

# Comparing the effluent organic matter removal of direct NF and powdered activated carbon/NF as high quality pretreatment options for artificial groundwater recharge

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## ABSTRACT

Direct nanofiltration and nanofiltration combined with powdered activated carbon known as the PAC/NF process were tested regarding the removal of effluent organic matter for reclamation of tertiary effluent from a municipal wastewater treatment plant. They can be regarded as a promising treatment alternative for high quality water reuse applications, especially for direct injection. The total removal for DOC was above 90% with permeate concentrations below 0.5 mg/l. Size exclusion chromatography and fluorescence EEM proved to trace origin of the organic matter even in low concentration ranges. The type and dosage of adsorbent influences the process performance significantly and allows process optimization.

**Key words** | DOC characterization, fluorescence EEM, nanofiltration, PAC-adsorption, PAC/NF process, water reclamation

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## INTRODUCTION

Many countries and regions of the world are facing water scarcity and deterioration of groundwater quality caused by climate change and continuous population growth especially in coastal areas. Since decades artificial groundwater recharge with reclaimed wastewater is applied in various arid regions as one of the most promising approaches to solve or minimize the complex problem of unsustainable water withdrawals. Depending on the recharge method the pretreatment requirements vary from secondary treatment for recharge basins to advanced treatment for direct injection wells (Asano *et al.* 2007). To inject directly in the aquifer requires a very high water quality especially regarding pathogens, bulk organics, and emerging pollutants such as pharmaceuticals and endocrine disruptors (Bouwer 2002; Ternes & Joss 2006; Toze 2006).

A proper treatment of effluent can be regarded as a crucial prerequisite for sustainable operation of reclamation systems as well as for public acceptance of water reclamation. In this light dense membrane systems like reverse

osmosis and nanofiltration provide not only good removal of bulk and trace organics (Drewes *et al.* 2002; Snyder *et al.* 2003) but also retain pathogens, especially viruses (Trussell *et al.* 2000). The removal of bulk organics influences on the one hand the fouling of membranes (Schäffer 2001; Amy 2007) with all its technical and economic implications, on the other hand wastewater effluent organic matter contributes to soil clogging (Bouwer 2002) and formation of disinfection by-products (Oliver 1983; Singer 1993).

Most of the high quality water reclamation systems rely on a combination of micro- or ultrafiltration and reverse osmosis (Metcalf & Eddy 2004; Bixio & Wintgens 2006; Asano *et al.* 2007). High investment and operation costs, the use of chlorinated chemicals to suppress membrane fouling and the brine produced are major drawbacks of the UF/RO process. Capillary nanofiltration combines advantages from UF and RO while reducing the disadvantages. It allows complete retention of all pathogens and most of the non biodegradable contaminants like endocrine disruptors and

pharmaceuticals while osmotic pressure relevant mono-valent 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 (Kazner *et al.* 2007a) and micro-pollutants (Kazner *et al.* 2007b) from municipal wastewater treatment plant effluents for water reclamation and water reuse. Especially due to advantages concerning membrane fouling the PAC/NF process has a real potential for wastewater reclamation (Meier & Melin 2005). Without further pre-treatment it can produce high quality water, which is definitively required for high quality water recycling purposes such as aquifer recharge water or industrial process water.

The objective of this study was to elucidate the fate and removal of effluent organic matter (EfOM) from tertiary effluent during direct nanofiltration compared to powdered activated carbon followed by nanofiltration applying advanced DOC characterization methods such as size exclusion chromatography and fluorescence excitation-emission matrix (FEEM) spectroscopy (Baker 2001; Her *et al.* 2003).

## MATERIALS AND METHODS

### Raw water quality

To evaluate the performance of the PAC/NF-process under realistic conditions a pilot plant has been installed at the WWTP Aachen Soers (460,000 p.e.) treating continuously about 500 L/h of tertiary effluent. The wastewater treatment plant with advanced biological treatment including nutrient removal as well as a final sand filtration already provides a high quality effluent with an average DOC of  $5.2 \pm 0.9$  mg/L, average COD of  $15.6 \pm 2.3$  mg/L, average conductivity of  $0.97 \pm 0.19$  mS/cm, and average pH of  $7.7 \pm 0.4$  (Kazner *et al.* 2007a).

### Characterization of organic matter

A MAXX SP III auto sampler provided the sampling of the 24 h composite samples with 200 mL collected each 30 min in a 10 L Duran glas bottle and stored at 7°C. The samples with activated carbon were taken as manually produced composite samples removing the PAC directly after

sampling with a 0.45 µm filter to interrupt the adsorption process. TOC and DOC were analyzed on a DIMA-TOC 100 total organic carbon analyzer (Dimatec Analysentechnik GmbH, Germany). For DOC measurement the samples were pre-filtered with 0.45 µm Acrodisc filters from Pall Corporation. A photometer of Varian Company, Model Cary 1 E was used for the measurement of UVA 254.

### Size exclusion chromatography

Specific characterization of the EfOM was performed by LC-OCD and LC-UVD respectively as published in Meier & Melin (2005).

### Fluorescence EEM spectroscopy

The FEEM spectroscopy was performed using a Fluoro-Max-3 spectrofluorometer from Horiba Jobin Yvon Inc., USA, with a xenon lamp as excitation source. The adapted protocol was based on work by Westerhoff *et al.* (2001). Depending on the DOC concentration the filtered samples were diluted to about 1 mg/l of DOC with 0.01M KCl solution with an adjusted pH of ~2.8 using HCl. The samples were measured at room temperature with the following range of wavelengths: Excitation: 240–450 nm in 10 nm intervals and Emission: 290–530 nm in 2 nm intervals. The sample EEMs were corrected by subtraction of the blank EEM (0.01 KCl, pH of 2.8 using HCl) to remove Raman scatter peaks.

### PAC/NF pilot plant

The pilot plant treated the WWTP effluent directly for more than 6,000 h of operation during May 2006 and April 2007. During operation of PAC/NF, powdered activated carbon was dosed in a CSTR and then retained by the nanofiltration. It was employed with a 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 a total membrane area of 20 m<sup>2</sup>. According to supplier's data the molecular weight cut-off of the composite membrane is 200 g/mol. It has an active layer of polyamide with a supporting layer of polyethersulfone. Depending on the permeate flux (20 to 25 L/m<sup>2</sup>·h) the

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%. The transmembrane pressure ranged between 1.5 and 4.0 bar. A schematic diagram of the pilot plant is shown in Figure 1.

Contact time in the PAC reactor was about 1 h and about 15 min in the cross flow recirculation loop. The powdered activated carbon used was Norit SAE Super. It has internal surface area of 1,300 m<sup>2</sup>/g with a mean particle diameter  $D_{50}$  of 15 μm. As low cost alternative, RWE lignite coke dust (LCD) with internal surface area of 300 m<sup>2</sup>/g and a mean particle diameter  $D_{50}$  of 24 μm was used. The adsorbents were pre-moistened to a drinking water content of 50% for improved handling and proper mixing.

## RESULTS AND DISCUSSION

### Removal of organic matter based on DOC and UV measurement

To determine the removal efficiency, two different removal rates were calculated:

- Adsorptive removal by the adsorption on PAC

$$R_{\text{adsorption}} = 1 - c_{\text{feed}}/c_{\text{raw water}}$$

- Total removal by the PAC/NF process  $R_{\text{total}} = 1 - c_{\text{permeate}}/c_{\text{raw water}}$

The average removal of DOC and UVA as well as concentrations at the different sampling points are given in Table 1. Direct NF provided already a high quality permeate with 0.3 mg/l DOC and a total removal of 93.4%. Addition of low adsorbent doses removed about 30% of the raw water DOC while the total removal increased only slightly. The different removal rates for DOC and UVA indicated that UV relevant molecules such as humic substances possess a higher affinity to adsorb. The average SUVA in the range of 2.4 to 2.7 L/mg·m was slightly above the typical effluent value of 2 L/mg·m. While adsorption reduced the SUVA to 2.2 L/mg·m, it increased again after NF to around 4 L/mg·m indicating a higher aromaticity on a very low DOC level.

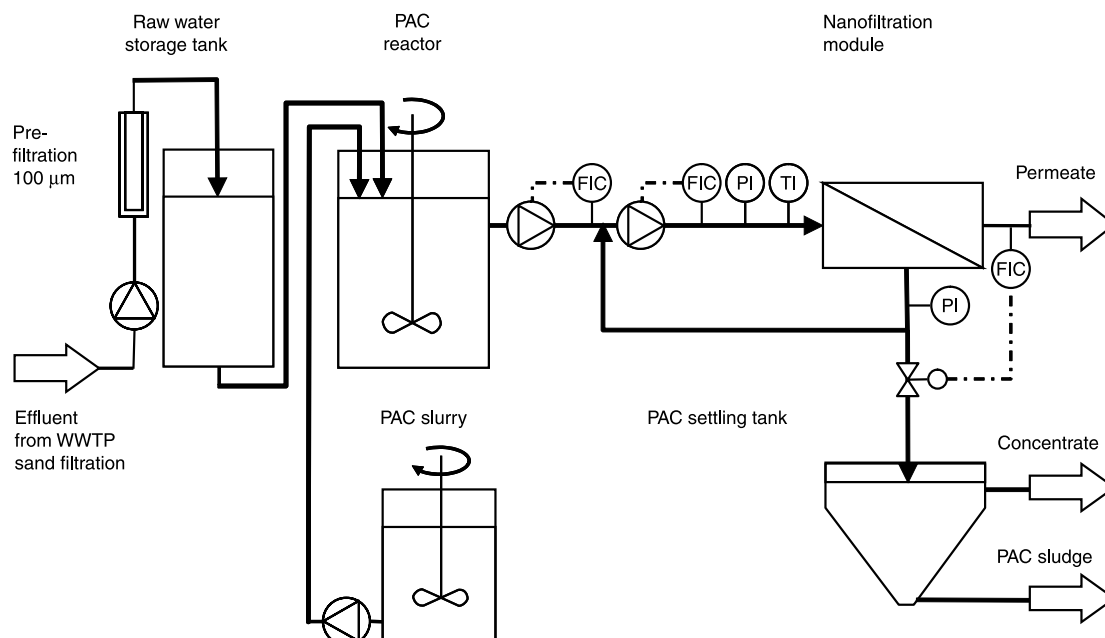


Figure 1 | Experimental set-up of the PAC/NF pilot plant.

### Size exclusion chromatography

### Nanofiltration

SEC for direct nanofiltration without PAC dosage showed as expected an incomplete rejection of low molecular weight neutrals and acids while large molecules such as

**Table 1** | DOC and UVA average concentrations, SUVA and removal rates

Parameter	Raw water	Adsorption		Nanofiltration	
	$C_{\text{influent}}$	$R_{\text{Ads.}}$	$C_{\text{Feed}}$	$R_{\text{total}}$	$C_{\text{Permeate}}$
<i>Without PAC</i>					
DOC	4.6 mg/L	–	–	93.4%	0.3 mg/L
UVA 254	0.126 $\text{cm}^{-1}$	–	–	90.0%	0.0126 $\text{cm}^{-1}$
SUVA	2.7 L/mg·m	–	–	–	4.2 L/mg·m
<i>With 25 mg/L PAC</i>					
DOC	5.7 mg/L	29.8%	4.0 mg/L	94.7%	0.3 mg/L
UVA 254	0.136 $\text{cm}^{-1}$	34.6%	0.089 $\text{cm}^{-1}$	90.4%	0.0130 $\text{cm}^{-1}$
SUVA	2.4 L/mg·m	–	2.2 L/mg·m	–	4.3 L/mg·m
<i>With 140 mg/L LCD</i>					
DOC	5.4 mg/L	18.5%	4.4 mg/L	92.6%	0.4 mg/L
UVA 254	0.133 $\text{cm}^{-1}$	28.6%	0.126 $\text{cm}^{-1}$	88.0%	0.0160 $\text{cm}^{-1}$
SUVA	2.5 L/mg·m	–	2.2 L/mg·m	–	4.0 L/mg·m

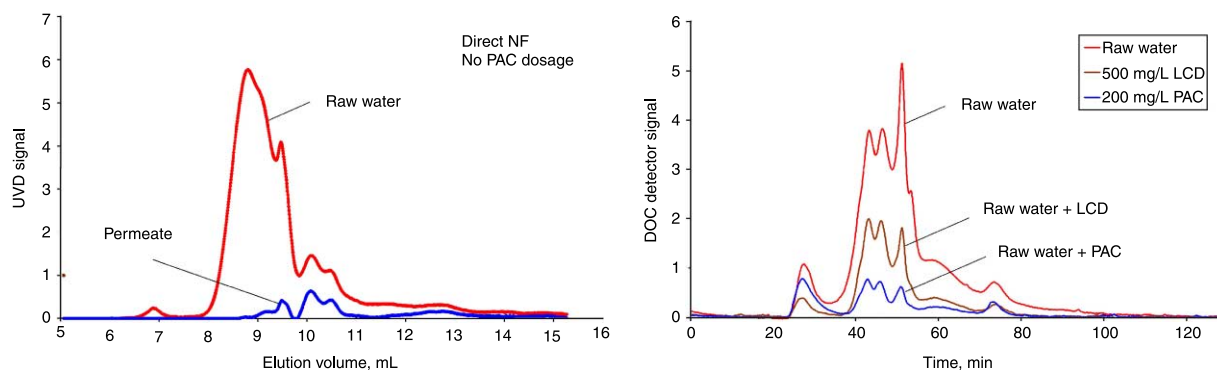
polysaccharides, proteins and humic substances were well removed (Figure 2a).

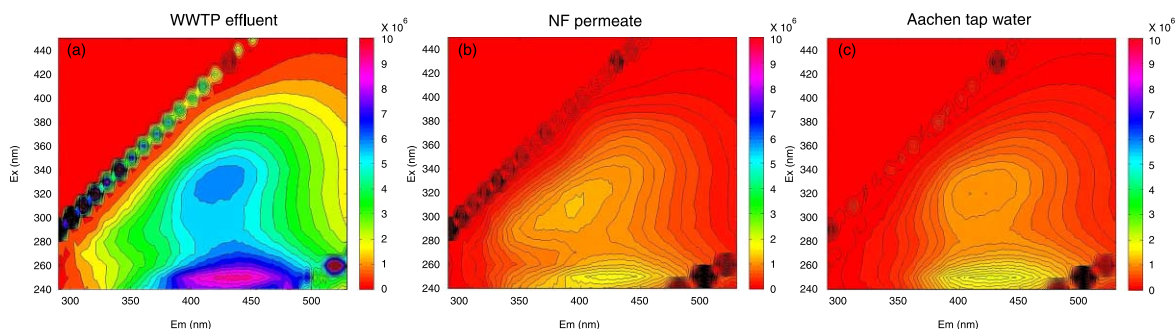
### Adsorption

Figure 2b depicts the different adsorption characteristics of the two adsorbents tested. The pore size distribution of lignite coke dust allowed a better adsorption of the fouling relevant high MW substances, whereas powdered activated carbon primarily removed humics and small size molecules illustrating that an adsorption step prior to NF has the potential to selectively reduce deficits of the nanofiltration.

### Fluorescence EEM spectroscopy

Water samples used for the EEM measurements presented in Figures 3 to 5 were taken on three different days but showed a similar composition of the WWTP effluent used as raw water for the pilot unit. All raw water assays exhibited dominating fulvic- and humic-like peaks at  $E_m/Ex = 440/250 \text{ nm}$  and  $424/340 \text{ nm}$  respectively and intensities of  $9.6$  to  $10.0 \times 10^6$  and  $6.2$  to  $6.4 \times 10^6$ . Long slopes from the peaks towards the lower excitation/emission range indicated the presence of proteins typical for wastewater influenced samples.

**Figure 2** | Size exclusion chromatograms for the NF removal and the adsorptive removal (Figure 2b adapted from Meier & Melin 2005).



**Figure 3** | Fluorescence EEMs for the direct NF treatment compared to Aachen tap water (DOC: WWTP effluent: 5.2 mg/L, permeate: 0.3 mg/L, tap water: 0.5 mg/L). Subscribers to the online version of Water Science and Technology can access the colour version of this figure from <http://www.iwaponline.com/wst>.

### Direct nanofiltration

Figure 3b illustrates the shift of the humic-like peak from  $Em/Ex = 430/330$  to  $390/310$  nm with an intensity of  $1.3 \times 10^6$  towards the protein-like substances through the removal of the humics by nanofiltration. The fulvic-like peak at  $Em/Ex = 430/250$  nm was reduced to an intensity of  $1.8 \times 10^6$ , but not significantly shifted. The DOC was reduced from 5.2 to 0.3 mg/l. The comparison with the Aachen tap water showed similar intensities of the drinking water with peaks at  $420/330$  nm ( $1.1 \times 10^6$ ) and  $430/250$  nm ( $2.0 \times 10^6$ ) which were more confined without the influence from protein-like compounds (Figure 3c). Although in the same range of intensities the position and extension of the permeate peaks clearly demonstrated the wastewater history of the NF permeate.

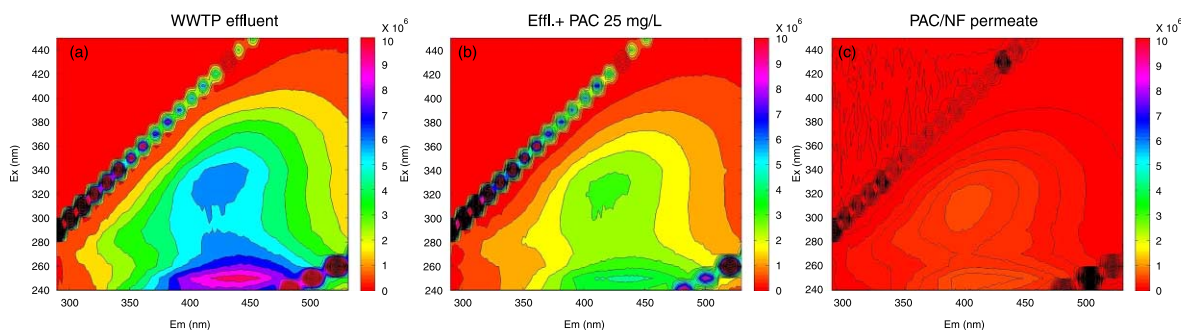
### PAC combined with NF

Figure 4 shows the series of EEM spectra with the effect of PAC dosage of 25 mg/l Norit SAE Super. While reducing

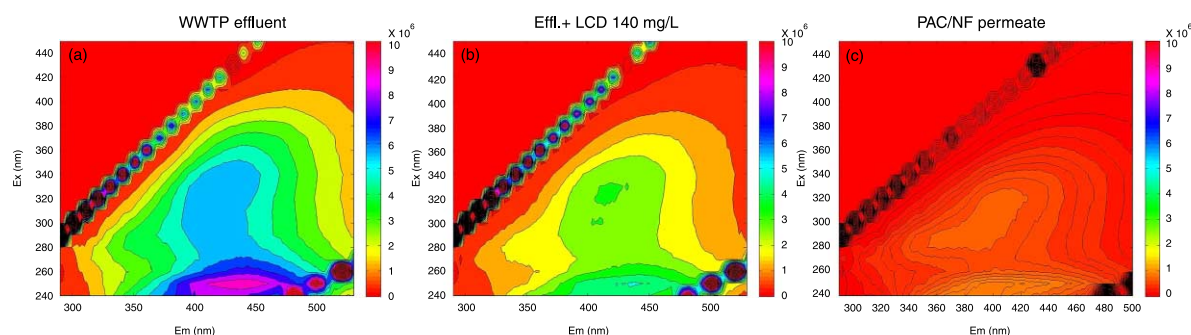
the peaks from  $6.4$  to  $3.1 \times 10^6$  ( $Em/Ex = 420/330$  nm) and  $10.0$  to  $4.5 \times 10^6$  ( $430/250$ ), PAC did not shift the peaks and partly removed the protein-like wastewater indicators. The PAC/NF permeate showed the highest quality of all samples measured. The peaks at  $Em/Ex = 400/310$  and  $408/250$  with intensities of  $5.8$  and  $7.1 \times 10^5$  (Figure 4c) were well below the Aachen drinking water. Still some of the protein-like substances remained in the permeate.

### LCD combined with NF

When applying lignite coke dust (Figure 5), organic matter was removed similarly as in the case of PAC. The broad peaks of the permeate sample at  $Em/Ex = 400/250$  and  $392/300$  with intensities of  $9.5 \times 10^5$  and  $7.1 \times 10^5$  were below the drinking water but exhibited stronger shifts towards the protein-like compounds. As expected from the adsorption pattern of LCD (Figure 2b) that showed a higher removal of the high molecular weight fraction, the



**Figure 4** | Fluorescence EEMs for the PAC/NF treatment (PAC dosage 25 mg/L; DOC: WWTP effluent: 5.7 mg/L, after PAC: 4.0 mg/L, permeate: 0.3 mg/L). Subscribers to the online version of Water Science and Technology can access the colour version of this figure from <http://www.iwaponline.com/wst>.



**Figure 5** | Fluorescence EEMs for the LCD/NF treatment (LCD dosage 140 mg/L; DOC: effluent: 5.6 mg/L, after LCD: 4.5 mg/L, permeate: 0.4 mg/L). Subscribers to the online version of Water Science and Technology can access the colour version of this figure from <http://www.iwaponline.com/wst>.

EEM of the LCD/NF permeate revealed a higher impact by wastewater-derived organic matter.

### Fluorescence index (FI)

On the basis of FEEM, the fluorescence index can be determined by the ratio of fluorescence intensity at emission 450 and 500 nm at excitation 370 nm (McKnight *et al.* 2001). It represents another tool to trace NOM origin of EEM samples. The effluent FI varied between 1.55 and 1.59. The FI increased during membrane treatment: NF permeate (1.81) compared to the PAC/NF permeate (1.69) and the LCD/NF permeate (1.61). All values reflect organic matter of autochthonous (microbial) origin known to be in the range of  $\sim 1.7$  to  $\sim 2.0$ . The FI of the tap water sample (1.39) showed the typical allochthonous (terrestrial) signature ( $\sim 1.3$  to  $\sim 1.4$ ).

### CONCLUSIONS

Direct nanofiltration as well as powdered activated carbon combined with nanofiltration can produce high quality water from tertiary effluent. DOC values below 0.5 mg/L and removal rates above 90% confirm the excellent quality suitable for direct injection.

Differences in the remaining organic matter can be detected with advanced characterization methods such as SEC and fluorescence EEM. Direct nanofiltration partly rejected the molecules with low molecular weights and exhibited FEEM spectra with a distinct wastewater impact. As PAC tends to adsorb the humic and fulvic substances as well as smaller size molecules while LCD adsorbs more of the larger molecules such as polysaccharides, PAC can be regarded as

more advantageous than LCD to counterbalance deficits of the membrane. Thus the PAC/NF process allows the fairly accurate adjustment of the permeate quality according to the site specific requirements through proper selection of the adsorbent and the dosage. Although the DOC values indicate a quality better than the original tap water, the applied advanced characterization methods show that even in very low DOC or organic matter concentration ranges the history of the water can be detected.

Ongoing research will cover the differences in the DBP formation potential and the behavior of the remaining organic matter in natural attenuation processes.

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