Influencing parameters for the operation of an MBR with respect to the removal of persistent organic pollutants

Lipp P.(1), Kreißel K.(1), Meuler S.(3), Bischof F.(4), Tiehm A.(2)
(1,2) Water Technology Center, Karlsruher Str. 84, 76139 Karlsruhe, Germany
(1) Department Technology (lipp@tzw.de), (2) Department Environmental Biotechnology (tiehm@tzw.de)
(3) Hans Huber AG, Industriepark Erasbach A1, 92234 Berching (mes@huber.de), Germany
(4) University of Applied Science Amberg-Weiden, Kaiser-Wilhelm-Ring 23, 92224 Amberg, Germany (bf@huber.de)

Abstract
Membrane bioreactors (MBR) are increasingly considered for de-centralized waste water treatment. In this study, the operation parameters on a pilot MBR were optimized, and the removal of organic pollutants such as pharmaceutical residues was studied. During the first phase of the research project, two membrane materials (polyethersulfone, polysulfonamide) were chosen for the manufacturing of plate modules and operation in a pilot plant, which was installed in a municipal wastewater treatment plant (20.000 p.e.).
Operation conditions were optimized with regard to flux, filtration time, aeration rate, sludge age, total suspended solids, etc. Both membranes were ultrafiltration membranes and therefore achieved a very good retention with regard to particles (microorganisms and turbidity). In comparison to the conventional wastewater treatment process the system performance with regard to COD removal was higher in the MBR. Analysis of samples taken from the MBR process tank and the filtrate of both membrane types showed an improved elimination of some specific organic pollutants. Due to the promising results, more process based MBR studies are encouraged.

Keywords
membrane bioreactor, persistent organic pollutants, operation parameters

Introduction
As part of the SMART Jordan Valley project [1], new integrated approaches for water management, aquifer recharge, and wastewater reuse are developed. Decentralized membrane bioreactor technologies combined with consecutive subsoil conditioning are studied with respect to the removal of persistent organic pollutants (POPs) and pathogenic organisms. Regarding the ubiquitous spreading of pharmaceutical active substances in the aquatic environment, it seems obvious that they enter the surface water with effluents of wastewater treatment plants (WWTP) due to incomplete elimination by conventional biological wastewater treatment [2]. Biodegradability varies significantly for the different pharmaceutical residues. For example, the antiepileptic drug carbamazepine was not removed in various WWTPs [3,4]. For diclofenac, in some wastewater treatment processes elimination rates of 50 - 90 % appeared, whereas only slight removal was observed in other WWTPs [3,4,5]. Other compounds such as the analgesics ibuprofen and naproxen or the lipid regulators gemfibrozil and bezafibrate were removed up to > 90 % [4,5,6].
Improvement of sewage treatment, for instance through membrane technologies, by higher solid retention times or combinations of aerobic and anoxic conditions, is considered to enhance biological elimination of pharmaceuticals and other degradable micropollutants to reduce their emission into aquatic environments [3,7,8,9]. In this research a MBR (Membrane Bioreactor) has been operated under the objective of an optimized elimination of POPs [9].

MATERIALS AND METHODS

Membrane bioreactor. The MBR pilot plant (Huber AG, Berching, Germany) consists of a process tank (volume 800 L) in which two plate and frame membrane modules of 2 m² membrane area each are submerged. Two different membrane types were tested in parallel. A schematic of the MBR process is shown in Figure 1. Membranes used were characterized with regard to surface properties (contact angle) and permeability. Details are given in Table 1. As depicted in Figure 2 (a) and (b) the modules consist of 25 plates with a space of 10 mm in between. The filtrate flux of both membranes was adjusted to 15 L/m²/h and kept constant during long term operation. For determination of critical flux it was increased up to 35 L/m²/h for short periods of less than 2 hours.

For mechanical cleaning of the membrane surface the filtration process is interrupted regularly for 0.5-1 min of relaxation time. Filtration time varied between 2 and 9 min. Membranes are aerated continuously (0.25-1.5 Nm³/m²/h) in order to support removal of depositions on the membrane surface. For biological degradation processes the process tank is aerated intermittently with 6 Nm³/h.

Analytical methods. COD was measured according to DIN 38409-H41 using cuvette tests LCK414 and 514 (Hach Lange). For the determination of NH4-N the cuvette test LCK304 has been used.

High-performance liquid chromatography with tandem mass spectrometric detection was used to determine the concentrations of all pharmaceuticals. A solid-phase extraction at pH 3 was performed using styrene divinylbenzene material. The limit of detection (LOD) is 10 ng/L for all pharmaceuticals in drinking water samples. However depending on the water type due to the need of dilution during sample preparation LOD may go up to 250 ng/L. More information about the analysis was previously published [10]. Detection of endocrine disrupting agents and organophosphorous compounds occurred by GC-MS after solid phase enrichment, with an additional step of derivatisation in case of the endocrine disruptors.

Contact angle was measured using an optical measuring system (OCA 15 Plus, Dataphysics GmbH, Filderstadt, Germany). A static captive bubble method as well as the sessile drop method was applied.

RESULTS AND DISCUSSION

Before operating membranes A and B in the MBR their clear water permeability and surface properties (contact angle) were determined. As can be seen from results in Table 1 there is not much difference between the two membranes regarding permeability and contact angle. Just membrane material and pore size/MWCO are different. However both membranes were operated in parallel in the MBR process tank. Conditions are given in Table 2.

The MBR was operated at a conventional wastewater treatment plant (CWWTP) where the feed water is only marginally affected by industrial wastewater. The chosen municipal WWTP has a capacity of 20.000 p.e. and consists of a mechanical screen (slit width 8 mm), a sand capture and grease removal in front of the activated sludge reactor. Denitrification and nitrification processes are realised by intermittent aeration of the activated sludge. The overall sludge age is 20 d, the mean content of total suspended solids (TSS) approximately 5-6 g/L. COD of the CWWTP feed is in the range of 400-700 mg/L, however during storm water events it may be lower (300-400 mg/L) and while cleaning the storm water basin it may increase up to 1000 mg/L. The efficiency of the plant with regard to COD and NH4-N removal is sufficient to cope with the standards. As shown in Table 3 the COD of the effluent is in the range of 25-40 mg/L.

In the filtrates of the MBR the COD values were lower in the range of 15-20 mg/L. Elimination for COD and NH4-N were larger than 95 %. More over the filtrate quality of the MBR is very good (< 0.2 NTU, < 100 Coliforms/100 mL).

Sludge age is an important design parameter for a WWTP and describes the mean retention time of the biomass in the activated sludge plant. At higher sludge age, also micro-organisms with a slow growth rate are present in the system. This gives the chance for specialists to adapt and eliminate more persistent substances. The higher sludge age is considered to be one reason for the higher pollutant removal by the MBR as compared to the cWWTP.
At sludge ages < 4 days there is almost no degradation of pharmaceuticals, however, at sludge ages between 10 and 15 days the elimination of a variety of substances is enhanced [4].
In MBR sludge ages of 25 days and more may be achieved without problems. This helps to enhance the elimination of persistent substances. An increased removal efficiency is also achieved by a higher content of TSS in the MBR. In MBR systems TSS may be 2-3 times higher than for CWWTP. However this requires a higher energy demand for the aeration of the sludge in the MBR. This is a drawback for the application of MBR that has to be looked at more thoroughly.

Within six months of operation a couple of tests were carried out with different operation conditions as given in Table 2. During the MBR operation the following observations have been made [11].
A mechanical cleaning of the modules had to be carried out in the beginning of the test runs because adverse sludge properties (TSS 20 g/L and sludge age 5 d) caused the blocking of the modules. Figure 2(c) illustrates the blocking. A chemical cleaning (caustic soda at pH 10; citric acid at pH 2) was not effective in this case. However it was required and effective in the case when coagulant aid had to be removed from the membrane surfaces. It had been added to the CWWTP to avoid floating sludge and caused a drastic pressure increase.
TSS-content of 10-12 g/L at sludge ages of 20-25 days allowed a stable operation of the MBR at reasonable transmembrane pressures for both membranes. Surplus sludge has to be regularly removed from the MBR process tank in order to keep sludge age and TS constant.
There is not much difference between the two membranes with regard to operation behaviour and elimination of substances.
The monitoring of the hydrodynamic influence (cake formation) gives information on the filtration performance of the membranes [12]. The authors observed a limiting value of $dP/dt=50$ mbar/h for the critical flux. With both membranes a critical flux of 30 $L/m^2/h$ has been determined. Higher fluxes cause higher TMP increase by irreversible fouling. Figure 3 shows the results for MBR-B.
During several runs a critical aeration rate of 0.5 Nm^3/h has been determined for the critical flux of 30 $L/m^2/h$. Even for lower fluxes aeration is required and cannot be replaced by a cross-flow with air/water.
A critical content of TSS of 12 g/L should not be exceeded in order to avoid blocking of the membranes.
Keeping conditions below critical values a stable operation is possible. Then a mechanical rinsing of the membranes is sufficient to recover permeability.

In order to determine the elimination of POPs during MBR treatment representative mixed samples were taken from the feed and the filtrates of the MBR under consideration of the hydraulic retention time (HRT). For comparison with the elimination during conventional treatment samples have been also taken from feed and effluent of the activated sludge plant of the CWWTP. Samples have been analysed for a number of 30 substances out of the groups of

analgesics, betablockers and trialkylphosphates. Half of the substances (e.g. phenacetin, clofibric acid, diazepam, betaxolol, propranolol, triethylphosphate) have not been detected in either samples. The analytical results (values given in ng/L) of the other substances are listed in Table 4. From these values elimination rates have been calculated and illustrated in Figure 4. In this graphics a standard deviation of 30 % is considered for the analytical results. As can be seen from Figure 4 some POPs were eliminated in both types of systems with no difference. However some substances out of all three groups showed a better elimination rate within MBR than CWWTP. These were Fenofibric acid (ffs), Gemfibrozil (gfz), Bisoprolol (bpo), Triphenylphosphate (tpp) and Tris(2-chloroethyl) phosphate (tcep).
The comparison of data showed no difference between the two membranes operated within the MBR.

Conclusions

Trace concentrations of persistent organic pollutants (POPs) have been detected in WWTP effluents and surface waters. Wastewater reuse and artificial groundwater recharge may result in significant pollutant accumulation over time. Therefore, the elimination of persistent pollutants represents a key factor in integrated water resources management in arid regions. Operation of MBR has shown that it is possible to increase the elimination of some POPs in the MBR compared to CWWTP. Sludge age and content of total suspended solids are important factors in this respect. For the operation of the MBR critical values for flux and aeration rate have to be considered. In the ongoing research it is intended to compare microfiltration with ultrafiltration membranes and run long term tests with critical flux to check operation stability.

Acknowledgement

The authors gratefully acknowledge funding by the German Federal Ministry of Education and Research (02WM0803). The study is associated with the joint research project “Sustainable Management of Available Water Resources with Innovative Technologies (SMART)”.

References

[1] SMART - Sustainable Management of Available Water Resources with Innovative Technologies (2007). http://www.iwrm-smart.org/.
[2] Ternes, T.A. (1998): Occurrence of drugs in German sewage treatment plants and rivers. Water Research, 32/11, 3245-3260.
[3] Joss, A., Zabczynski, S., Gobel, A., Hoffmann, B., Loffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A., Siegrist, H. (2006). Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. Water Research, 40 (8), 1686-1696.
[4] Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., Kroiss, H. (2005a). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Research, 39 (19), 4797-4807.
[5] Radjenovic, J., Petrovic, M., Barcelo, D. (2007). Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. Analytical and Bioanalytical Chemistry, 387 (4), 1365-1377.
[6] Jones, O.A.H., Voulvoulis, N., Lester, J.N. (2005): Human pharmaceuticals in wastewater treatment processes. Critical Reviews in Environmental Science and Technology, 35/4, 401-427.

[7] Clara, M., Kreuzinger, N., Strenn, B., Gans, O., Kroiss, H. (2005b). The solids retention time - a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. Water Research, 39, 97-106.
[8] Zwiener, C., Frimmel, F.H. (2003). Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen, and diclofenac. Science of the Total Environment, 309 (1-3), 201-211.
[9] Lipp, P., Stieber, M., Meuler, S., Bischof, F., Tiehm, A. (2007): Development of innovative processes for waste water treatment by MBR with respect to the removal of persistent organic pollutants. In: 6th IWA Specialist Conference on Wastewater Reclamation and Reuse for Sustainability, 9-12 Oct. 2007, Antwerp (Belgium): 4 pages (Proceedings CD).
[10] Sacher, F., Lange, F.Th., Brauch, H.-J., Blankenhorn, I. (2001): Pharmaceuticals in Groundwaters – Analytical Methods and Results of a Monitoring Program in Baden-Württemberg, Germany. Journal of Chromatography A, 938/1-2, 199-210.
[11] Kreißel, K.: Untersuchungen zu den Einsatzmöglichkeiten von zwei verschiedenen Membranen zur Abwasserbehandlung mittels Membranbioreaktor unter Berücksichtigung der Entfernung ausgewählter Spurenstoffe. Diplomarbeit University of Karlsruhe 2008.
[12] Le-Clech, P., Jefferson, B., Judd, S. J., (2003). Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of membrane bioreactor. Journal of Membrane Science, 218, 117-129.

LIST OF TABLES AND FIGURES

Table 1: Membrane specification for MBR

properties		**membrane type A MBR-A**	**membrane type B MBR-B**
material (active layer)		polyethersulfone	polysulfonamide
pore size / MWCO*		38 nm pore size	150 kD
contact angle,			
sessile drop	°	68.6±7	67.6±5.8
captive bubble	°	43.2±4.2	46.6±3.0
permeability (20°C)			
(clear water),	L/m²/h/bar	350-620	320-510
membrane area,	m²	2	2

MWCO = molecular weight cut off

Table 2: MBR operation and sludge conditions

Parameters		**MBR-A and MBR-B**
filtrate flux	L/m²/h	10, 15, 20, 25, 30
transmembrane pressure	mbar	-20 … -800
filtration time interval	min	4.5 or 9
time for relaxation	min	0.5 or 1
air for cleaning	Nm³/h	0.5 - 3
sludge age	d	5 - 30
sludge loading	g/g/d	0.05 – 0.06
TSS within process tank of MBR	g/L	6-12
hydraulic retention time HRT	h	5 - 24
Temperature	°C	13-16

Table 3: feed and filtrate water properties

Parameters		**Feed CWWTP**	**Filtrate CWWTP**	**Filtrate MBR-A and MBR-B**
COD,	mg/L	400-700	25-40	15-20
total N,	mg/L	60-80	3-4	3-4
total P,	mg/L	10	1-2	-

Table 4: Elimination of POPs by conventional waste water treatment plant and MBR

Parameter		unit	Feed CWWTP	Effluent CWWTP	Feed MBR	Filtrate MBR-A	Filtrate MBR-B
Analgesics							
Bezafibrate	(bzf)	ng/L	**960**	**190**	**540**	< 50	< 50
Carbamazepine	(cmz)	ng/L	**2000**	**2200**	**1800**	**1600**	**1600**
Diclofenac	(dcf)	ng/L	**4700**	**2200**	**3400**	**1500**	**1500**
Fenofibric acid	(ffs)	ng/L	**1100**	**530**	**1300**	< 50	< 50
Gemfibrozil	(gfz)	ng/L	**2600**	**880**	**1500**	< 50	< 50
Ibuprofen	(ibf)	ng/L	**11000**	**1200**	**11000**	**72**	**79**
Indomethacine	(inm)	ng/L	< 200	< 100	**130**	**57**	**54**
Ketoprofen	(kpf)	ng/L	**750**	**420**	< 100	< 50	< 50
Naproxen	(npx)	ng/L	**1000**	**200**	**1300**	**65**	**62**
Betablockers							
Atenolol	(ato)	ng/L	**600**	**260**	**350**	**150**	**140**
Bisoprolol	(bpo)	ng/L	**310**	**180**	**200**	**50**	< 50
Metoprolol	(mpo)	ng/L	**1700**	**1300**	**1100**	**840**	**770**
Sotalol	(sto)	ng/L	**580**	**580**	**400**	**460**	**480**
Trialkylphosphates							
Triphenylphosphate	(tpp)	ng/L	< 250	< 130	**1200**	< 125	**180**
Tris(2-chloroethyl) phosphate	(tcep)	ng/L	< 250	**130**	**140**	< 125	< 130
Tris(2-chloropropyl) phosphate	(tcpp)	ng/L	**740**	**400**	**1100**	**470**	**490**

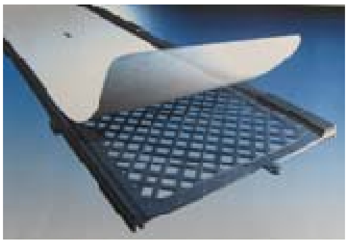
(a)  (b)  (c) 

Figure 1: view of a single membrane plate (a), the top of a clean plate and frame module (b) and a blocked membrane module (c)

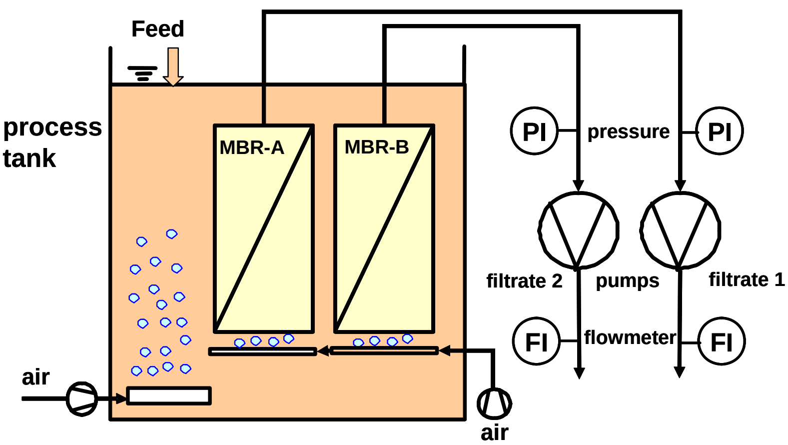


Figure 2: Schematic illustration of MBR instrumentation

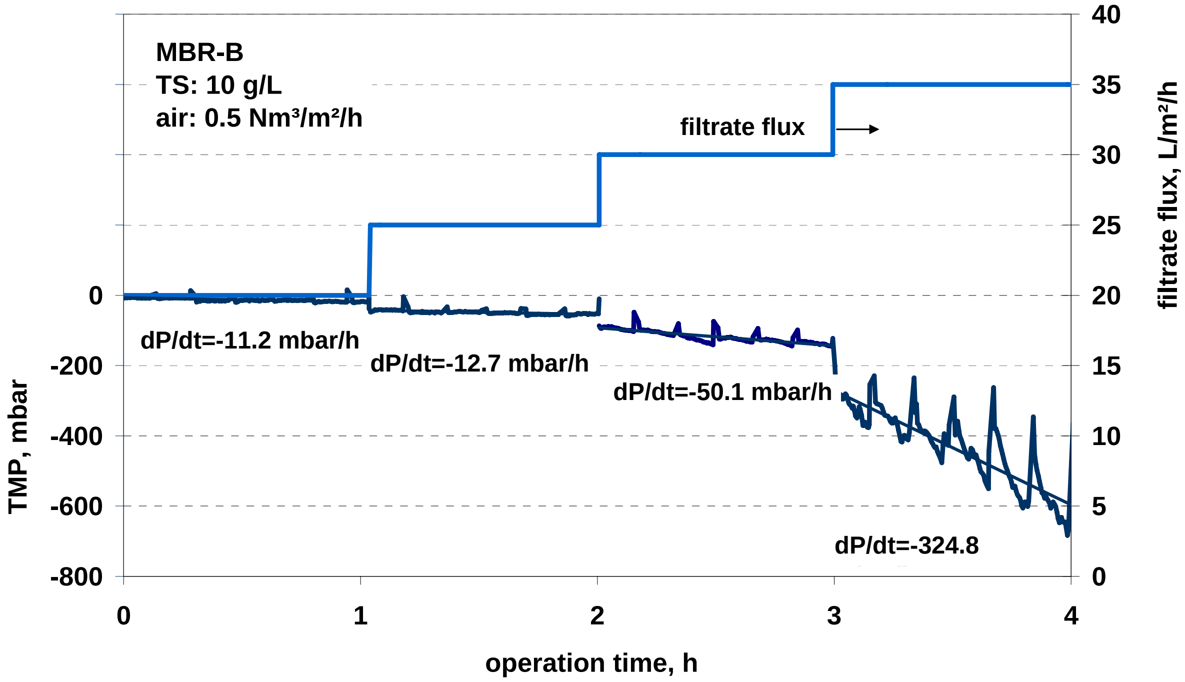


Figure 3: determination of critical flux

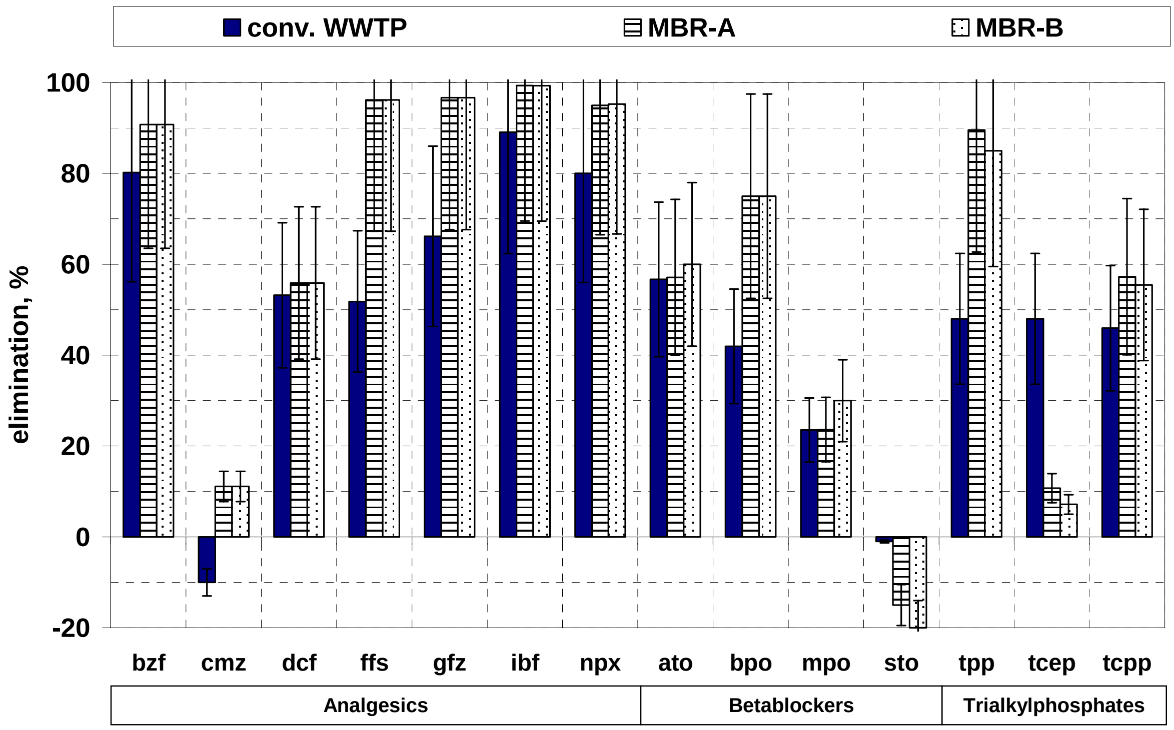


Figure 4: Elimination of POPs by conventional wastewater treatment and MBR