

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

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ABSTRACT

Membrane bioreactors (MBR) are increasingly considered for decentralized 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

1. 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 [3–5]. Other compounds such as the analgesics ibuprofen and naproxen or the lipid regulators gemfibrozil and bezafibrate were removed up to >90% [4–6].

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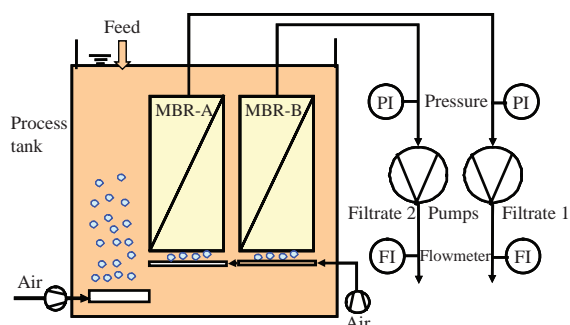


Fig. 1. Schematic illustration of MBR instrumentation.

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 [3,7–9]. In this research a membrane bioreactor (MBR) has been operated under the objective of an optimized elimination of POPs [9].

2. 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 Fig. 1. Membranes used were characterized with regard to surface properties (contact angle) and permeability. Details are given in Table 1. As depicted in Fig. 2a 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 h.

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 LCK514 (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.

3. 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 was 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.

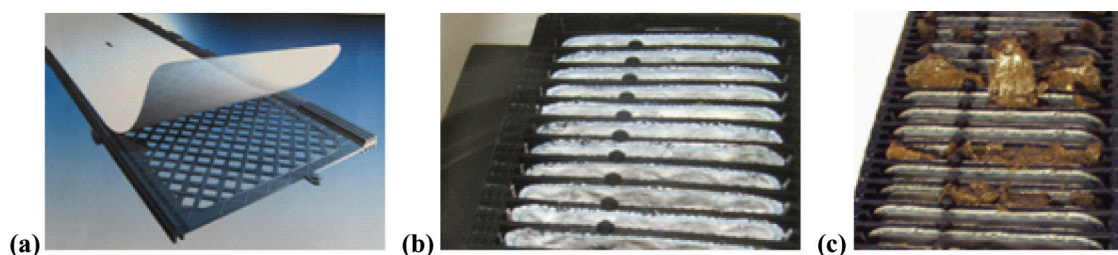


Fig. 2. View of a single membrane plate (a), the top of a clean plate and frame module (b) and a blocked membrane module (c).

Table 1
Membrane specification for MBR

Properties	Membrane type A MBR-A	Membrane type B MBR-B
Material of active layer	Polyethersulfone	Polysulfonamide
MWCO* (pore size, nm)	150 kD (38 nm)	150 kD (no value available)
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/m ² /h/bar)	350–620	320–510
Membrane area (m ²)	2	2

* MWCO = molecular weight cut off.

The chosen municipal CWWTP 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. The mean daily throughput of the plant is 2,500 m³. 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

Table 2
MBR operation and sludge conditions

Parameters		MBR-A and MBR-B
Filtrate flux	L/m ² /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	Nm ³ /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	–
Turbidity (NTU)	–	–	<0.2
Coliforms (1/100 mL)	–	–	<100

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 microorganisms 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 6 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

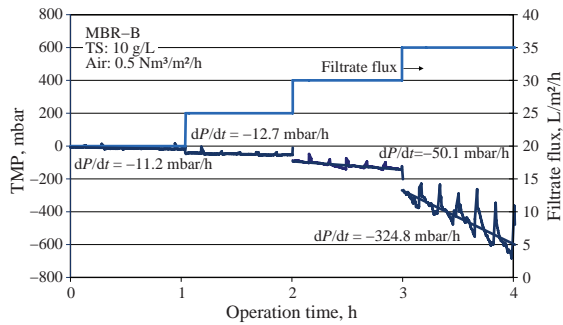


Fig. 3. Stepwise increase of filtrate flux from 20 to 35 L/m²/h to determine critical flux.

5 d) caused the blocking of the modules. Fig. 2c 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 in the MBR process.

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 (TMPs) for both membranes. Surplus sludge has to be regularly removed from the MBR process tank in order to keep sludge age and TS constant.

A comparison of the results showed that there is not much difference between the two membranes with regard to operation behaviour and elimination of substances.

3.1. MBR optimization

In order to optimize MBR operation with regard to performance and energy demand several runs were carried out to maximize flux and minimize aeration input. The initial value of 15 L/m²/h has been recommended as flux for long term operation by Huber AG.

This value is also realised in many other practical applications.

From literature it is known that the membrane filtration process is limited by a critical flux where the increase in TMP is too high for an economic operation [12]. The authors observed a limiting value of TMP increase of $dP/dt = 50$ mbar/h for the critical flux. With both membranes a critical flux of 30 L/m²/h has been determined. Higher fluxes cause higher TMP increase by irreversible fouling. Fig. 3 shows the results for MBR-B.

During several runs critical flux has been determined for two different aeration rates 0.25 and 1.5 Nm³/m²/h and two intervals for filtration/relaxation (see Table 4). Critical flux was 30 L/m²/h for the lower aeration rate but was not reached for the higher aeration rate. Within another set of runs flux has been kept constant at 30–35 L/m²/h for both membranes and aeration rate has been varied (see Table 5). There was not much difference between the membranes or the filtration/relaxation intervals. For this flux range a critical aeration rate of 0.5 Nm³/m²/h has been determined. Even for lower fluxes aeration is required. Runs without air caused a blocking of the membranes. A blocking of the membranes could also not be hindered by a cross-flow with air/water along the membrane surfaces.

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 for TSS, flux and aeration a stable operation of the MBR process is possible. Under such conditions a mechanical rinsing of the membranes is sufficient to recover permeability.

3.2. Elimination of POPs

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

Table 4
TMP increase (mbar/h) as a function of flux, aeration rate and filtration/relaxation – interval for both membranes

Flux (L/m ² /h)	Filtration/relaxation 4.5 min/0.5 min		Filtration/relaxation 9 min/1 min	
	Aeration rate 0.25 Nm ³ /m ² /h	Aeration rate 1.5 Nm ³ /m ² /h	Aeration rate 0.25 Nm ³ /m ² /h	Aeration rate 1.5 Nm ³ /m ² /h
10	<10	<10	–	–
15	10	<10	–	–
20	26	12	12–32	<10
25	32	<10	12	<10
30	82–85	15	35–50	<10
35	>200	–	>200	<10

Table 5

TMP increase (mbar/h) as a function of aeration rate and filtration/relaxation – interval and membrane material at a flux of 30–35 L/m²/h

Aeration rate Nm ³ /m ² /h	Filtration/relaxation 4.5 min/0.5 min		Filtration/relaxation 9 min/1 min	
	MBR-A	MBR-B	MBR-A	MBR-B
1.5	<10	32	<10	<10
1.0	<10	15	<10	<10
0.75	<10	<10	25	20
0.5	<10	25	<10	<10
0.25	60	123	35	83

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, beta-blockers 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 6. From these values elimination rates have been calculated and illustrated in Fig. 4. In this graphics a standard deviation of 30% is considered for the analytical results. As can be seen from Fig. 4 some POPs were

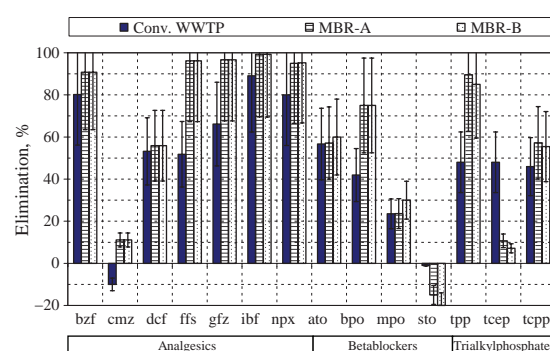


Fig. 4. Elimination of POPs by conventional wastewater treatment and MBR.

Table 6

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
<i>Analgesics</i>						
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	11,000	1200	11,000	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
<i>Betablockers</i>						
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
<i>Trialkylphosphates</i>						
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

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-chloropropyl) phosphate (tcpp).

The comparison of data showed no difference between the two membranes operated within the MBR.

4. Conclusions

Trace concentrations of 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 TSSs 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.

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