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Capillary nanofiltration coupled with powdered activated carbon adsorption for high quality water reuse

C. Kazner, J. Meier, T. Wintgens and T. Melin

ABSTRACT

Direct capillary nanofiltration was tested for reclamation of tertiary effluent from a municipal wastewater treatment plant. This process can be regarded as a promising treatment alternative for high quality water reuse applications when combined with powdered activated carbon for enhanced removal of organic compounds. The nanofiltration was operated at flux levels between 20 and 25 L/(m^2 h) at a transmembrane pressure difference of 2–3 bar for approximately 4,000 operating hours. The study was conducted with PAC doses in the range from 0 to 50 mg/L. The plant removal for DOC ranged from 88–98%. The sulfate retention of the membrane filtration process was between 87 and 96%. The process provided a consistently high permeate quality with respect to organic and inorganic key parameters.

Key words | capillary membrane, nanofiltration, PAC-adsorption, PAC-NF-process, water reclamation, water reuse and recycling

C. Kazner
J. Meier
T. Wintgens
T. Melin
Department of Chemical Engineering,
RWTH Aachen University,
Turmstrasse 46,
Aachen 52056,
Germany
E-mail: *kazner@ivt.rwth-aachen.de*;
meier@ivt.rwth-aachen.de;
wintgens@ivt.rwth-aachen.de;
melin@ivt.rwth-aachen.de

INTRODUCTION

High quality water reclamation, e.g. for groundwater recharge, mostly relies on a combination of ultrafiltration and reverse osmosis (Metcalf & Eddy 2004; Bixio & Wintgens 2006). Besides high investment costs, the UF-RO process often demands the use of chlorinated chemicals to suppress membrane fouling. Furthermore economic treatment methods for the brine containing disinfection by-products and micropollutants are still required.

Capillary nanofiltration combines advantages from UF and RO. The operation of a NF module allows complete retention of all pathogens and most of the not biodegradable contaminants like endocrine disruptors and pharmaceutically active compounds while osmotic pressure relevant monovalent ions are not retained.

A process combination of powdered activated carbon (PAC) and direct nanofiltration (NF) called PAC-NF process is currently tested as process for removal of bulk organics and micropollutants from municipal wastewater treatment plant effluents for water reclamation and water reuse.

According to Meier *et al.* (2002) the advantages of this hybrid process over simple membrane processes are:

- The adsorption with PAC provides pre-cleaning, which results in a better permeate quality concerning the organic contaminants and also in a reduced membrane fouling due to the removal of substances causing membrane fouling such as effluent organic matter (EfOM).
- The PAC acts as a filter aid and prevents potential foulants from getting into contact with the membrane.
- Compared to fixed-bed adsorption, the PAC-dosage can be adjusted to the feed quality. Also the PAC is loaded before the membrane unit and in the retentate on a higher concentration level.

Especially due to advantages concerning membrane fouling the PAC-NF process has a real potential for wastewater reclamation (Meier & Melin 2005). It can produce high quality water without further pre-treatment, which is definitively required for high quality water

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recycling purposes such as aquifer recharge water or industrial process water.

The present study aims to investigate the performance of the PAC-NF process with low adsorbent concentrations to remove organic compounds from tertiary effluent. Furthermore the pilot study examines the optimum long term operation conditions of the novel PAC-NF process.

METHODS

Adsorbents

Four different commercially available adsorbents were used for the study (Table 1). Ranging from lignite coke dust (LCD) to powdered activated carbon (PAC) the adsorbents were chosen to cover a broad spectrum of quality regarding inner surface, pore size and particle size distribution as well as raw material. The powdered activated carbon used for the pilot tests was pre-moistened to a drinking water content of 50% (ETC engineering & technology consulting GmbH, Burgau, Germany) for improved handling and proper mixing.

Water samples

Effluent from the WWTP Aachen Soers was used as raw water for the batch adsorption and pilot tests. Samples were taken as 24 h composite samples from the pilot plant influent (WWTP effluent) and the permeate and as grab samples or 24 h composite samples from the membrane feed and the concentrate (both 0.45 μm filtered).

An auto sampling unit of MAXX GmbH provided the sampling of the 24 h composite samples with 200 mL each 30 min collected in a 10 l Duran glas bottle and stored at 7°C. The samples with activated carbon were taken as grab samples or as manually produced composite samples removing the PAC directly after sampling with a 0.45 μm filter to interrupt the adsorption process.

DOC and UVA_{254} were used to quantify bulk EfOM (TOC-measurement: Model multi N/C, Analytik Jena AG, Jena, Germany; Model C-MAT 5,500, Ströhlein, Kaarst, Germany; DIMA-TOC 100, Dimatec, Essen, Germany). Specific characterization of the EfOM was performed by LC-OCD and LC-UVD respectively (Meier & Melin 2005).

COD, chloride, sulfate, ammonium, nitrate and total P were determined with Lange cuvette tests and a Hach Lange spectrophotometer. Sulfate as important parameter for evaluation of the membrane performance was also measured by means of ion chromatography. A photometer of Varian Company, Model Cary 1 E was used for the measurement of UVA_{254}.

Membrane

The experiments are run with the capillary nanofiltration membrane NF50 M10 from Norit X-Flow (Futselaar *et al.* 2002) in a 8″ capillary module with a capillary diameter of 1.5 mm and an membrane area of 20 m^2. The molecular weight cut-off (MWCO) of the Norit X-Flow NF 10 M10 is 200 D.

Batch adsorption tests

The 0.45 μm filtered WWTP effluent samples with a DOC_0 of 4.5 mg/L were shaken with different PAC doses for 24 h at ambient temperature.

Pilot plant tests

The PAC-NF pilot plant treated directly the effluent from the sand filtration of the municipal WWTP Aachen Soers. Depending on the permeate flux (20 to 25 L/m^2 h) the

Table 1 | Characteristics of the used adsorbents

Parameter	Unit	LCD	PAK 1,000	PAK 1,000 K	SAE Super
Supplier		RWE	CarboTech	CarboTech	Norit
Raw material		Lignite	Coconut	Mineral coal	Diverse
Inner surface	m^2/g	300	> 900	> 1,000	1,300
D_{50}	μm	24	–	–	15
Price	€/t	300	875	950	1,200

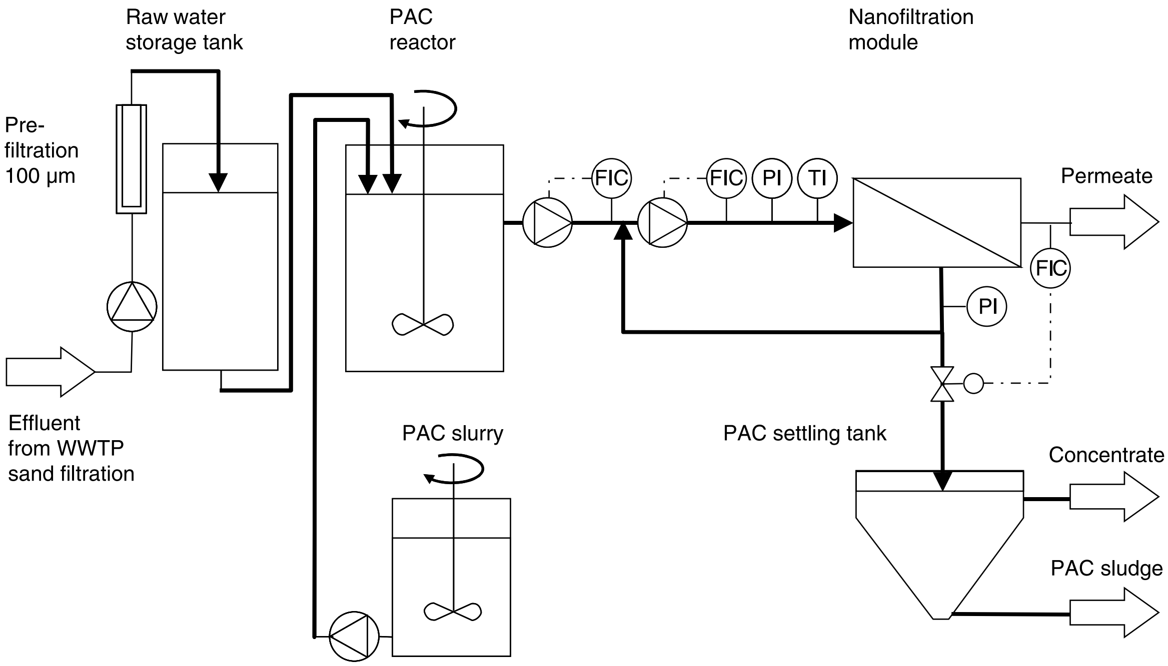

Figure 1 | Experimental set-up of the pilot plant.

permeate production varied between 400 and 500 L/h. The membrane was operated in cross flow mode with a cross flow velocity of 1.2 m/s and a recovery of 75%. Contact time in the PAC reactor was about 1 hour and about 15 min in the cross flow recirculation loop.

During the 4,000 hours of operation reported subsequently Norit SAE Super was used as powdered activated carbon. Lignite coke dust will be investigated in the next period of pilot tests.

The flow sheet of the pilot plant is shown in Figure 1.

RESULTS AND DISCUSSION

Characterization of the raw water

The raw water was characterized by a total amount of 51 composite samples taken in the period of May to December 2006. Table 2 gives the results from the measurement. The wastewater treatment plant with advanced biological treatment including nitrogen and phosphorus removal as well as a final sand filtration provides a high quality effluent. The average DOC was

Table 2 | General parameters of the WWTP effluent used as raw water for the study

Parameter	Unit	Average ± standard deviation	85 percentile
COD	mg/L	15.6 ± 2.3	17.3
DOC	mg/L	5.2 ± 0.9	6.0
UVA_{254}	m^{-1}	0.13 ± 0.02	0.15
Conductivity	mS/cm	0.97 ± 0.19	1.17
pH	–	7.7 ± 0.4	8.4
Sulfate	mg/L	94 ± 21	118
Chloride	mg/L	133 ± 38	168
Ammonium NH_4-N	mg/L	0.04 ± 0.04	0.04
Nitrate NO_3-N	mg/L	5.8 ± 1.7	7.5
Total P	mg/L	0.09 ± 0.06	0.14

Table 3 | General operational parameters and experimental conditions of the pilot tests

Parameter	Duration h	Flux L/(m^2 h)	PAC mg/L	TMP bar	Permeability L/(m^2 h bar)	SO_4-rejection %
Phase 1	760	20	0	1.9 ± 0.3	11.3 ± 1.7	96.6 ± 1.7
Phase 2	550	25	0	2.5 ± 0.2	10.5 ± 0.9	94.2 ± 1.8
Phase 3	550	25	50	2.9 ± 0.5	9.1 ± 1.8	90.0 ± 1.3
Phase 4	450	20	0	2.7 ± 0.3	7.5 ± 0.8	89.4 ± 2.2
Phase 5	540	20	25	2.6 ± 0.2	7.9 ± 0.6	86.6 ± 2.3
Phase 6	190	20	50	2.8 ± 0.3	7.2 ± 0.9	89.3 ± 0.4
Phase 7	480	20	10	2.9 ± 0.3	6.9 ± 0.9	88.6 ± 2.1
Phase 8	260	19	10	2.6 ± 0.3	7.2 ± 0.8	86.1 ± 0.3

5.2 mg/L indicating a very high degree of treatment. Also the typical effluent parameters COD (15.6 mg/L), Ammonium (0.04 mg/L), Nitrate (5.8 mg/L) and total Phosphorus (0.09 mg/L) show the good quality of the effluent from the WWTP Aachen Soers. The average SDI was 5.6, the modified fouling index MFI was 86 (Meier & Melin 2005).

General operational parameter

The results and the experimental conditions are given in Table 3 and Figure 2.

Flux

Earlier studies testing the capillary NF membrane with high PAC doses in the range of 200 mg/L revealed a critical flux in the range of 15 to 20 L/(m^2 h) (Meier & Melin 2005) which proved to be valid also for lower PAC doses.

The first experiment was conducted without PAC for 750 hours at a flux of 20 L/(m^2 h) and a TMP of 1.9 bar and subsequently for about 500 hours at a flux of 25 L/(m^2 h) and a TMP of 2.5 bar. After the PAC dosage a slight TMP increase up to 2.9 bar was observed while the permeability dropped from about 11 L/(m^2 h bar) to 9 L/(m^2 h bar). With 25 L/(m^2 h) the flux was proven to be above the critical flux

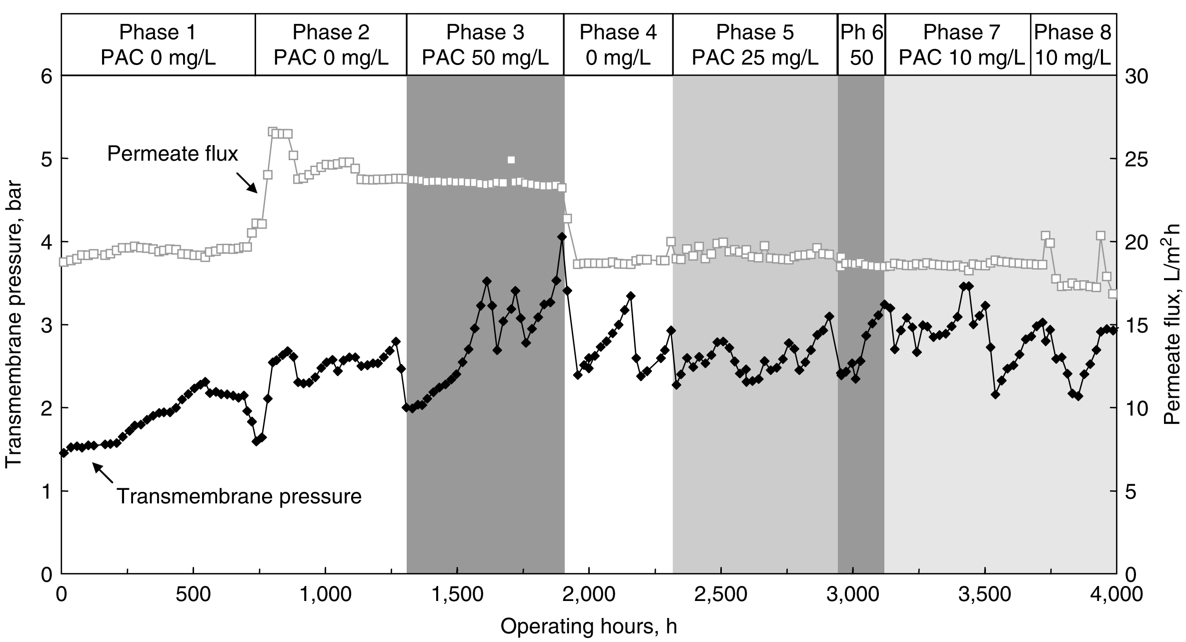

Figure 2 | Phases and operational characteristics of the PAC-NF pilot plant tests (daily averages of online measurements).

Table 4 | Average permeate concentrations during the phases of the pilot tests

Parameter	Flux L/(m^2 h)	PAC mg/L	COD mg/L	DOC mg/L	UVA_{254} cm^{-1}
Phase 1	20	0	3.6	1.0	0.012
Phase 2	25	0	3.5	0.5	0.020
Phase 3	25	50	2.5	0.6	0.011
Phase 4	20	0	4.1	0.9	0.024
Phase 5	20	25	4.5	1.1	0.020
Phase 6	20	50	3.0	0.3	0.012
Phase 7	20	10	4.1	0.8	0.018
Phase 8	19	10	3.8	0.8	0.022

and was therefore reduced to 20 L/(m^2 h). Thereafter the permeability was in the range of 7 to 8 L/(m^2 h bar).

Sulfate rejection

With an initial sulfate rejection of 96.6% the membrane has shown optimum performance. Presumably due to development of a PAC cake layer the sulfate rejection decreased by 4% after dosing of PAC and could not be recovered when PAC dosage was interrupted in phase 4. It seems that even several multi step chemical cleanings were not able to completely remove the PAC layer attached to the membrane. With continuing PAC dosage a further decline in sulfate rejection was observed with a minimum of 86% in the last period of the pilot tests.

Permeability recovery

Depending on permeability decline the module was chemically cleaned–on average every two weeks–with a multi step cleaning procedure consisting of an enzymatic, oxidative (H_2O_2), acidic and caustic step.

Removal rates and permeate quality

To determine the removal efficiency, the quality of the permeate and three different removal rates are used:

- membrane retention by the nanofiltration;
- adsorptive removal by the adsorption on PAC in the PAC reactor;
- total removal by the complete PAC-NF process.

The removal rates are calculated as follows:

$$\text{Membrane retention } R_{\text{membrane}} = 1 - \frac{c_{\text{permeate}}}{c_{\text{concentrate}}}.$$

$$\text{Adsorptive removal } R_{\text{adsorption}} = 1 - \frac{c_{\text{feed}}}{c_{\text{rawwater}}}.$$

$$\text{Total removal } R_{\text{plant}} = 1 - \frac{c_{\text{permeate}}}{c_{\text{rawwater}}}.$$

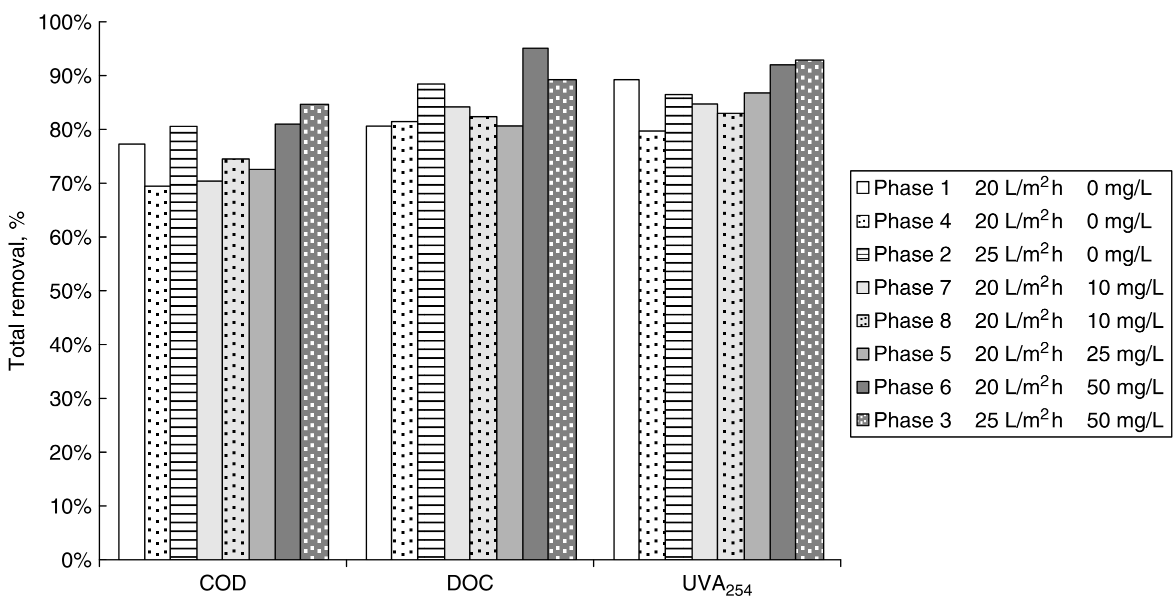

Figure 3 | PAC-NF- pilot plant Soers: Total removal of organic substances ($R_{plant} = 1 - C_{permeate}/C_{raw\ water}$).

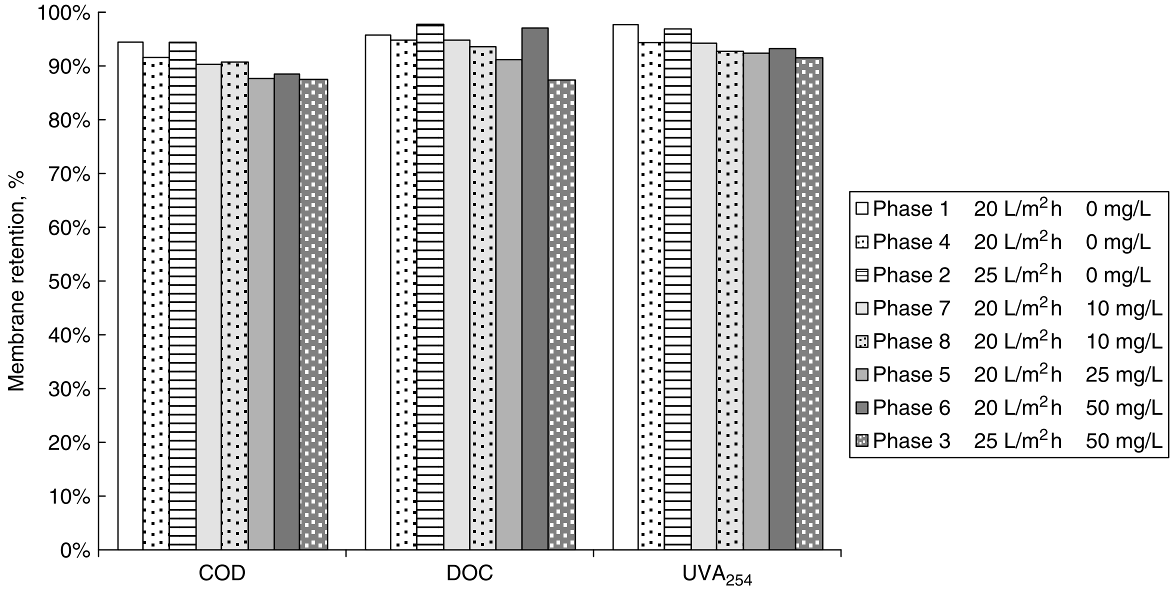

Figure 4 | PAC-NF pilot tests: membrane retention of organic substances ($R_{membrane} = 1 - C_{permeate}/C_{concentrate}$).

The membrane retention describes the performance of the membrane and thus relates to the concentration of the retentate. However the adsorptive removal and the total removal relate to the raw water. Therefore total removal is not the sum of adsorptive removal and membrane retention.

Permeate quality

The permeate produced by the PAC-NF process proved to be of very high quality with average DOC concentrations between 0.3 (PAC dose 50 mg/L) and 1 mg/L (no PAC). The dynamic of the DOC is also reflected by the COD and UVA_{254} concentrations (Table 4).

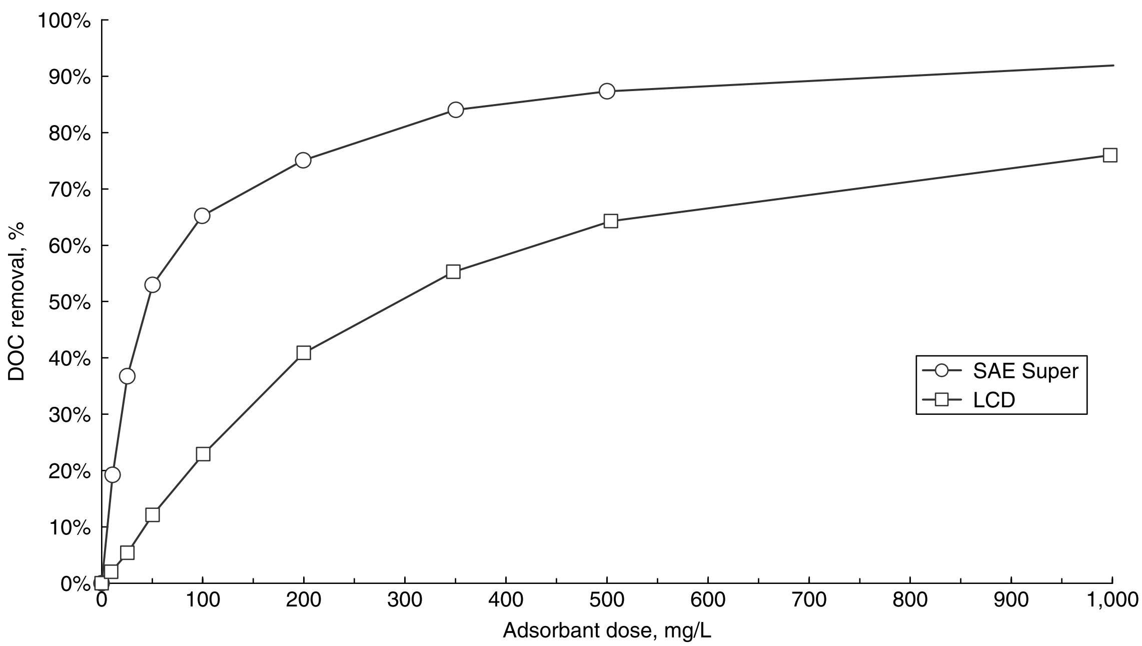

Figure 5 | Batch adsorption tests: DOC adsorption vs. adsorbent dose ($DOC_0 = 4.5$ mg/L).

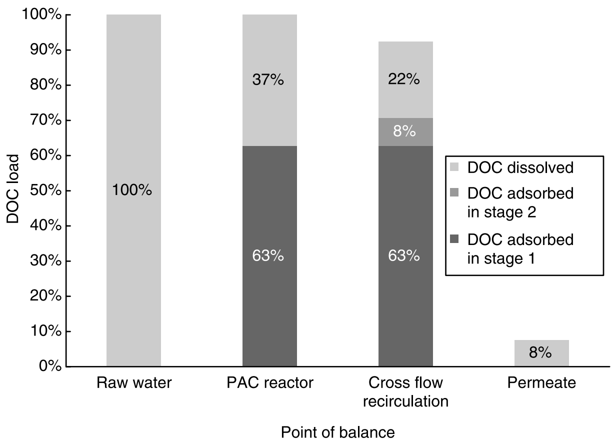

Figure 6 | PAC-NF pilot tests: DOC mass balance (PAC dose 50 mg/L).

Removal rates

The average total DOC and UVA_{254} removal rates clearly show the influence of the operational conditions (Figure 3). The total removal reaches maximum values of 90 to 95% in phase 3 and 6 with the highest PAC dose of 50 mg/L. The virgin membrane showed also relatively high total removal rates in the range of 81–89% which could not be completely recovered by chemical cleaning after PAC dosage (phase 4). With total removal rates between 81 and 84%, PAC doses below 50 mg/L do not lead to a significant increase in DOC removal, although the UVA_{254} values indicate a small influence of low PAC concentrations. The increasing removal of bulk organics by adsorption to PAC is largely compensated by a decreasing membrane retention due to the build-up of a cake layer and resulting effects such as an increased concentration polarization. In cases of higher PAC dosage, the adsorptive EfOM removal outweighs the cake layer formation effects.

With small reductions in retention rates, the membrane retention reflects whether PAC was dosed or not (Figure 4). In phases without PAC dosage the average membrane retention was in the range of 95–98% (DOC) and 94–98% (UVA_{254}). With PAC dosage the average membrane retention slightly went down to 87–97% (DOC) and 91–94% (UVA_{254}). The poorest membrane retention was observed in phase 3 when combining high PAC dosage with a high flux of 25 L/(m^2 h) which lead to a constant increase of the transmembrane pressure.

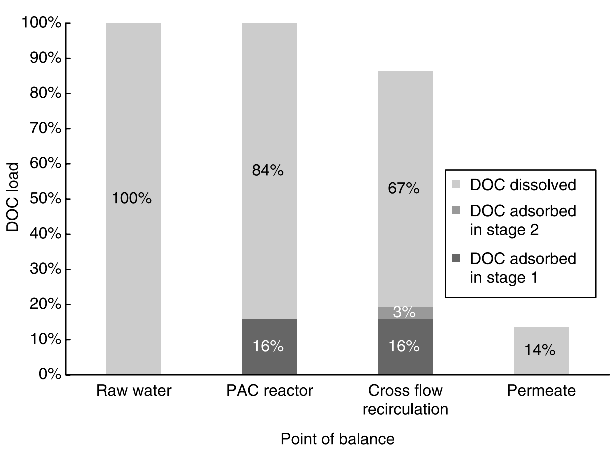

Figure 7 | PAC-NF pilot tests: DOC mass balance (PAC dose 10 mg/L).

Adsorption studies

Adsorption efficiency

DOC batch adsorption tests were executed for lignite coke dust (LCD) and powdered activated carbon SAE Super (PAC). The specialized PAC removes already in low doses high percentages of the EfOM, e.g. 20% with 10 mg/L and 53% with 50 mg/L. LCD demands much higher dosage rates to reach the same adsorption rates. With a dosage of 100 mg/L LCD removes 23% of the EfOM and 55% with a dose of 350 mg/L. This clearly verifies the impact of the adsorbent characteristics (Figure 5).

Brine concentrations

The dosage of PAC reduced also in the pilot tests the EfOM significantly. In comparison of phase 2 (no PAC) and phase 3 (PAC 50 mg/L) the average brine concentration was reduced from 25 mg/L to 5 mg/L whereas the removal occurred in two steps. About 50 to 60% of the EfOM are already removed in the PAC reactor with a contact time of 60 minutes. Further 8% were adsorbed on the preloaded PAC in the cross flow recirculation loop as the PAC concentration increased to 200 mg/L (Figure 6). Thus PAC dosage of 50 mg/L leads to a 75% reduction of the brine DOC load while 10 mg/L only adsorb 22% of the brine DOC (Figure 7).

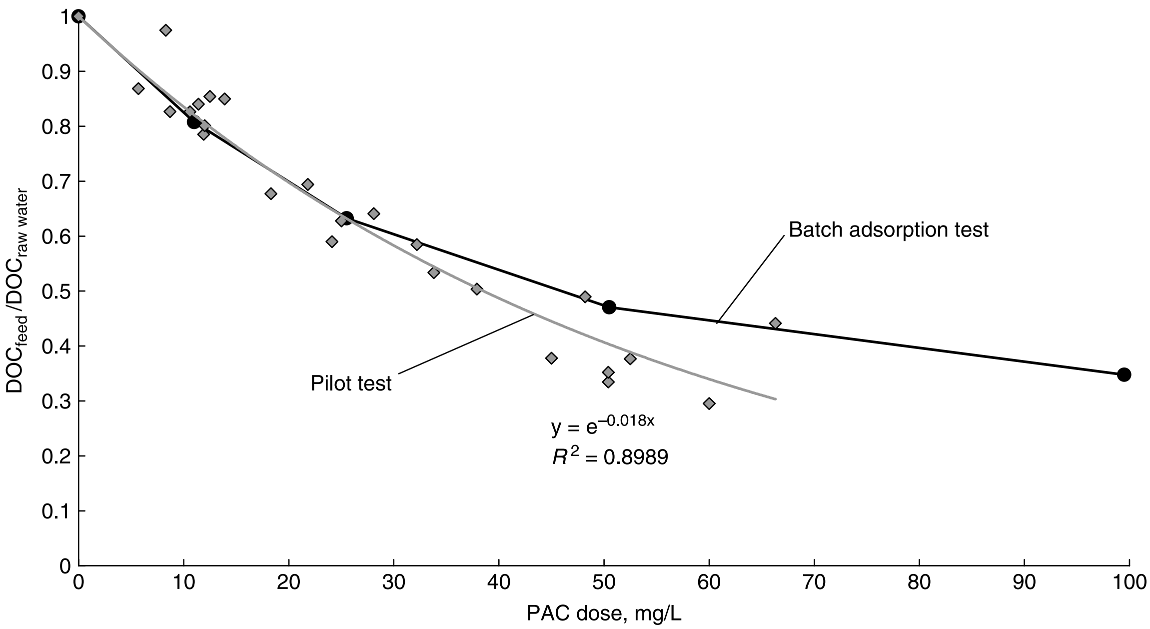

Figure 8 | Comparison of DOC adsorption in PAC-NF pilot test and batch test (regression equation for pilot test).

The direct comparison of the adsorptive removal in the batch test to the pilot test shows a similar gradient of the two curves. During the pilot tests with higher raw water concentrations and PAC doses of about 50 mg/L, a few values were even below the batch adsorption curve (Figure 8).

The impact of the PAC addition on the treated effluent has been investigated in a former study (Meier & Melin 2005) by means of LC-OCD (Liquid chromatography organic carbon detection) analysis which shows the different molecular mass fractions and how those are affected by the adsorbent (Figure 9).

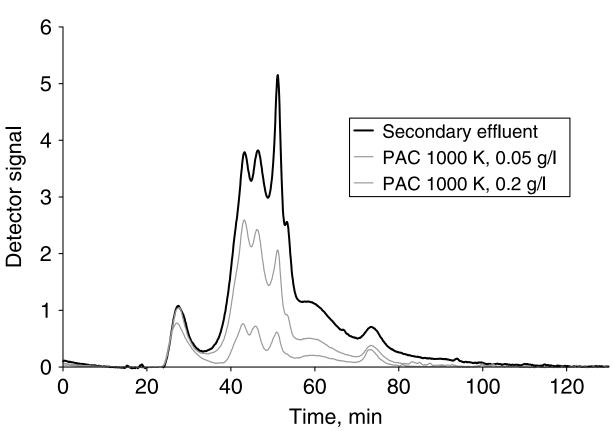

Figure 9 | Result of LC-OCD analysis of two different PAC concentrations (from Meier & Melin 2005).

CONCLUSIONS

The hybrid process of adsorption on PAC in combination with nanofiltration can be regarded as a reliable treatment concept for high quality water production and combined brine treatment similarly to the combination of a GAC filter and nanofiltration (Roorda *et al.* 2005). With relatively low PAC doses of about 50 mg/L most of the EfOM can be removed. Besides the sum parameter DOC the removal of organic trace substances in the PAC-NF is of major interest as they are of concern particularly in indirect potable reuse applications (Bixio & Wintgens 2006; Ternes & Joss 2006). Within further ongoing experiments the behavior of pharmaceutically active compounds and endocrine disruptors are investigated. First results indicate a high removal performance of selected substances in the range of 88 and 99.9% (Kazner *et al.* 2007; Lehnberg *et al.* 2007) when PAC was added prior to NF.

Removal rates of above 90% for a broad range of key parameters prove that PAC-NF can be regarded as a promising alternative to dual membrane processes including RO, if a high degree of desalination is not required. A rough cost estimate shows that the dosage of 50 mg/L PAC will cause additional operational costs of about 0.06 €/m^3. As the PAC-NF process applies a low pressure membrane with an average TMP of 2 to 3 bar the combination of adsorption and subsequent nanofiltration can be expected to compete also economically with dual membrane processes.

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