

Influence of hybrid coagulation-ultrafiltration pretreatment on trace organics adsorption in drinking water treatment

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ABSTRACT

The treatment of raw water by hybrid coagulation-ultrafiltration was investigated. Coagulation-ultrafiltration removed high molecular weight organics, preferentially humics. Adsorption of the trace compound cis-1,2-dichloroethene, present in raw water, on granular activated carbon was improved considerably as compounds competing for adsorption space had been removed. This was shown in isotherms and breakthrough curves. Aeration during filtration did not affect membrane performance as expressed in permeability. However, aeration in the submerged membrane container resulted in a release of organic matter from the flocs, which resulted in higher concentrations of dissolved organic carbon in the filtrate.

Key words | adsorption, coagulation, drinking water treatment, granular activated carbon, hybrid process, ultrafiltration

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ABBREVIATIONS

BV	bed volumes ($\text{m}^3 \text{m}^{-3}$)
c	concentration (mg l^{-1} or mol l^{-1})
c_0	initial concentration (mg l^{-1})
c_{eq}	liquid-phase concentration at adsorption equilibrium (mg l^{-1})
CDOC	chromatographic detectable organic carbon (ppb)
DCE	cis-1,2-dichloroethene ($\mu\text{g l}^{-1}$)
DOC	dissolved organic carbon (mg l^{-1} or ppb)
FNU	formazine nephelometric unit
GAC	granular activated carbon
HPC	heterotrophic plate count (ml^{-1})
HOC	hydrophobic organic carbon (ppb)
K_F	Freundlich parameter ($\mu\text{g g}^{-1}$)
LC-OCD	liquid chromatography-organic carbon detection
I_{det}	detection limit
m	mass of adsorbent (mg)
MWCO	molecular weight cut-off (Dalton)
n	number of measurements

n_F	Freundlich exponent
NOM	natural organic matter
OC	organic carbon (ppb)
P	membrane permeability ($\text{l m}^{-2} \text{h}^{-1} \text{kPa}^{-1}$)
P_0	initial permeability ($\text{l m}^{-2} \text{h}^{-1} \text{kPa}^{-1}$)
q	solid-phase concentration at adsorption equilibrium (mg g^{-1})
TMP	transmembrane pressure (hPa or kPa)
TOC	total organic carbon (ppb)
UF	ultrafiltration
UVA_{254}	ultra violet absorbance at 254 nm (m^{-1})
V	volume of solution (ml)

INTRODUCTION AND PROBLEM DESCRIPTION

Objectives of investigation

Adsorption of trace organics on granular activated carbon (GAC) is influenced by adsorption competition between the respective compound and background organic matter. The so-called 'fouling' effect is caused by high molecular weight humic

substances and may result in a lower adsorption capacity for trace organics compared with single solute adsorption. The Mühlheim process (Sontheimer *et al.* 1978) is one of the treatment processes in which high molecular weight organics are oxidized by ozonization in order to enhance adsorption capacity of GAC for trace organics. A combination of coagulation and ultrafiltration may decrease the concentration of natural organic matter (NOM) in raw water and consequently result in improved adsorption conditions for trace organics as well. Because of the pore size of the ultrafiltration membrane this hybrid process is able to remove particles bigger than $0.1\ \mu\text{m}$ from raw water and therefore constitutes an effective barrier against bacteria, viruses and parasites in the water treatment process.

The objectives of the investigations were to determine and optimize substantial operating parameters of a coagulation-ultrafiltration unit for the decrease of concentrations of organic substances which might impact adsorption of trace organics on granular activated carbon.

The Dresden Hosterwitz water treatment plant

The Dresden Hosterwitz water treatment plant is situated on the River Elbe and offers an installed maximum capacity

of $60,000\ \text{m}^3\ \text{d}^{-1}$. When the plant is utilizing full treatment capacity, river water is treated by coagulation, sedimentation and dual media filtration and is infiltrated for groundwater recharge (see Figure 1). After the withdrawal from the wells, the water is further stabilized by neutralization/aeration over a mechanical aeration installation and purified by an adsorption step with GAC. Before delivering the water to the distribution network the water is disinfected with chlorine and the pH is adjusted.

Today the delivery quantity usually amounts only to $10,000\text{--}20,000\ \text{m}^3\ \text{d}^{-1}$, corresponding to 15–30% of the installed treatment capacity. Thus the cost-intensive river water treatment is not economically or technically practical. Consequently, at deliveries less than $20,000\ \text{m}^3\ \text{d}^{-1}$, river water treatment is taken out of operation and a raw water mixture of bank filtrate and groundwater is treated directly by aeration and GAC-adsorption.

In this case the quality of the raw water mixture depends on the rates of groundwater and river bank filtrate drawn off which are affected by the groundwater level. As a consequence of soil passage of the bank filtrate, bacteria plate counts on nutrient rich agar are usually less than $10\ \text{ml}^{-1}$ in raw water. HPC determined according to *Standard Methods* (2005) amounts then to approximately

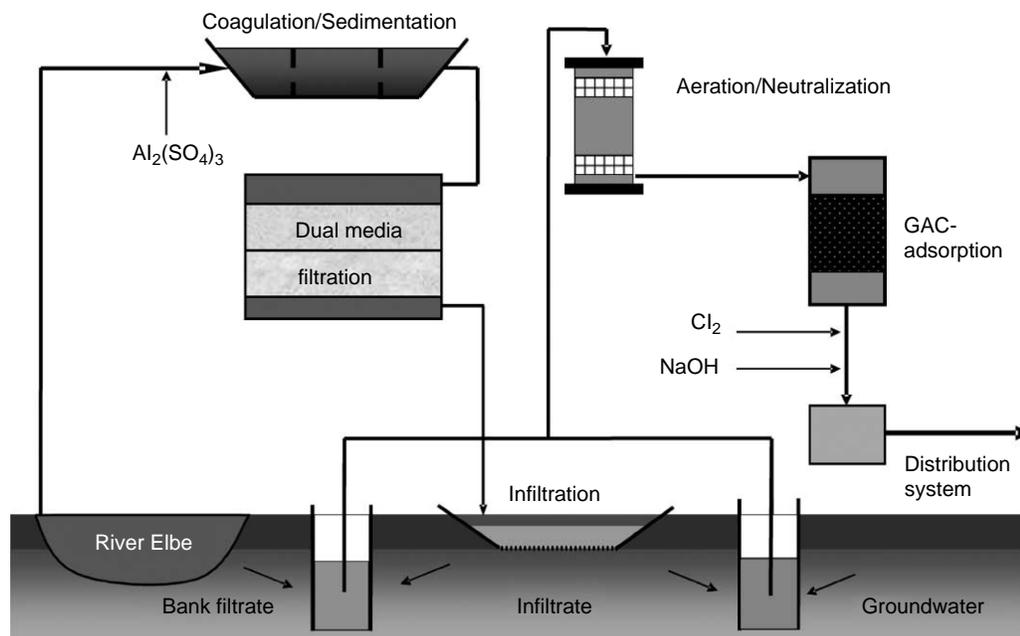


Figure 1 | Schematic of the water treatment plant Dresden Hosterwitz.

10^5 ml^{-1} (Uhl & Schaule 2004). Only exceptionally are coliform bacteria detected. During the investigations, turbidity was usually below 0.4 FNU and pH was between 6.7 and 7.1. In the raw water, DOC (dissolved organic carbon) was usually determined to be between 1.3 and 2.0 mg l^{-1} . Owing to microbial degradation processes during bank filtration and mixing with groundwater, UVA_{254} (ultraviolet absorbance at 254 nm) was reduced by 80% compared with the river water and measured between 2.7 and 4.2 m^{-1} . During the period of investigations, the organic trace compound cis-1,2-dichloroethene (DCE) was found in a range from 0.3 to $7.5 \text{ } \mu\text{g l}^{-1}$ in the raw water. This volatile solvent is used in different production processes and may also occur as a result of metabolization of tetra- and trichloroethene under anaerobic environmental conditions. The origin of the measured DCE concentrations could not be found during this investigation. However, subsequent measurements by others in different wells of the treatment plant described higher levels of DCE in wells located further away from the river. This indicates pollution of the groundwater with the trace organic or its parent compounds. DCE is considered as a hazardous substance with long-term health effects on humans and therefore should be removed from drinking water. The maximum contaminant level for DCE in drinking water is defined at $70 \text{ } \mu\text{g l}^{-1}$ by WHO guidelines.

During aeration, DCE is partly stripped out (on average 48%) and the remainder is removed during further treatment. Owing to the adsorption competition between the adsorbable trace compound and background organic matter, the

run time of the GAC-filters is limited by the early breakthrough of DCE. It is measurable after approximately 16,000 bed volumes, causing high costs for GAC reactivation. In order to increase treatment safety and reduce total treatment costs, the introduction of a hybrid coagulation-ultrafiltration process is considered.

METHODS

Pilot plant for ultrafiltration with submerged membranes

In order to investigate the process of hybrid coagulation-ultrafiltration and its effects on a following adsorption step a pilot plant with submerged membranes was operated in the Dresden Hosterwitz water treatment plant for a period of about 10 months.

The ultrafiltration pilot plant was equipped with Zee-Weed 500c submerged membranes from Zenon. The flow scheme is depicted in Figure 2. Prior to UF-treatment, coagulation of the raw water is possible. The dosing point for the coagulant is directly in front of a mixing section, in which a homogeneous interference of the coagulant as well as the destabilization of the colloidal and dispersed material is achieved by cross-sectional changes. The following U-tube has a diameter six times larger than the pipe diameter and provides a retention time of approximately 9 min for aggregation of micro flocs and/or larger floc complexes.

Subsequently, the coagulated water is fed to the membrane container, in which three UF membrane

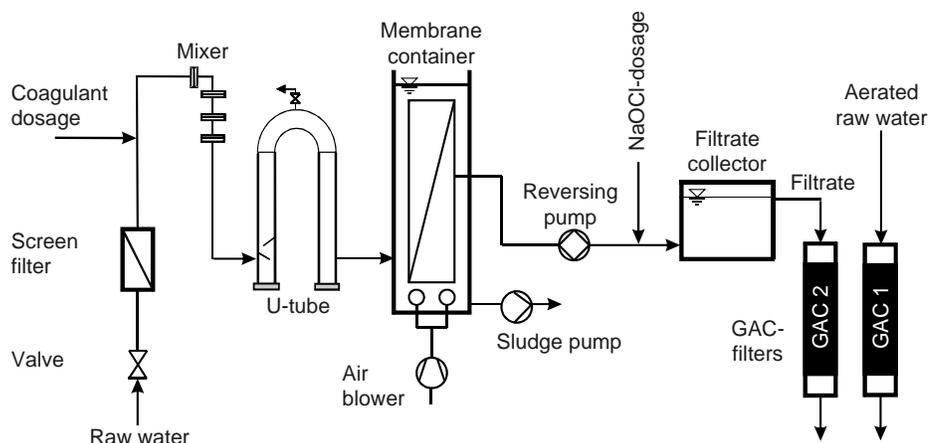


Figure 2 | Schematic of the pilot plant.

elements with submerged capillary membranes of a total filter area of 60 m² are installed. The ultrafiltration membrane has a molecular weight cut-off of 200,000 Dalton (MWCO at 50%) with a nominal pore size of 0.04 µm. The membranes can be aerated during backflush as well as during filtration by an air blower. The vacuum necessary for filtration is generated by a reversing pump. For the protection of the capillary membranes the installation is automatically taken out of operation if the transmembrane pressure (TMP) of 500 hPa is exceeded. The filtrate is led into a closed collector with a volume of 1 m³ serving as reservoir for backflush and filtrate sampling. Mean residence time of the water in the collector was approximately 25 min. Total solids content in the membrane container can be adjusted by a sludge pump which can be operated both intermittently and continuously.

The adsorption stage consisted of two filter columns with an inner diameter of 0.15 m which were both filled similarly to the full scale GAC filters with freshly reactivated GAC to a bed depth of 2 m and operated with a water head of approximately 0.7 m. The first filter (GAC 1) was operated with aerated raw water, like the GAC filters of the full scale plant. The second filter (GAC 2) was operated with the filtrate from the UF pilot plant. In this way the effects of coagulation/UF pretreatment could be compared with the conventional technology.

The pilot plant for ultrafiltration with submerged membranes was operated with the following filtration parameters:

Filtration: 2.4 m³ h⁻¹, 20 min.

Backflush: 3.3 m³ h⁻¹, 30 s with an aeration rate of 0.75 m³ (m² h)⁻¹.

This resulted in a net flux of 36 l m⁻² h⁻¹. The total solids content in the membrane container was kept at

0.5 g l⁻¹ by adjusting the speed of the sludge pump. Chemical cleanings of the membrane with hydrochloric acid and/or citric acid were necessary after operation times of 6 to 12 weeks, since the TMP approached the limit value of 500 hPa. During these in-place cleanings the UF equipment was taken out of operation and the filtrate collector and the filtrate pipeline were disinfected with sodium hypochlorite. Special backflushes with automatic chemical addition were not carried out. The investigations were separated into three phases whose respective operating parameters are summarized in Table 1.

In the first experimental phase the influent to UF was raw water without pre-aeration, and aluminium sulphate with a coagulant dosage of 1 mg Al³⁺ l⁻¹ was used. During filtration the air blower was operated with a cycle of 1 min aeration and 2 min break. In the second phase aerated raw water was used as influent to the pilot plant and the UF run without aeration during filtration. In the third phase, aerated raw water was flocculated with three different doses of ferric chloride and again no aeration during filtration was carried out.

To study the impact of pretreatment by coagulation/UF on the adsorption of DCE, the two GAC-filter columns were operated for about 6 months during experimental phase 1 as explained in the previous paragraph. A filtration rate of 10 m h⁻¹ was adjusted resulting in an empty bed contact time of approximately 12 min.

Laboratory tests and measurements

For determination of DOC and UVA₂₅₄, samples were filtered through polycarbonate membrane filters with nominal pore size of 0.45 µm. DOC was analysed according

Table 1 | Overview of the experimental phases

Phase	UF Influent	Coagulant	Aeration in membrane tank
1	Non-aerated raw water	Aluminium sulphate 1.0 mg Al ³⁺ l ⁻¹ = 0.037 mmol l ⁻¹	1 min aeration/2 min break, aeration rate 0.5 m ³ (m ² h) ⁻¹
2	Aerated raw water	Aluminium sulphate 1.0 mg Al ³⁺ l ⁻¹ = 0.037 mmol l ⁻¹	No aeration during UF
3	Aerated raw water	Ferric chloride 1.5 mg Fe ³⁺ l ⁻¹ = 0.027 mmol l ⁻¹ 2.0 mg Fe ³⁺ l ⁻¹ = 0.036 mmol l ⁻¹ 4.0 mg Fe ³⁺ l ⁻¹ = 0.071 mmol l ⁻¹	No aeration during UF

to DIN EN 1484 (DIN German Institute for Standardization 1998) by a Tekmar Teledyne device (Apollo 9000) operating with a method precision of $\pm 6\%$. UVA₂₅₄ was analysed by an Agilent spectrophotometer equipped with a 10 mm cuvette according to DIN 38404 C3 (German Standard Methods 2005). Detection limits are $I_{\text{det}} \text{ DOC} = 0.2 \mu\text{g l}^{-1}$ and $I_{\text{det}} \text{ UVA}_{254} = 0.0 \text{ m}^{-1}$. Aluminium was measured by inductively coupled plasma mass spectrometry (ICP-MS) according to EN ISO 17294 (DIN German Institute for Standardization 2007) and iron was analysed by a photometric method according to DIN 38406 E1 (German Standard Methods 1983). Detection limits are $I_{\text{det}} \text{ Al}^{3+} = 0.02 \text{ mg l}^{-1}$ and $I_{\text{det}} \text{ Fe}^{3+} = 0.05 \text{ mg l}^{-1}$, respectively.

Quantitative analysis of NOM fractions was performed by liquid chromatography-organic carbon detection (LC-OCD) with a detection limit of 5–50 ppb per compound. This method combines high sensitivity size-exclusion chromatography with high sensitivity organic carbon detection (Huber & Frimmel 1991). A full TOC characterization of a sample includes the partitioning of TOC (total organic carbon) into DOC, HOC (hydrophobic OC), POC (particulate OC) and CDOC (chromatographable, hydrophilic OC). CDOC is fractionated by LC-OCD in the following fractions: ‘humics’ consists of intact and oxidized humic substances (350–10,000 g mol^{-1}); ‘building blocks’ are hydrolysis products of humics (300–500 g mol^{-1}); ‘neutrals and amphiphilics’ include aldehydes, ketones, alcohols and amino acids ($< 350 \text{ g mol}^{-1}$); ‘biopolymers’ represent NOM composed of polysaccharides, amino sugars and proteins ($> 20,000 \text{ g mol}^{-1}$); ‘acids’ consist of low molecular weight aliphatic organic acids ($< 350 \text{ g mol}^{-1}$).

DCE was analysed by a certified drinking water laboratory by gas chromatography with a purge-and-trap system according to DIN EN ISO 15680. Detection limit is $0.1 \mu\text{g l}^{-1}$ and method precision is $\pm 10\%$.

To quantify adsorption equilibrium of DCE with activated carbon, adsorption isotherms were determined. An adsorption isotherm describes the dependence of the solid-phase concentration q on the liquid-phase concentration c_{eq} at equilibrium. Solid-phase concentrations are calculated by a mass balance (Equation (1)), when the volume of solution V and the mass of adsorbent m are known.

$$q = \frac{V}{m} \cdot (c_0 - c_{\text{eq}}). \quad (1)$$

The concentration difference between the respective compound in the liquid before adsorption and at equilibrium ($c_0 - c_{\text{eq}}$) is measured. The Freundlich isotherm Equation (2), where K_F is the Freundlich parameter and n_F is the Freundlich exponent, characterizes the equilibrium.

$$q = K_F \cdot c_{\text{eq}}^{n_F} \quad (2)$$

For the determination of adsorption isotherms of the trace compound, DCE concentrations were spiked to initial concentrations of $12 \mu\text{g l}^{-1}$. The isotherms were determined for DCE in aerated raw water and in filtrate after coagulation/UF. Test conditions are listed in Table 2.

RESULTS AND DISCUSSION

Membrane performance

During the entire test period of 10 months a net flux of approximately $36 \text{ l m}^{-2} \text{ h}^{-1}$ was observed. By adjustment of a concentration of total solids of approximately 0.5 g l^{-1} in the membrane container a yield of more than 99.5% was achieved. Figure 3 shows a typical operation diagram of the pilot plant in experimental phase 1.

TMP is mainly dependent on the viscosity of the raw water and the membrane resistance at the beginning of a filtration phase with constant flux. TMP increases with filtration time due to the formation of deposits on the membrane while the real flux stays constant. Permeability, normalized to 20°C , describes the temperature independent relationship of the real flux at 20°C to TMP. For the characterization of the filtration behaviour in the respective experimental phase, the rate of permeability decrease was

Table 2 | Adsorption test conditions

Activated carbon	Norit ROW 0.8 Supra, powdered in ball mill
Solution volume V	250 ml
Mass/volume ratio	0, 4, 8, 16, 32, 40, 60, 120, 240 mg l^{-1}
Shaking	200 rounds per minute for 48 h

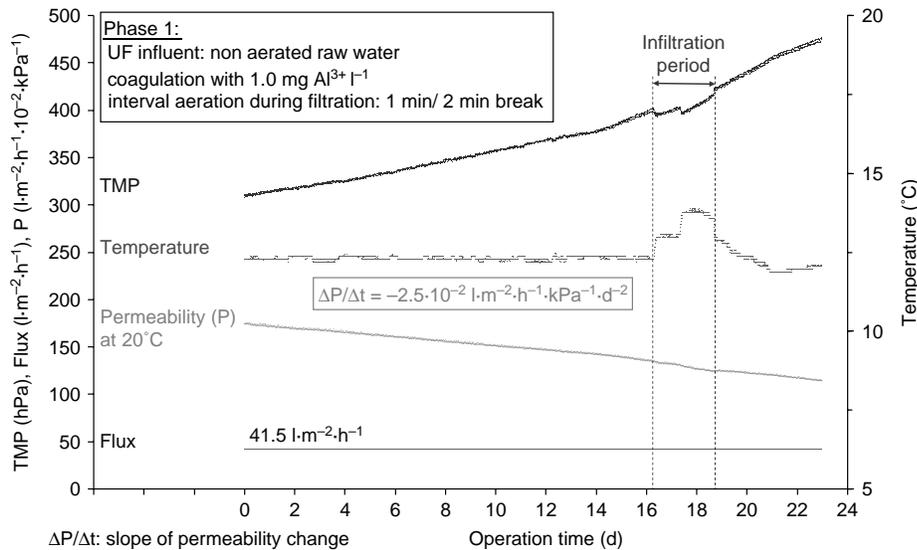


Figure 3 | Operation diagram of the UF pilot plant (Phase 1).

determined as change in permeability at 20°C per unit of time (day). In the period shown the change in permeability is $2.5 \cdot 10^{-2} \text{ l} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{kPa}^{-1} \cdot \text{d}^{-1}$.

A comparison of the permeability change in the three experimental phases is represented in Figure 4. The slope of permeability change is defined as change in permeability per unit of time ($\Delta P/\Delta t$).

Comparison of the slopes of phase 1 (non-aerated raw water, but aerated during UF treatment) and phase 2 (aerated

raw water, not aerated during UF treatment) shows that air bubbling in the membrane container does not have a considerable impact on the rate of permeability decrease during UF treatment. This is in accordance with the results of Choksuchart *et al.* (2002) who found that interval aeration during filtration does not improve UF filtration performance.

The impact of the type of coagulant on the rate of permeability decrease during filtration can be seen clearly. Comparing phase 2 with phase 3b shows that, at nearly

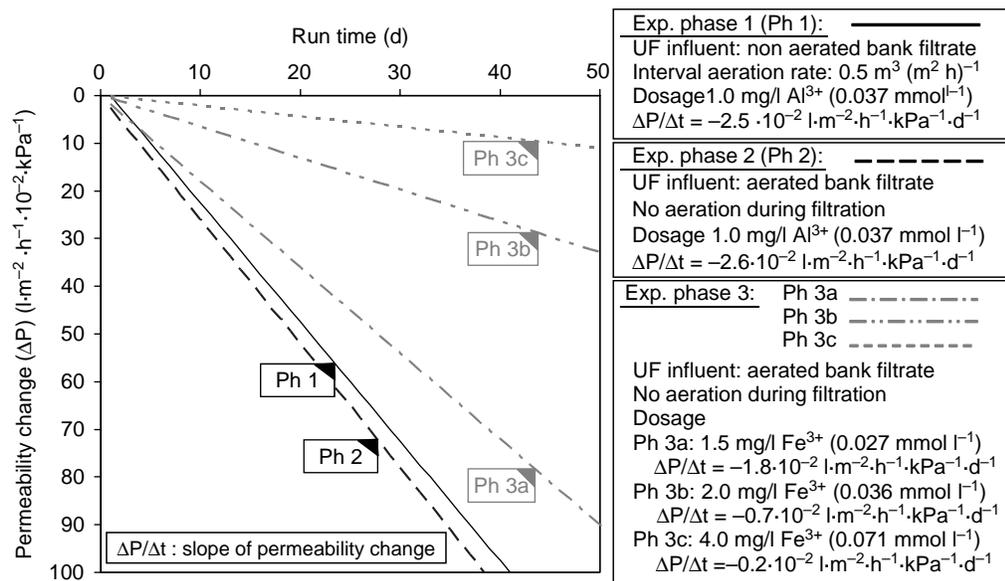


Figure 4 | Change in permeability ($\Delta P = P_0 - P$) under different experimental conditions.

similar mole concentrations of coagulant ($0.037 \text{ mmol l}^{-1} \text{ Al}^{3+}$ and $0.036 \text{ mmol l}^{-1} \text{ Fe}^{3+}$), the dosage of aluminium results in a rate of permeability decrease of $2.6 \cdot 10^{-2} \text{ l m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ per day which was approximately four times higher than the rate when iron is used. The reason for the better membrane performance with iron as coagulant is probably the different structure of iron and aluminium hydroxide flocs. Iron hydroxide flocs are larger than aluminium hydroxide flocs and have a smaller floc density; that is, their structure is more complex (see Jefferson *et al.* 2004).

An increase of coagulant dosage from 1.5 to 2.0 and $4.0 \text{ mg Fe}^{3+} \text{ l}^{-1}$, respectively, as carried out in phase 3, resulted in a minor permeability decrease and thus in an improvement of membrane performance. The reason for this effect may be that with increasing coagulant dosage a better removal of dissolved and colloidal substances was achieved (results not shown here) which may block membrane pores. A further cause may be the increase of the floc volume with increased coagulant concentration, as shown by Chakraborti *et al.* (2003) for coagulation with aluminium salts. With the more complex floc structure the surface layer at the membrane becomes more porous and consequently a lower rate of permeability decrease occurs. Machenbach *et al.* (2002) likewise found a dependence of permeability on coagulant dose (aluminium).

A strong impact of the raw water matrix on membrane performance can be seen from the fact that when raw water was produced by treated and infiltrated river water, the decrease in permeability during membrane filtration was more pronounced than when bank filtrate was used as raw water (see Figure 3).

Filtrate quality

As expected, suspended solids were removed completely by the UF treatment. Turbidity in the filtrate was always lower than 0.1 FNU. Also, HPC-bacteria and pathogens were removed effectively. However, it was found that a re-growth could take place when the membranes were flushed with filtrate for cleaning, which was probably because the filtrate collector was not hermetically closed. Therefore, later, the filtrate pipe and filtrate collector were disinfected during chemical cleanings of the membrane which proved successful to prevent re-growth.

The remaining coagulant concentration in the filtrate was usually below the detection limit ($I_{\text{det}} \text{ Al}^{3+} = 0.02 \text{ mg l}^{-1}$ and $I_{\text{det}} \text{ Fe}^{3+} = 0.05 \text{ mg l}^{-1}$, respectively).

From the experience of other researchers, it could be expected that with the operation of UF with coagulation the concentration of NOM measured as DOC and UVA_{254} will be reduced (e.g. Machenbach *et al.* 2002). Figure 5 shows the removal of NOM during the different experimental phases, measured as UVA_{254} and DOC. During phase 1, while operating the ultrafiltration with intermediate aeration and using aluminium as coagulant (1 mg l^{-1} corresponding to $0.037 \text{ mmol l}^{-1} \text{ Al}^{3+}$), an average removal of UVA_{254} of 12% was achieved (significant on a 95% level). DOC removal was 4% on average, which was proven at a 67% level, but not significant at a 95% level. Further lab investigations showed that there was a release of already flocculated organic substances during UF filtration, due to the shear forces caused by the air bubbles in the membrane container (results not shown here).

Consequently, the pilot plant in the second experimental phase was operated without aeration during filtration. In order to use the positive effects of aeration, such as the removal of surplus carbonic acid, stripping of the trace compound DCE and addition of oxygen before adsorption, aerated raw water was fed to the UF. With these test conditions and similar aluminium dosage as used in phase 1, an increase of UVA_{254} removal up to 16% could be achieved while DOC removal was on average about 9%. When operating the pilot plant with aerated raw water and

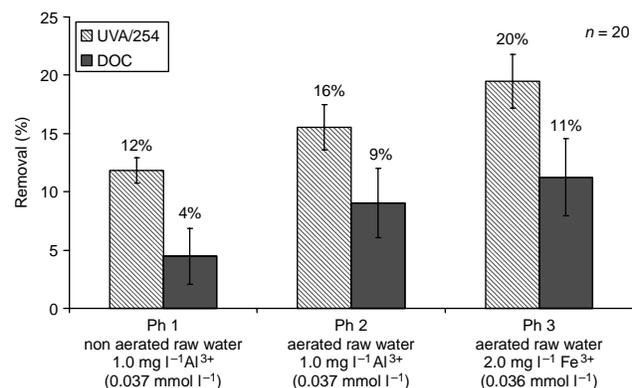


Figure 5 | Removal of organic matter by coagulation/UF; error bars represent 67% confidence interval.

coagulation with iron salts (phase 3), at a dosage of 2 mg l^{-1} iron (corresponding to $0.036 \text{ mmol l}^{-1} \text{ Fe}^{3+}$) an UVA_{254} removal of 20% and a DOC removal of 11% were observed. These results show that – as already expected – iron salts seem to be more effective for removal of organic matter than aluminium salts, as is very often experienced.

DCE was removed by aeration of the raw water and by aeration during UF owing to stripping effects. A DCE removal of approximately 28% could be achieved by interval aeration in the membrane container in experimental phase 1. This corresponds to approximately two-thirds of the stripping performance which can be reached by open aeration over a mechanical aeration installation (48%) as used in the water treatment plant. This is important to note, as when the UF pretreated water is fed to the following adsorption step (column GAC 2, see Figure 2), it contains DCE concentrations different from those in the influent of column GAC 1. Consequently, the following adsorption stage is loaded with higher concentrations of DCE by the filtrate from UF compared with aerated raw water from conventional treatment technology. If the UF is loaded with aerated raw water (as in experimental phase 2 and 3) and operated without intermediate aeration during filtration, the DCE concentration in the filtrate is equal to the DCE concentration in the effluent of the aeration step.

Impact of pretreatment by coagulation/UF on DCE adsorption

As already known, organic background significantly affects the range of adsorption capacity for a particular compound (Sontheimer *et al.* 1988). The so-called ‘fouling’ effect is caused by the slow adsorption-desorption kinetics of humic substances and the consequential long-term preloading of the carbon. This pre-adsorption is very slow but may lead to a considerable reduction of the adsorption capacity for chlorinated hydrocarbons. The impact can be adequately described by a change of the Freundlich parameter K_F (Zimmer *et al.* 1989).

DCE adsorption isotherms were determined in order to compare the effect of pretreatment by hybrid coagulation/UF with conventional treatment (aeration) on trace compound adsorption. Figure 6 shows the two DCE adsorption isotherms in phase 1 both for the filtrate of the UF plant and for the aerated raw water.

Treatment by coagulation/UF has a clear effect on concentration and composition of background organic matter, which influences adsorption of trace organics such as DCE. Comparison of the two adsorption isotherms shows that for the effluent of coagulation/UF, the DCE solid phase concentration is much higher than for aerated raw water at the same liquid phase concentrations. This is

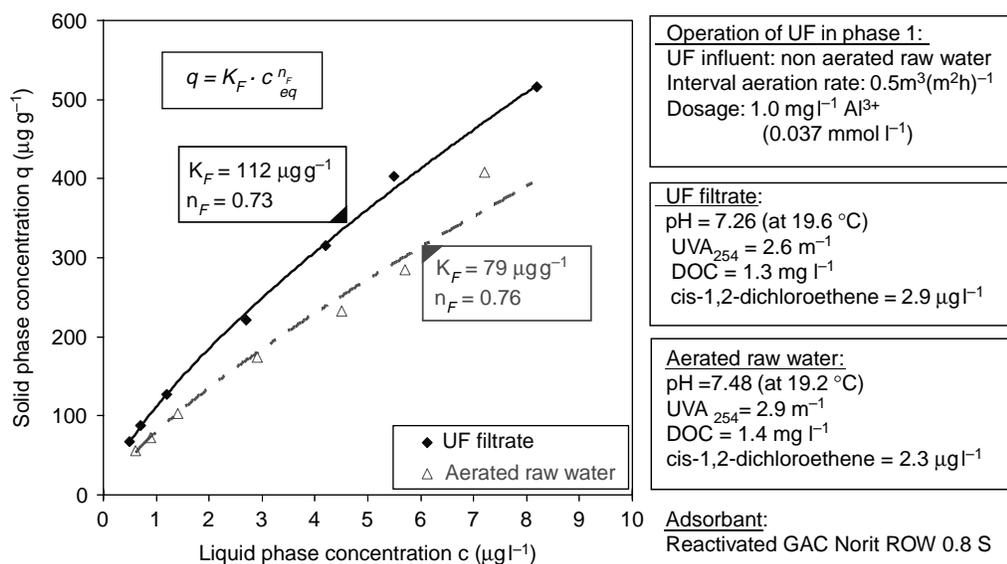


Figure 6 | DCE adsorption isotherms in experimental phase 1.

reflected in the much higher Freundlich parameter K_F when DCE is adsorbed from UF filtrate than from aerated raw water ($112 \mu\text{g g}^{-1}$ versus $79 \mu\text{g g}^{-1}$).

To explain the impact of treatment by coagulation/UF on adsorption capacity of GAC for the trace organics, fractions of the organic background were analysed by LC-OCD analyses in experimental phase 1. Figure 7 shows the effects of coagulation/UF and GAC adsorption, single and combined treatment, compared with the treatment by aeration/GAC adsorption.

Comparison of TOC and DOC (1,505 ppb vs. 1,490 ppb) shows that the raw water only contains a very small amount of particles. Of the DOC, 79% (1,179 ppb) can be fractionated as CDOC by LC-OCD, while HOC contributes 21%. CDOC contains 31% humics (363 ppb), 45% building blocks (559 ppb) and 21% neutrals and amphiphilics (298 ppb). The concentration of further fractions such as biopolymers and low molecular acids is low (summarized as 3%).

With adsorption of aerated raw water at GAC1 (treatment as used in the water treatment plant) a DOC abatement of 476 ppb (32%) was determined, while with coagulation/UF and adsorption at GAC2, 628 ppb (42%) of DOC could be removed. HOC concentration is affected nearly equally by aeration and adsorption at GAC1 (aeration/GAC1) and coagulation/UF followed by adsorption at GAC2 (UF/GAC2). The effect of aeration/GAC1 on CDOC was a 25% (289 ppb) decrease, while with

UF/GAC2 a reduction of CDOC of 36% (428 ppb) was achieved. This is due to a better removal of humics and building blocks as well as amphiphilics during UF/GAC2 compared with aeration/GAC2.

The effect of coagulation/UF on NOM is mainly a result of the removal of humics. This fraction was shown to be responsible for the so-called fouling processes at GAC and lowers the adsorption capacity of GAC for trace compounds. Therefore the removal of humics by coagulation/UF may result in the improvement of adsorption capacity of GAC for DCE.

The improvement of DCE adsorption by coagulation/UF was seen in the breakthrough curves of the pilot GAC filters. Filter GAC 2, which was operated with UF filtrate (see Figure 2), showed a higher adsorption capacity for DCE compared with the filter GAC 1, which was operated with aerated raw water. From Figure 8 it can be seen that, despite higher DCE concentrations in the UF filtrate than in aerated raw water, breakthrough took place about 2,700 bed volumes later in filter GAC 2 than in filter GAC 1 operated with aerated water. Consequently, the run-time of the filter adsorber downstream of the UF pretreatment can be extended for approximately 20% compared with conventional treatment technology.

Figure 8 also shows that, after breakthrough of DCE, in both filters effluent concentrations much higher than the influent concentrations were measured, which is due to the displacement of already adsorbed DCE by more easily adsorbable organics.

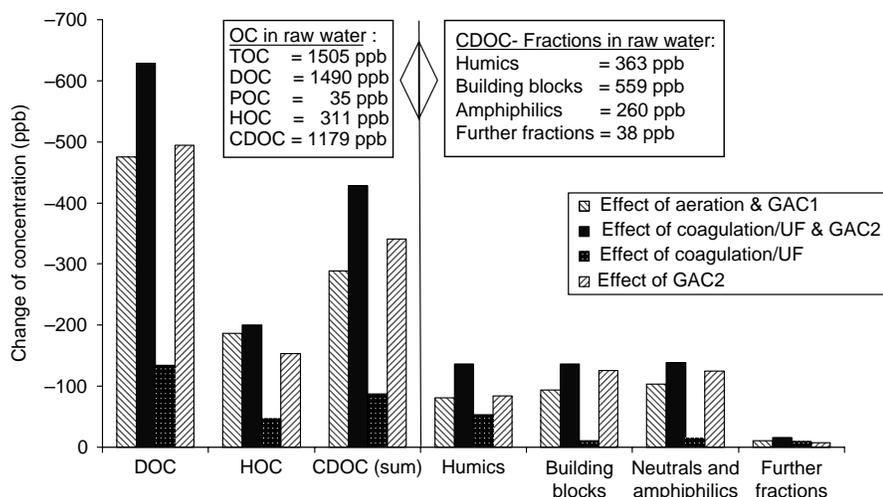


Figure 7 | Effects of treatment on organic fractions compared with raw water in phase 1.

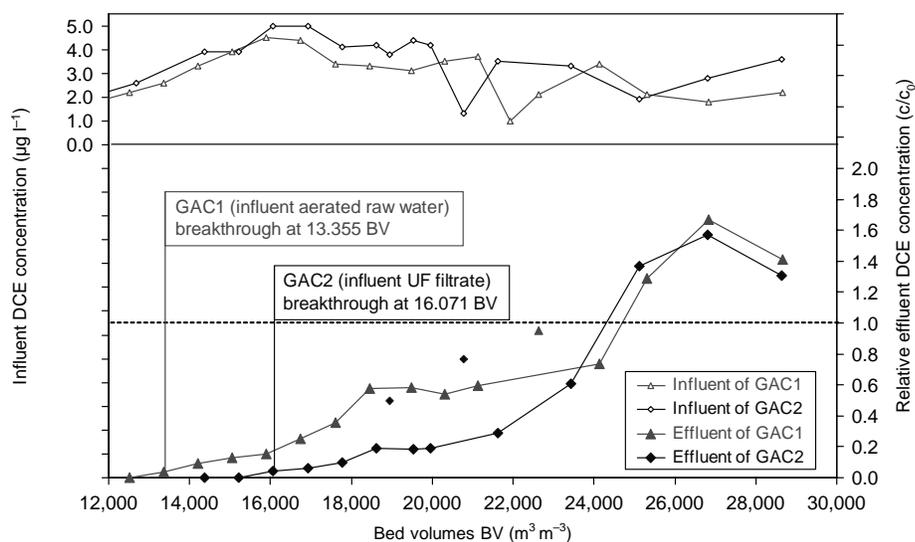


Figure 8 | DCE break-through curves of GAC-filters.

CONCLUSIONS

The investigations showed that the application of a hybrid coagulation/UF process is an interesting option for drinking water treatment.

The filtration behaviour of the submerged membrane showed a clear dependence on the type and dose of coagulant. A substantially lower rate of permeability decrease was observed when iron was used, compared with aluminium sulphate. An increase of iron dosage improved membrane performance, expressed as a lower rate of permeability decrease. A significant influence of aeration during filtration on the permeability could not be found.

The attainable elimination of organic matter is affected by the type and dose of coagulant. However, differences are not very pronounced. Aeration in the membrane container obviously led to a release of already flocculated organic substances, measurable as an increase of DOC and UVA₂₅₄ in the filtrate. Since the aeration did not contribute to an improvement of the filtration characteristics during filtration, it is not regarded as an effective measure in coagulation/UF-treatment.

Pretreatment of non-aerated raw water by hybrid coagulation-ultrafiltration clearly improved the adsorption capacity of the following activated carbon filter stage for the trace compound DCE. This effect is mainly caused by the removal of humics during coagulation/UF as was

found out with LC-OCD analysis. Run-times of the GAC adsorber downstream of UF pretreatment can be extended for approximately 20% compared with conventional treatment technology.

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REFERENCES

- Chakraborti, R. K., Gardner, K. H., Atkinson, J. F. & v. Bentschoten, J. E. 2003 *Changes in fractal dimension during aggregation*. *Wat. Res.* **37**, 875–883.
- Chokschart, P., Héran, M. & Grasmick, A. 2002 Surface water clarification with an immersed membrane system: effect of coagulation/aeration on flux enhancements. *Berichte Aus Dem IWW Rheinisch-Westfälisches Institut für Wasserforschung Gemeinnützige GmbH, Bd.37a*. eds.:

- IWW Rheinisch-Westfälisches Institut für Wasserforschung GmbH, Eigenverlag, Mülheim an der Ruhr, Germany, pp. 653–660.
- DIN German Institute for Standardization 1998 *Water analysis: Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)*; German version EN 1484–1997.
- DIN German Institute for Standardization 2007 *Water Quality: Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Part 1: General guidelines* (ISO 17294–1:2004).
- German Standard Methods for the Examination of Water, Waste Water and Sludge* 1983 Cations (group E); determination of iron (E 1). DIN German Institute for Standardization.
- German Standard Methods for the Examination of Water, Waste Water and Sludge* 2005 Physical and physical-chemical parameters (group C). Part 3: Determination of absorption in the range of the ultraviolet radiation, Spectral absorptions coefficient (C 3). DIN German Institute for Standardization.
- Huber, S. A. & Frimmel, F. H. 1991 *Flow injection analysis of organic and inorganic carbon in the low-ppb range*. *Anal. Chem.* **63**, 2122–2130.
- Jefferson, B., Jarvis, P. & Parsons, S. A. 2004 The effect of coagulant type on natural organic matter floc structure and strength. In: Hahn, H. H., Hoffmann, E. & Ødegaard, H. (eds), *Chemical Water and Wastewater Treatment VIII. Proceedings of the 11th Gothenburg Symposium, Orlando, Florida, USA*. IWA Publishing, London, pp. 151–159.
- Machenbach, I., Leiknes, T. & Ødegaard, H. 2002 Coagulation/submerged hollow-fibre ultrafiltration for NOM removal. *Berichte Aus Dem IWW Rheinisch-Westfälisches Institut für Wasserforschung Gemeinnützige GmbH, Bd.37a*. Hrsg.: IWW Rheinisch-Westfälisches Institut für Wasserforschung GmbH, Eigenverlag, Mülheim an der Ruhr, Germany, pp. 661–668.
- Sontheimer, H., Heilker, E., Jekel, M., Nolte, H. & Vollmer, F. H. 1978 The Mülheim process. *J. Am. Wat. Wks Assoc.* **70**(7), 393–396.
- Sontheimer, H., Crittenden, J. C. & Summers, R. 1988 *Activated Carbon for Water Treatment*. Engler-Bunte-Institut der Universität Karlsruhe (TH), Karlsruhe, Germany.
- Standard Methods for the Examination of Water and Wastewater* 2005 21st edition, Chapter 9215 C. American Public Health Organisation/American Water Works Association/Water Environment Federation.
- Uhl, W. & Schaule, G. 2004 *Establishment of HPC(R2A) for regrowth control in non-chlorinated distribution systems*. *Int. J. Food Microbiol.* **92**, 317–325.
- Zimmer, G., Brauch, H.-J. & Sontheimer, H. 1989 Activated-carbon adsorption of organic pollutants. In: Suffet, I. H. & McCarthy, P. (eds), *Chemical Aquatic Humic Substances (Advances in Chemistry Series 219)*. American Chemical Society, Washington DC, pp. 579–596.

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