a function of  $[Al_T]$  and operating mode for both pH values of pH 5.25 and pH 6.75 (Figure 8a and b, respectively). The HA removal ratios of 0.15 at most were observed for the experiments performed with no PACl dosing and at high HA loads at pH 6.75 (indicated as control, Figure 8b). Addition of  $[Al_T]$  in the contact and direct scheme had shown higher levels of more than 0.7 retentions for both pH levels. The similar data for a conventional scheme was shown in Figure 4. Comparing the obtained removal ratios, it was concluded that coagulation followed by a flocculation and sedimentation step did not result in additional HA removal above the 0.7 ~ 0.8 barrier.

## DISCUSSION AND CONCLUSIONS

Two of the main bottlenecks in a direct application of UF for surface water treatment are irreversible fouling and low retention of HA by UF without coagulation. Hence, coagulation achieves dual goals in minimizing membrane fouling and increasing HA retention. The performed research was initiated in order to optimize UF water treatment with capillaries operated in inside-out mode. The presented study is an attempt to assess the relative importance of four parameters that were deemed significant for efficient HA retention. The parameters under investigation included three operation modes, two PACl concentrations, two HA doses at two pH levels of pH 5.25 and pH 6.75. The chosen pH levels corresponded to coagulation domains of ‘charge neutralization’ and ‘sweep coagulation’. Variations in operating modes were inspired by rapid sand filtration and included in-line coagulation, coagulation followed by flocculation, and coagulation followed by flocculation and sedimentation.

The membrane performance was assessed by degree of fouling and HA removal ratio. In-line coagulation followed by UF results in a relatively moderate increase in TMP levels and prolonged runs between backwashes. Additional flocculation slightly improved the HA removal ratio to the highest degree of 0.7 ~ 0.8 retention on average, not compromising the run length. The HA removal ratio was virtually equal for direct and conventional modes. However, application of the latter resulted in capillary clogging. Two important derivatives of that observation are: 1) efficient HA retention might be achieved with low PACl doses when coagulation is followed by flocculation; and 2) the addition of a sedimentation step as a useful unit operation for the removal of agitated flocs seems not to be efficient.

Alteration of pH and  $[Al_T]$  doses to achieve either charge neutralization or sweep coagulation mechanisms yielded virtually similar results in terms of TMP and HA removal. However the sweep coagulation was deemed favourable in the comparison of the permeability curves. The possible explanation lies in PACl experimental solubility data, provided by Pernitsky & Edzwald (2003). With low solubility of  $Al(OH)_4^-$  at pH 6.75, more than 0.99 of  $Al_T$  was in a form of  $Al(OH)_3$  precipitate. The significant hydrolysis products at pH 5.25 were  $Al(OH)^{2+}$  and  $Al_{13}O_4(OH)_{24}^{7+}$ . Therefore charge neutralization at pH 5.25 is realized via the

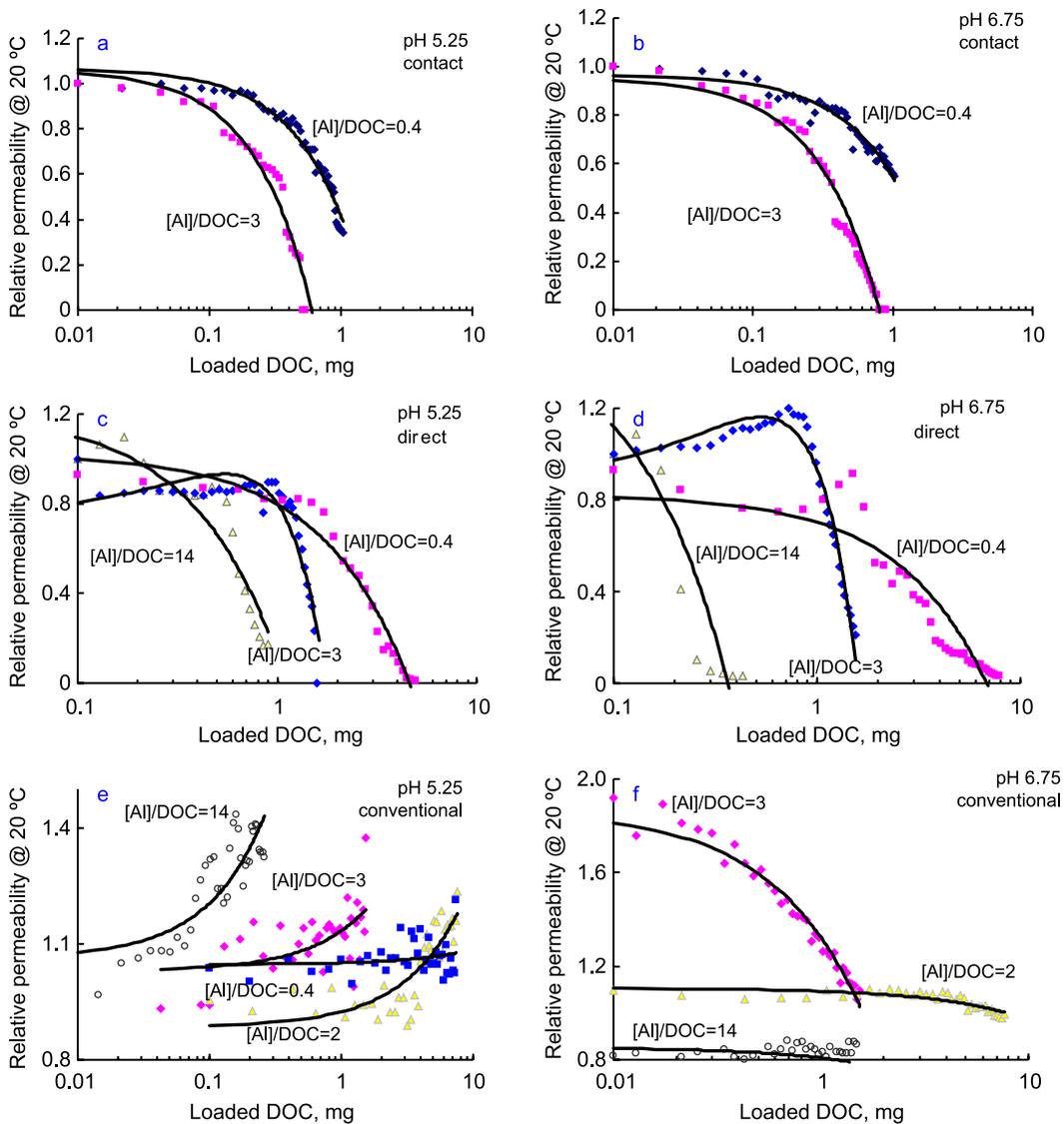


Figure 7 | The relative permeability at the begin funnel as a function of loaded HA.

formation of  $-\text{COO}^- \text{Al}(\text{OH})_2^+$  and  $-\text{COO}^- \text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  flocs. The flocs with smaller dimensions accumulated inside the capillary cause a more significant TMP increase.

The limited advantage of charge neutralization was partially explained by a low carboxylic acidity of the stock HA solution. The sweep flocs are of bigger dimensions, but their contribution to permeability decrease was minor. The sweep coagulation mechanism can be as effective as limiting the production of large flocs that could clog the

capillary. It is reasonable to assume that the dimensions of HA-PACl flocs were affected by the  $[\text{Al}_T]/\text{DOC}$  mass-to-mass ratio. The low  $[\text{Al}_T]/\text{DOC}$  ratio of 0.4 with the direct treatment scheme was found to be the favourable combination. The observation was consistent for both pH levels. Increasing that ratio resulted in incomplete removal and provided a rapid clogging of the membrane capillary and increasing TMP values. As changing the  $[\text{Al}_T]/\text{DOC}$  ratio resulted in predictable changes in HA removal and degree of fouling, we claimed that the  $[\text{Al}_T]/\text{DOC}$  parameter might

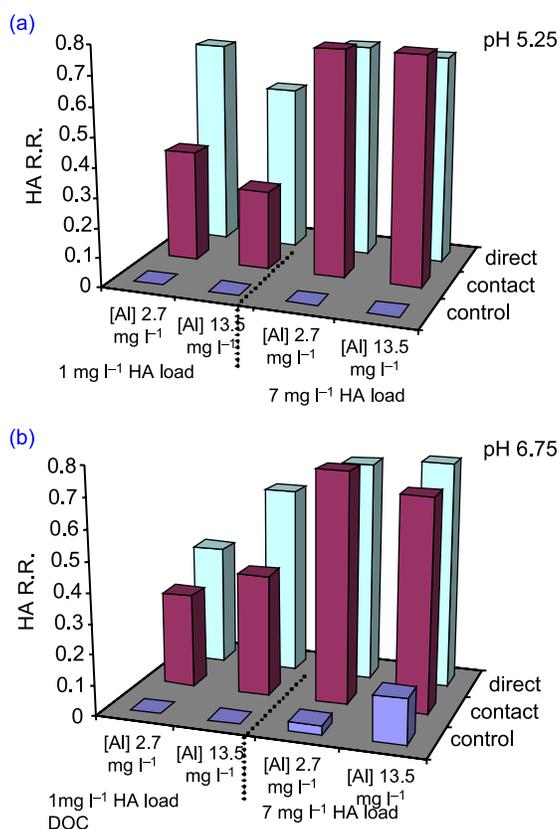


Figure 8 | HA R.R. as a function of load and  $[Al_3]$  dosage for different operating modes.

be a valuable coagulation parameter. The other important finding is that the optimization of the Camp-number, or  $G * t$  values, respectively, might be the key to obtaining medium-sized flocs as needed to achieve high removal levels at minimal fouling.

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