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Removal of Endocrine Disruptors and Cytostatics from Effluent by Nanofiltration in Combination with Adsorption on Powdered Activated Carbon

C. Kazner*, K. Lehnberg**, L. Kovalova***, T. Wintgens*, T. Melin*, J. Hollender***, W. Dott**

* RWTH Aachen University, Dept. of Chemical Engineering, Turmstrasse 46, 52056 Aachen, Germany
(E-mail: *kazner@ivt.rwth-aachen.de; wintgens@ivt.rwth-aachen.de; melin@ivt.rwth-aachen.de)*
** RWTH Aachen University Hospital, Institute of Hygiene and Environmental Health Pauwelstr. 50, 52050 Aachen, Germany
(E-mail: *kai.lehnberg@rwth-aachen.de; wdott@ukaachen.de)*
*** Swiss Federal Institute of Aquatic Science and Technology (Eawag), Überlandstr. 133, 8600 Dübendorf, Switzerland
(E-mail: *Lubomira.Kovalova@eawag.ch; Juliane.Hollender@eawag.ch*)

Abstract
Direct capillary nanofiltration also in combination with an upstream powdered activated carbon treatment was tested for high quality water reuse of tertiary effluent from a municipal wastewater treatment plant. Two endocrine disruptors (BPA and EE2) and two cytostatics (CytR and 5-FU) were spiked in concetrations of 1 to 2 µg/L to evaluate the process performance. In direct NF the real total removal of the micropollutants was between 5 and 40%. Adsorption to the membrane played a major role leading to a seemingly total removal between 35 and 70%. Addition of powdered activated carbon and lignite coke dust largely reduced the influence from adsorption to the membrane and increased the total removal to >95 to 99.9% depending on the PAC type and dose. The cytostatics showed already in direct NF a very high removal due to unspecified losses. Further investigations are ongoing to understand the underlying mechanism. The PAC/NF process provided a consistently high permeate quality with respect to bulk and trace organics.

Keywords
Cytostatics; endocrine disruptors; nanofiltration; powdered activated carbon; PAC/NF

INTRODUCTION

Recent research proved the efficiency of membrane and activated carbon treatment for the removal of organic trace pollutants, such as pharmaceuticals, from secondary and tertiary effluents (Kazner *et al.*, 2007, Snyder *et al.*, 2007). Especially in indirect potable reuse and water reclamation by managed aquifer recharge these substances are causing concern due to potential harm to the users (Asano and Cotruvo, 2004).

Some endocrine disruptors (EDCs) show already effects in very low ng/L-concentrations which are close or sometimes even below the limit of quantification. Wenzel *et al.* (1999) report that 17α-ethinylestradiol (EE2) might cause environmental effects in concentrations below 1 ng/L. Eco-toxicological and environmental data classify EE2 as being highly relevant to the environment. While conventional sewage treatment plants remove between 50 to 95% of EE2 (Andersen *et al.*, 2003, Johnson *et al.*, 2005, Ternes and Joss, 2006) effluent concentrations may still range in environmentally relevant concentrations. Bisphenol A (BPA) is another environmentally relevant chemical with endocrine disrupting effects - however not due to its high activity but to the significantly higher effluent concentrations typically in the low µg/L range.
Cytostatic agents represent a further group of chemicals causing environmental concern as many of these chemotherapeutic drugs feature carcinogenic, mutogenic, and reprotoxic effects and are therefore categorized as CMR-drugs. Recent research focused on the presence and fate of cytostatics in hospital wastewater as the main source of discharge (Mahnik et al., 2007, Lenz et al., 2007). Mahnik et al. (2004) measured 20 to 120 µg/L of 5-fluorouracil (5-FU) in the effluent from

a hospital. The presence of these compounds in the effluent of municipal WWTPs is not yet well investigated. Yu et al. (2006) detected a low biodegradation of less than 60% for 5-FU whereas Mahnik et al. (2007) observed a high 5-FU elimination of >90% in a lab scale test. They assume that 5-FU is biodegraded or metabolized by microorganism.

Dense membrane processes like reverse osmosis and nanofiltration as well as activated carbon are among the processes supposed to have the best potential to retain micropollutants with endocrine disrupting effects (Ternes and Joss, 2006). Depending on a large variety of factors, between 41 and >99% of EE2 (Weber, 2004) and between 1.9 and 99.7% of BPA (Gallenkämper, 2005, Zhanga et al., 2006) can be removed by nanofiltration. The removal of potentially harmful cytostatics in dense membrane processes was not yet investigated. Additionally there is a lack of knowledge of the fate of EDCs in large scale polishing systems. One concern is that compounds sorbing to the membrane can lead to an uncontrolled break through. The objective of this study is therefore to elucidate to which extent direct capillary nanofiltration can remove endocrine disruptors (EDCs) and cytostatics and whether process improvement by pre-treatment with adsorption on powdered activated carbon can be achieved.

MATERIALS AND METHODS

Selected pharmaceuticals and other trace organics

The present study selected 17α-ethinylestradiol (EE2) and bisphenol A (BPA) as endocrine disruptors and 5-fluorouracil (5-FU) and cytarabine (CytR) as cytostatics to test the performance of the PAC/NF process. The compounds were spiked to the WWTP effluent at concentrations of about 1 µg/L to show effects which cannot be measured reliably at ambient concentrations. Table 1 summarizes the selected target compounds which were chosen due to molecular weights close to the MWCO of the membrane or due to the low removability in other processes.

Table 1. Selected organic micropollutants (molecular weight (MW) in g/mol)

Analytes	Short name	Use	MW	pK_a	Log K_{OW}
Bisphenol A	BPA	Industrial chemical	228.3	9.7	3.2
17α-Ethinylestradiol	EE2	Hormonal contraceptive	296.4	10.2	4.1
Cytarabine	CytR	Cytostatic drug	243.2	4.4	- 2.2
5-Fluorouracil	5-FU	Cytostatic drug	130.1	8.0	- 0.9

Analytical methods

All samples were taken as 24 h composite samples. An auto sampling unit of MAXX GmbH provided the sampling of the influent and permeate samples with 200 mL each 30 min collected in a 10 l Duran glas bottle and stored at 7 °C. The feed and retentate samples containing activated carbon were manually produced composite samples removing the PAC directly after sampling with a 0.45 µm filter to interrupt the adsorption process. Pharmaceutical concentrations in the influent, feed, permeate, and retentate were analyzed by using SPE enrichment prior to LC-MS-MS detection. For the detection of the EDCs and the cytostatics two different methods were employed. Oasis HLB SPE-cartridges were used for the EDCs while cytostatics were concentrated with ENV+ SPE-cartridges. Separation was performed with HPLC (Agilent 1100) with a reverse phase column (Thermo HyPurity C18) for EDCs and a HILIC column (ZIC HILIC) for cytostatics. The substances were detected with an Applied Biosystems triple quadrupole mass spectrometer (API 3000). All samples were quantified with 13C doted internal standards.

DOC measurement was performed on a DIMA-TOC 100 total organic carbon analyzer (Dimatec Analysentechnik GmbH, Germany). The DOC samples were pre-filtered with 0.45 µm Acrodisc filters from Pall Corporation.

Characterization of the influent water quality

To evaluate the performance of the PAC/NF process under realistic conditions regarding the effluent matrix, a pilot plant has been installed at the WWTP Aachen Soers (460,000 p.e.) treating continuously about 400 to 800 L/h of tertiary effluent from the sand filtration. 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 with an average DOC of 5.2 ± 0.9 mg/L, average COD of 15.6 ± 2.3 mg/L, average conductivity of 0.97 ± 0.19 mS/cm, and mean pH of 7.7 ± 0.4 (Kazner *et al.*, 2007).

PAC/NF pilot plant

The pilot plant treated the effluent directly for about 2400 h of operation from July to November 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 an 8" capillary module with a capillary diameter of 1.5 mm and a total membrane area of 20 m². 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 (15 to 25 L/m²·h) the permeate production varied between 300 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 65 to 85 %. The transmembrane pressure ranged between 1.7 and 3.3 bar. A schematic diagram of the pilot plant is shown in Fig. 1.

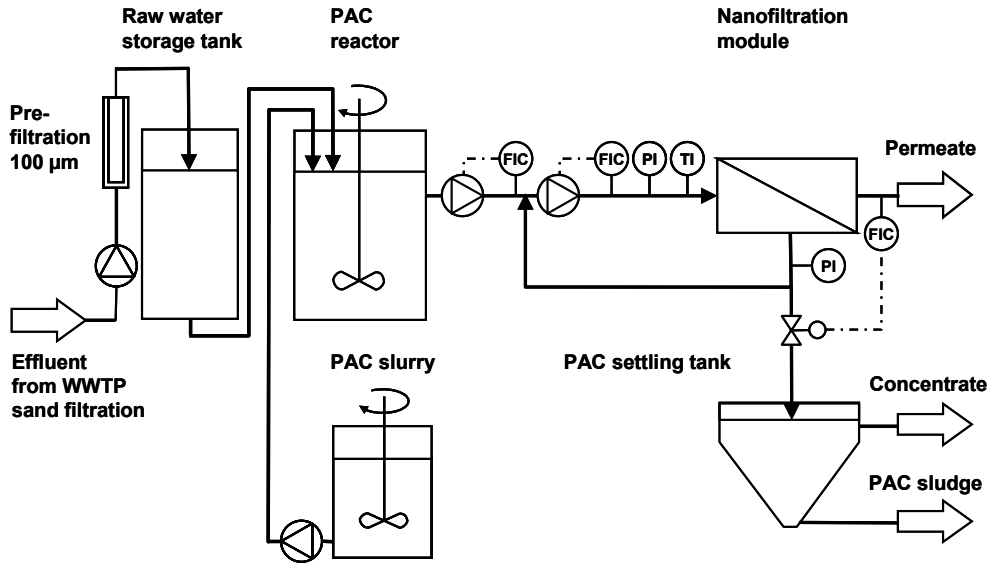

Figure 1. Experimental set-up of the PAC/NF pilot plant

Contact time in the PAC reactor was about 1.2 h and about 15 min in the cross flow recirculation loop. Norit SAE Super was used as powdered activated carbon. It features an inner surface of 1300 m²/g with a mean particle diameter D_{50} of 15 µm. As low cost alternative, RWE lignite coke dust with an inner surface of 300 m²/g and a mean particle diameter D_{50} of 24 µm was applied. The adsorbents were pre-moistened to a drinking water content of 50% for improved handling and proper mixing. The selected micropollutants were spiked from a 10 L duran glas bottle with an Ismatec Reglo Analog peristaltic pump in the stirred raw water storage tank.

RESULTS AND CONCLUSIONS

Removal rates. To evaluate the process performance three different removal rates were used:

- Adsorptive removal by the adsorption on PAC $R_{adsorption} = 1 - c_{feed}/c_{raw\ water}$
- Membrane retention by the NF membrane $R_{NF} = 1 - c_{permeate}/c_{retentate}$
- Total removal by the PAC/NF process $R_{tot} = 1 - c_{permeate}/c_{raw\ water}$

Direct nanofiltration

Bisphenol A and 17α-ethinylestradiol. As known from literature (Bellona et al., 2004) direct NF (without activated carbon) showed an incomplete removal of the target compounds (e.g. EE2, see Fig 2). An overview of the results from the direct NF filtration pilot tests is given in table 2. The average membrane retention varied largely between -5% and 45% for BPA and between 54 and 72% for EE2 depending on the operating conditions. The best performance in terms of permeability was observed at a flux of 20 L/(m²·h) and a recovery of 75 %. With increasing permeate flux a slight decrease of the real total removal was observed. As described by Nghiem et al. (2004 and 2005) it was proven that large amounts of the compounds were sorbed to the membrane and a substantial part of the total removal was due to sorption effects. This was relevant for all selected compounds.

Table 2. General operational parameters and experimental conditions of the direct NF pilot tests and retention of BPA and EE2 (R_{tot*} = total removal corrected, without adsorption to NF and plant)

Flux	Recovery	TMP	Permeability	BPA retention, %			EE2 retention, %		
L/(m²·h)	%	bar	L/(m²·h·bar)	R_{NF}	R_{tot}	R_{tot*}	R_{NF}	R_{tot}	R_{tot*}
15	75	1.9	8.8	44.5	58.5	17.0	71.6	67.3	39.3
20	75	2.0	10.0	28.8	43.1	9.5	62.6	52.9	29.5
25	75	2.9	8.9	17.0	37.1	5.0	62.6	52.1	31.0
20	65	2.6	8.7	-5.1	35.4	-1.6	53.6	43.4	27.9

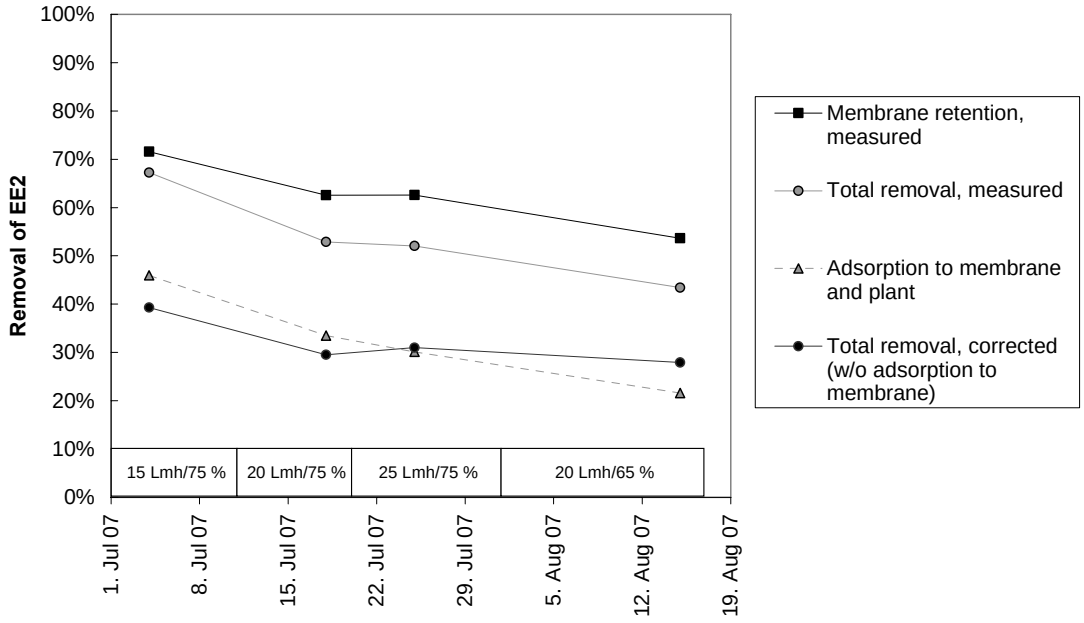

Figure 2. Average removal of EE2 in direct NF with spiked effluent (spiking conc. ~ 1 µg/L)

Under changing operation conditions permeate concentrations sometimes exceeded the retentate concentrations presumably due to desorption from the membrane. When the feed concentrations were reduced to about 0.1 µg/L (1/10 of the average spiking concentration), the adsorption of EE2 to the membrane stopped while the adsorption of BPA decreased by 20 %.

Repeating the set point of a 20 L/m²·h flux and a 75 % recovery with a pre-fouled chemically cleaned membrane, no saturation of the membrane was observed (see Fig 3) when applying continuous spiking for two weeks. The initial high adsorption to the membrane (BPA 30 %, EE2 40%) diminished and leveled off at 10 to 20%. The portion of trace compounds found in the retentate was rather stable at 25 to 30% for BPA and about 35% for EE2.

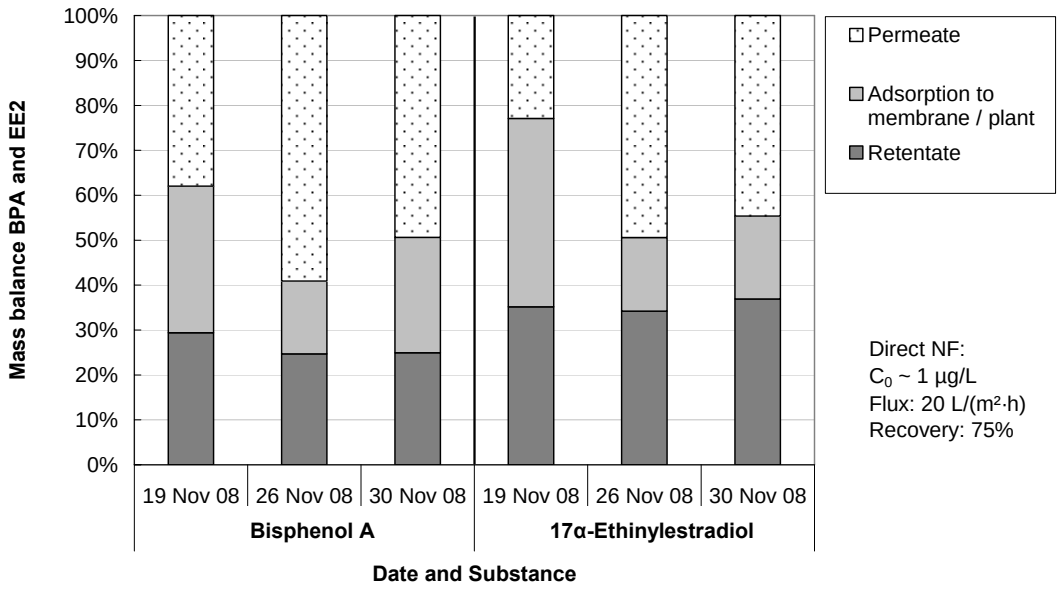

Figure 3. Mass balance of BPA and EE2 in long-term spiking test (2 weeks continuous spiking with pre-fouled membrane after chemical cleaning)

Cytarabine and 5-Fluorouracil. Due to health concerns, the cytostatics were only applied during the tests with a flux of 20 L/m²·h and a recovery of 75%. With an average raw water concentration of 2.5 µg/L 5-FU and 1.6 µg/L CytR only 4% of the spiked 5-FU and 24% of the spiked CytR were detected. The real total removal of the highly polar compounds was relatively low (see Table 3).

Table 3. General operational parameters and experimental conditions of the direct NF pilot tests and retention of CytR and 5-FU (R_{tot*} = total removal corrected, without adsorption to NF)

Flux	Recovery	TMP	Permeability	CytR retention, %			5-FU retention, %		
L/(m²·h)	%	bar	L/(m²·h·bar)	R_{NF}	R_{tot}	R_{tot*}	R_{NF}	R_{tot}	R_{tot*}
20	75	2.5	10.0	80.8	46.6	18.0	97.2	59.8	27.0

In a subsequent test for chemical stability and biodegradation no significant losses were detected. When checking the adsorbability to the membrane the cytostatics also showed less affinity to the membrane material than for instance the selected EDCs. A conclusive explanation for the significant losses cannot yet be given.

Powdered activated carbon in combination with nanofiltration

Bisphenol A and 17α-ethinylestradiol. Addition of a wide range of PAC and LCD was tested for a more stable removal of the target compounds. It proved substantial performance improvement with removal rates above 90 - 95% at a low PAC dosage of 10 to 50 mg/L as shown before in lab scale tests (Lehnberg et al., 2007). At the highest PAC dosage of 100 mg/L a 2.5 to 3 log unit removal of BPA and EE2 was detected. Adsorption to the membrane and desorption effects were less prevalent. While the DOC was only partly adsorbed at low PAC doses, the EDCs featured a significantly higher adsorbability to the tested PAC (see Fig 4).

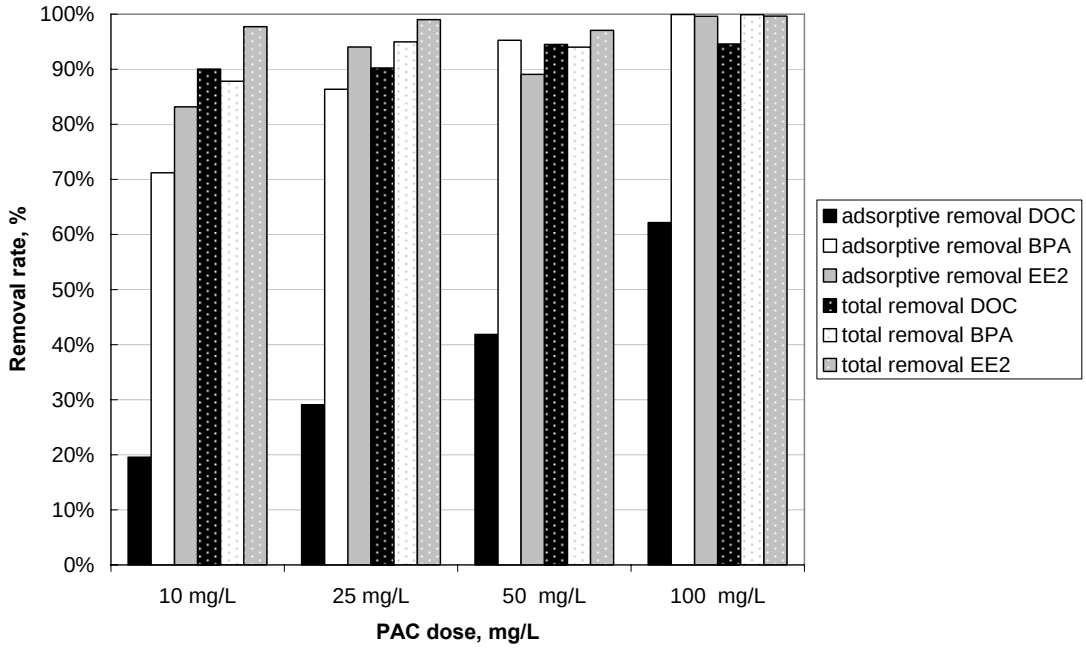

Figure 4. Adsorptive and total removal of DOC, BPA and EE2 with dosage of PAC

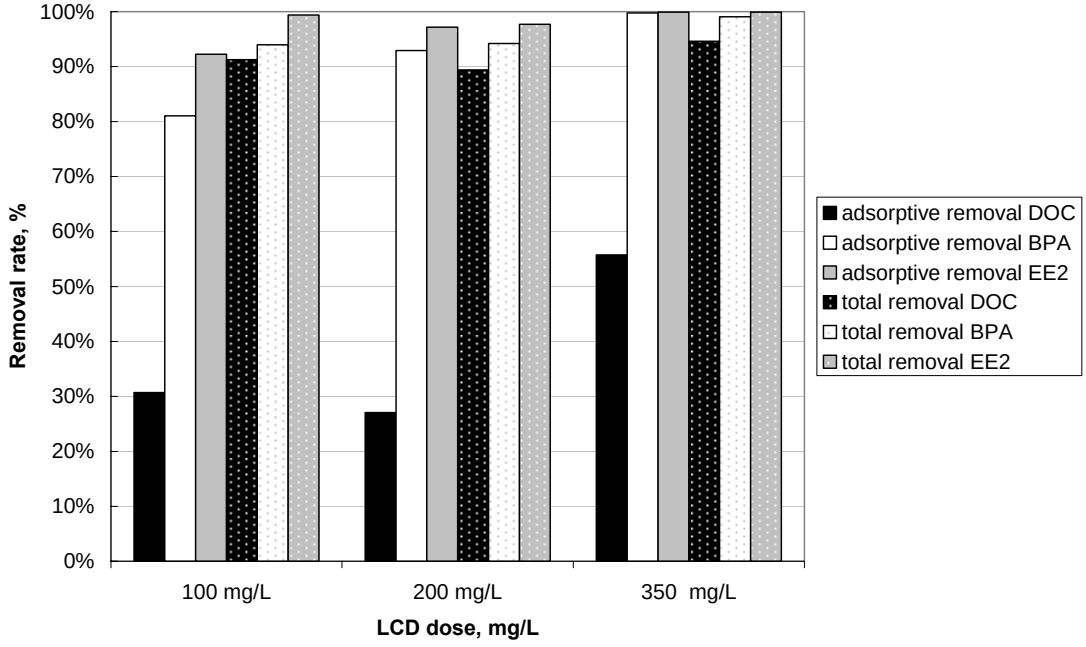

Figure 5. Adsorptive and total removal of DOC, BPA and EE2 with dosage of PAC

As known from former tests with lignite coke dust (Kazner et al., 2008) a three to four times higher

dose than PAC is required for achieving a similar removal of bulk organics. This proved to be also valid for the selected EDCs. When applying 100 to 200 mg/L LCD the combination of adsorptive removal and membrane retention eliminated 94 to 99% of the targeted micropollutants. Although suspended solids concentrations above 200 mg/L are somewhat problematic from an operational perspective 350 mg/L (corresponding to 100 mg/L PAC) were tested and showed a 99.9% removal of BPA and EE2.

Figure 6 shows the comparison of the lab adsorption tests with the adsorption in the pilot unit. While there were no large differences regarding temperature, pH, NOM level, and mixing, the contact time in the PAC reactor was considerably smaller than in the lab tests. The kinetic influence was more important in the low concentration range of 10 to 25 mg/L, presumably due to a greater competition between NOM and EDCs. At high PAC concentrations the differences between the lab and the pilot test diminish clearly reaching a complete removal of the EDCs at 100 mg/L.

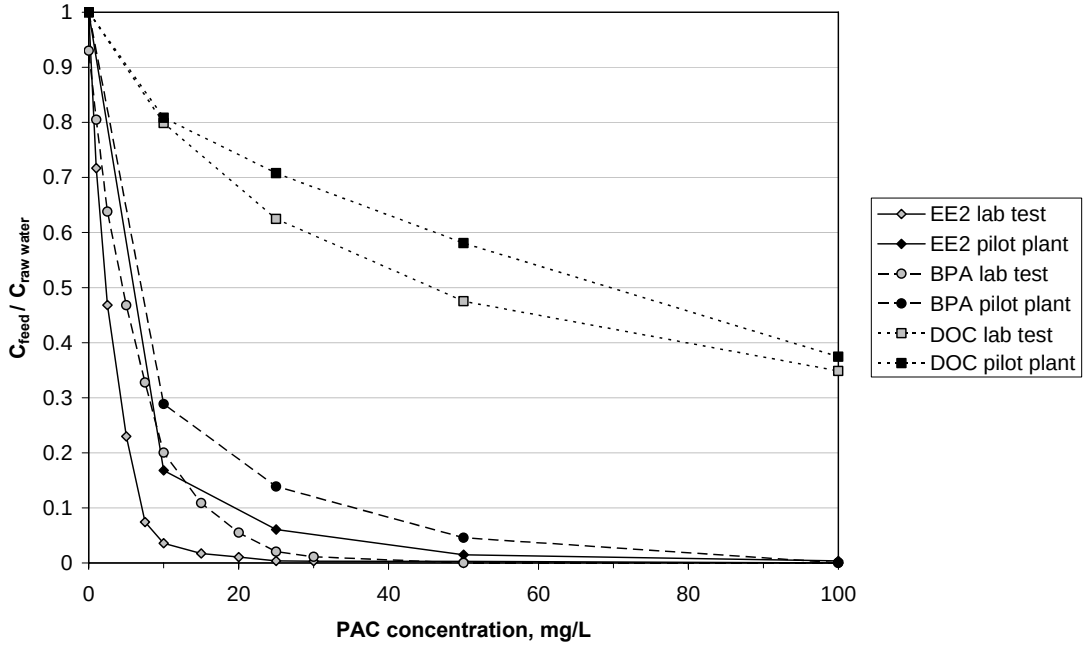

Figure 6. Comparison of adsorption of DOC, EE2 and BPA in lab test and pilot test (contact time in lab test 24 h and in pilot test 1.2 h)

Cytarabine and 5-Fluorouracil. As the permeate and retentate concentrations were already close to the limit of detection when applying direct NF, the combination with powdered activated carbon is not considered as a necessary process improvement. For practical reasons the foreseen tests were therefore omitted.

CONCLUSIONS

The endocrine disruptors EE2 and BPA showed in direct nanofiltration relatively low real total removal of 30 to 40% for EE2 and 5 to 17% for BPAwas between 5 and 40%. Adsorption to the membrane played a major role leading to a seemingly total removal between 35 and 70%. In pilot scale and moreover in full scale NF plants, the permeate concentration depends not only on the operation conditions such as flux, transmembrane pressure, NOM level and ionic strength (Nghiem *et al.*, 2004) but also on the ever changing equilibrium between adsorption and desorption to the membrane which can lead to peaks in the permeate.

The process performance can highly be improved by combining NF with an upstream PAC adsorption step. Low carbon doses of 10 to 50 mg/L PAC can increase the removal to >95 to 99%. Due to the low remaining retentate concentrations, the impact of feed variation is largely reduced.

Through selection of the adsorbent and the dosage, the PAC/NF process allows the exact adjustment of the permeate quality according to the site specific requirements. Adsorption of the EDCs to the powdered carbon occurs relatively fast and reaches about 80 to 90% of the adsorptive capacity in the equilibrium already after about one hour contact time. Powdered activated carbon in combination with nanofiltration proved to produce high quality water from tertiary effluent suitable for a wide range of challenging applications.

The investigated cytostatic drugs CytR and 5-FU showed surprisingly high losses of 76 and 96% in the NF plant. The cause of these losses could not finally be explained and will be subject of future research.

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