GOOD REMOVAL CAPACITIES FOR HORMONES AND MEDICINE RESIDUES

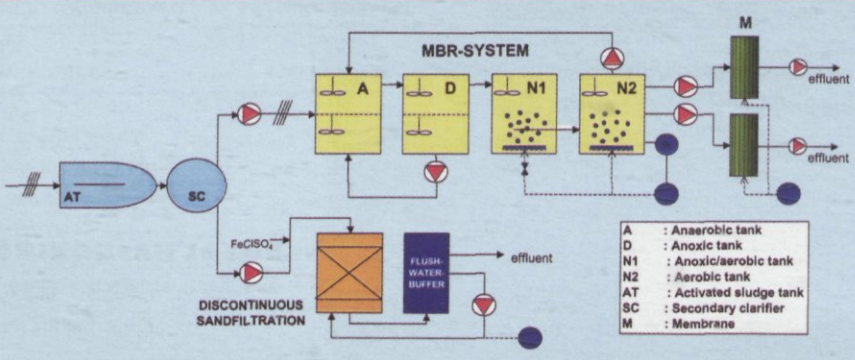
MBR-research at WWTP Leeuwarden for the post treatment of effluent

The Frisian capital Leeuwarden wants to make the city canals more attractive and wants the water in the centre to be separated from the surrounding (nutrient rich) surface water by means of a special water separation construction. These constructions allow the boats and canoes to pass but will minimize the flow of surface water to the centre. To improve the water quality of the canals in Leeuwarden, it is the intention to transport treated effluent of the WWTP Leeuwarden to the canals of the city centre of Leeuwarden. The intention is to make the canals suitable for recreation and to develop ecological areas.

The WWTP has been renovated entirely in 2001, but the effluent still contains too many contaminants to be able to use it as recreation water. Also there was a concern for micro-contaminants. In the middle of 2003 the three-year study on WWTP Leeuwarden into the post treatment of the effluent of WWTP has started. Two systems for treating the effluent, sand filtration (SF) and membrane bioreactor (MBR), have been examined more closely. The research of the MBR is carried out by Wetterskip Fryslân and Vitens at the WWTP of Leeuwarden. Two subjects for research are the specific biological population, which may develop in the MBR and the removal of organic micro-contaminants. This article focuses on the MBR research project.

MBR-pilot at WWTP Leeuwarden.

Figure 1: Lay out MBR for post treatment effluent of WWTP Leeuwarden.



System description

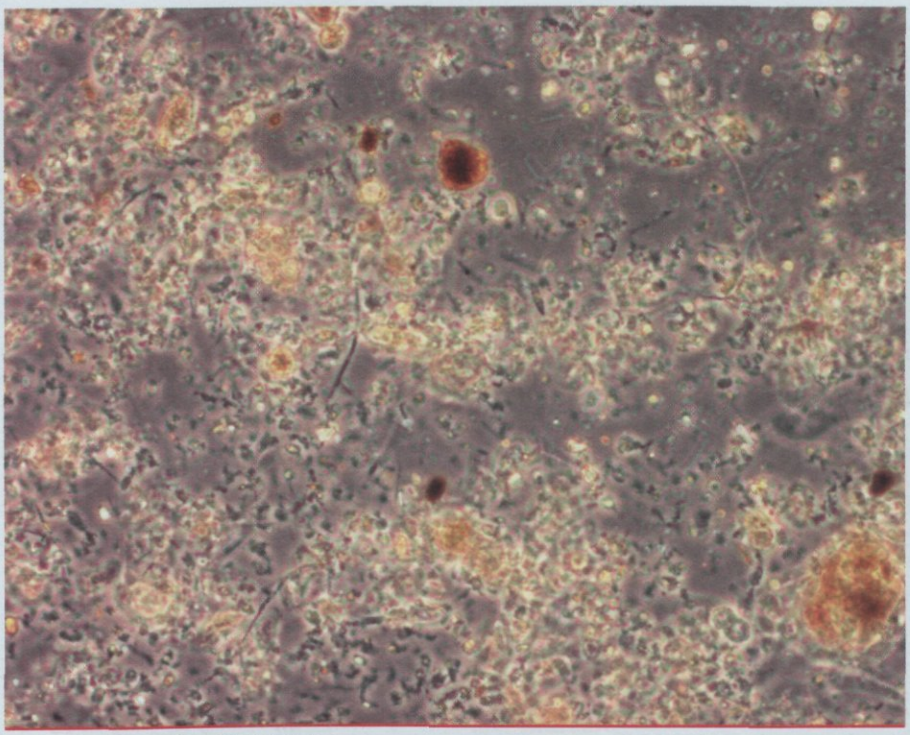
Normally MBR is applied as an integral purification technique, meaning treatment of WWTP influent. At the WWTP site of Leeuwarden however the MBR is used for effluent treatment. The MBR system (see figure 1) is equipped with X-Flow ultra filtration side-stream membranes (0.03 µm pore size) and has a capacity of 8 m³/h.

The MBR was designed with respectively an anaerobic, anoxic and aerobic compartment. However, the very low BOD content in the effluent of the WWTP and the cleaning of the membranes with air, in combination with the recirculation flows, ensured aerobic conditions in all compartments. Consequently the MBR is not capable to remove phosphate and nitrogen biologically at this time.

Unique micro-organisms

The research workers expect that treating the WWTP-effluent in a MBR, enables the development of a unique bacterial population due to extreme high sludge ages. Microscopic analyses (see photograph) show a typical picture of this type of sludge.

The sludge quantity increases very slowly. In 1.5 year time, sludge concentration has increased from 2 to 4.5 g SS/l. Still no sludge has been withdrawn from the system and sludge age is at this point infinite. From the determination of the ash content of the sludge it appears that the non-organic part has increased to 50%, while normal activated sludge shows values between 30 and 40%. It is very likely that the sludge is mineralising itself as a consequence of the low BOD load and therefore the sludge shows a relative low activity and slow growth.



MBR sludge Leeuwarden with high sludge age.

Table 1: Analyse methods and detected compounds of micro-contaminants in influent and effluent of MBR at WWTP Leeuwarden.

analyses	analysing method	detected compounds	laboratory
79 non-volatile compounds	GC-MS	benzylbutylphtalate, bi-sethylhexylphtalate, di-butylphtalate, di-ethyl-phtalate, di-isobutylphtalate, di-n-octylphtalate	Wetterskip Fryslân
phenols en alcohols	GC-MS	- not detected -	Wetterskip Fryslân
organosulfides	GC-MS	CS_2 and di-methylsulfide	Wetterskip Fryslân
steroids, nitrogen compounds	GC-MS	indole, nicotine, caffeine, cholesterol, di-hydrocholesterol	Wetterskip Fryslân
chloorphenol	GC-MS	- not detected -	Omegam
50 volatile compounds*	GC-MS	chloroform, tetra-chloorethene	Wetterskip Fryslân
fenylureum-herbicides	HPLC	diuron	Wetterskip Fryslân
41 pesticides (watersoluble)	LC-MS	di-azinon, carbendazim, furalaxyl, imidacloprid, simazine, propoxur, metzachloor	Wetterskip Fryslân
organophosphor, organonitrogen pesticides	GC-MS	di-azinon	Wetterskip Fryslân
heavy metals	ICP	e.g. chromium, copper, lead, nickel, zinc, iron, aluminium, arsenic	Wetterskip Fryslân
medicines	LC-MS	carbamazepine, coffeine, di-clofenac, erythromycine, gemfibrozil, metoprolol, naproxen, sotalol, sulfamethoxazol	Omegam
oestrogenic compounds	ER-Calux	bisphenol A, estron, EEQ**	Aquasense***
toxicity research	bio-essays	(not applicable)	RIZA

* volatile organohalogens, volatile aromates (eg. BTEX) and chlorinated benzenes

** EEQ = 17ß-oestradiol equivalents

*** analysed by Biodetection Systems, Amsterdam and Waterlaboratorium, Haarlem

Membrane performance

Since the start-up of the pilot MBR in September 2003, the permeability has shown a continuous decrease from 400 l/m²/h/bar at the start to 100 l/m²/h/bar in December 2004 (Figure 2). Chemical cleaning with hypochlorite and citric acid of the membranes to improve the membrane performance, only shows a positive effect for a short period of time. In September 2004 the air supply unit of the membrane tank, which ensures a continuous cleaning of the membranes, was also cleaned. This cleaning has improved the performance of the membranes for a much longer period and the permeability was 'stabilized' to a value around 100 l/m²/h/bar.

Sampling and analysing methods of micro-cantaminants

In 2004 influent and effluent of the MBR have been analysed for micro-contaminants at the laboratory of Wetterskip Fryslân and Omegam for determination of micro-contaminants. Specific analyses of hormones were performed by AquaSense and RIZA determined the ecotoxicity of the samples. In Table 1 an overview is given of the analysis techniques and the detected compounds of each method.

As shown, several persistent micro-contaminants were detected. The Dutch government has made a list of Maximum Tolerable Risk (MTR) values for the most abundant micro contaminants. This list is used to determine the minimal quality level of surface water. These MTR values are also used as a guideline for the determination of the quality level of the WWTP effluent. In general most of these compounds are already below the MTR values, except for simazine, cholesterol, diisobutylphtalate and di-n-octylphtalate.

Although the amount of measurements is limited, so far removal efficiencies tend to be low for the measured herbicides pesticides and phtalates. However steroids and nitrogen compounds appear to be effectively removed.

Furthermore it has to be noted that a lot of pesticide compounds could not be measured since their detection limit is relative high. Since the detection limits of some compounds are higher then the MTR values it still may be that individual compounds are exceeding the MTR value, but have not been detected. For example p,p-DDT has an MTR value of 0.9 ng/l, but its detection limit is 0.1 µg/l, so about 100 times higher.

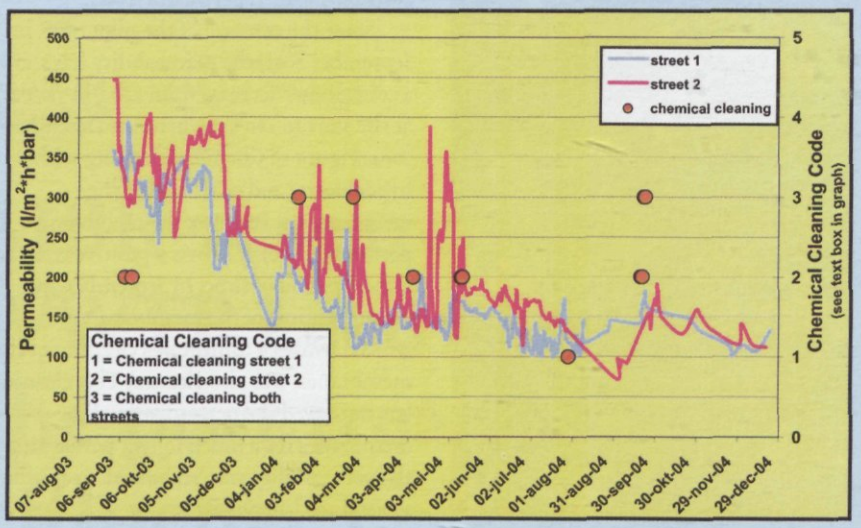


Figure 2: Permeability of membranes in street 1 and 2 of the MBR Leeuwarden.

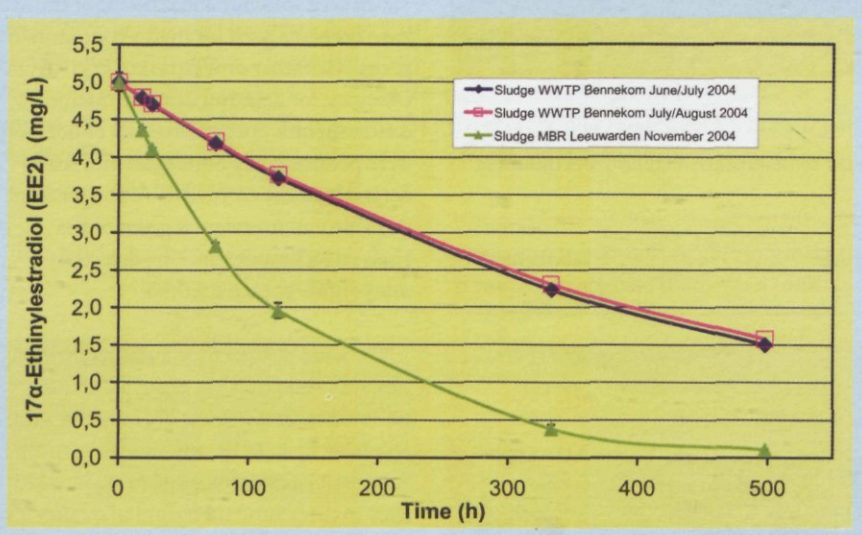


Figure 3: Degradation activity of EE2 by MBR sludge (WWTP Leeuwarden) in comparison to activated sludge (WWTP Bennekom).

The single measurement by Omegam so far showed similar medicine compounds as observed in a research by RIZA, such as analgetics (e.g. naproxen), ß-blockers (e.g. sotalol), cholestorol reducing medicines (gemfibrozil) and anti-epileptica (carbamazepine). Most of these detected medicine compounds show a reasonable removal, except for carbamazepine.

Hormone removal

Aquasense has reported that the absolute hormone WWTP effluent concentrations in the effluent of WWTP Leeuwarden were already very low compared to other WWTPs. However the post treatment by the MBR ensured even lower concentrations and ensured a high total hormone removal efficiency of on average 90% (ER-Calux method).

An additional hormone degradation activity test figure 3 was performed at the Wageningen University. It was shown that specific degradation activity of EE2 (17α-ethinylestradiol) by the MBR sludge was three times higher than activated sludge from the WWTP of Bennekom, while adsorption characteristics were identical.

Toxicity reduction

Measurements conducted by RIZA showed that the toxicity of the surface water and the effluent of the WWTP in Leeuwarden was relative low. The ECf50 factor is the concentration factor which causes at 50% of the organisms a toxic effect. The higher the number the lower the toxicity. As can be seen in table 2 the WWTP effluent samples should be concentrated at least 70 times to see 50% effect.

The effluent and the canal water have been tested again on two occasions (data between brackets) showing consistent values for the WWTP effluent and fluctuating values for the canals. The MBR effluent was only measured once and it showed on average a decrease of 1.5 times in toxicity in comparison to the MBR influent.

Discussion and conclusion

The pilot MBR is now running for 1.5 years on effluent of the WWTP. The preliminary results show a total hormone removal about 90% (ER-Calux method) and a good removal of medicine, steroids and nitrogen compounds. Furthermore it is shown that the high sludge age and low feed conditions have clearly selected a specific biological population with a three times higher hormone (EE2) degradation capacity in comparison to activated sludge.

Removal efficiencies tend to be low for the measured herbicides, pesticides and phtalates. However most of the detected compounds are already below the MTR value.

Looking at the measured data, simazine, diisobutylphtalate and di-n-octylphtalate exceed their MTR value in WWTP effluent and cannot be effectively removed under the present conditions with the MBR. These compounds are therefore of concern and should be monitored more frequently in order to determine if advanced treatment is required. It has to be noted that a lot of pesticide compounds could not be measured since their detection limit are relative high (even higher then MTR values). The low level of toxicity measured by RIZA in the same samples at least confirms that either these compounds were not present or had a very low concentration.

Table 2: ECf50 values of influent and effluent of MBR at WWTP Leeuwarden compared to canals of the city centre of Leeuwarden (August 9th, 2004).

	daphnia IQ test	algae test	bacterial test
effluent WWTP (= influent MBR)	216 (219 / 162)	74 (70 / 105)	71 (64 / 104)
effluent MBR	337	81	113
Canal City centre Leeuwarden	190 (841 / 400)	22 (40 / 209)	138 (170 / 333)

Previous research by RIZA showed that little is known about the environmental risk of the detected medicine compounds. Therefore new research should determine the chronical and specific effects of these medicine compounds on the aquatic environment. The acute toxicity of the detected medicine compounds however seems to be minimal since bio-essays of the same samples showed low toxicity.

In terms of ecotoxicity a reduction (1.5 times) has been observed by the application of a MBR. Then again the toxicity of the WWTP effluent was already very low and in case of Algae and Daphnia toxicity lower than the surface water in the canals of Leeuwarden. Therefore the need for MBR technology to further purify the effluent on this matter will be low.

Nevertheless, since the cultivated MBR sludge shows indeed good removal capacities for hormones and medicine residues, research will be continued and focussed on this specific subject.

Last but not least, in general efforts should be made to realise reliable measurement techniques, especially for pesticide compounds, which should have a detection limit below the MTR value of the specific compound.

Progress

The current situation will be more closely examined and focussed on the removal of hormones and the removal of micro-contaminants. A second EE2 activity test at Wageningen University is yet under investigation. Since the amount of measurements is very limited monitoring should be extended to determine the actual quality of the WWTP effluent and monitoring is required to support the current findings.

In the following research phase the research will be focused at the combined disposal of micro-contaminants and nutrients. For that purpose methanol will be dosed as a carbon source. Because it is the intention to preserve the unique biomass, which has been created up to now, the biomass will be put into a separate vessel in which it will be cultivated and preserved by a continuous feed of WWTP effluent. Also a lab-scale installation will be applied to perform specific micro-contaminant removal tests using the cultivated MBR sludge. ¶

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