# Full scale membrane bioreactor treatment of hospital wastewater as forerunner for hot-spot wastewater treatment solutions in high density urban areas

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## ABSTRACT

Membrane Bioreactors (MBR) are a very attractive option for the treatment of hospital wastewater and elimination of pharmaceuticals in high density urban areas. The present investigation showed that, depending on the substance, between 19% and 94% of the level of antibiotics found in the environment originate from hospitals. Because of their ecotoxic potential, hospital wastewaters can have a significant impact on the environment. The segregation of these wastewaters and their separate treatment at the source can reduce the entry of drugs in waterways and enable water reuse after adequate polishing treatment processes.

**Key words** | hospital, hot-spot wastewater treatment, membrane bioreactor, pharmaceuticals urban areas

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## INTRODUCTION

Organic trace and ultra trace pollutants such as pharmaceutical residues and industrial chemicals gain increasing importance within the current eco-political discussion worldwide. Regardless of the achieved high standard of wastewater treatment, the mandatory configurations of wastewater treatment techniques have to be expanded in order to reliably remove trace pollutants. Therefore, adequate and eco-friendly treatment technologies have to be identified and tested. As further option, hot-spot wastewater treatment solutions have to be considered – particularly for high density urban areas. The hot-spot treatment compensates missing treatment capacity and efficiency of municipal wastewater treatment plants (WWTP) – especially with regard to trace and ultra trace pollutants. Thus, the separate treatment of highly concentrated wastewater flows will allow minimising the operating and financial expenditures for municipal wastewater treatment. In the following, the specific hospital wastewater treatment exemplary shows how effective hot-spot wastewater treatment can be.

doi: 10.2166/wst.2011.010

## MATERIAL AND METHODS

### Mass balance in the catchment area

To compile a mass balance on the pharmaceuticals' entry from a hospital in a wastewater stream that is representative for high density urban areas, the catchment area should not contain any industrial sources. Following sampling points should be available in the catchment area: hospital effluent, effluent of the hospital WWTP, influent and effluent of the municipal WWTP. The drug quantities found in the hospital effluent must be compared and verified with the amount of active pharmaceutical ingredients distributed by the hospital pharmacy. In this comparison, the excretion rates as well as pharmaco-kinetic parameters need to be considered. These values can for example be found in the Documed data base (Documed 2009).

The methodology for the pharmaceuticals mass balance was performed after Feldmann *et al.* (2008). The study was undertaken at the Waldbröl hospital, Germany, with a capacity of 342 beds. The wastewater is treated with a membrane

bioreactor (MBR) before being sent to the municipal WWTP. The hospital capacity is 33.5 beds per 1000 inhabitants in the investigated catchment area. This is a high capacity compared the German national average of 6.2 beds per 1000 inhabitants.

To determine the hospital contribution for a particular target compound, the measured concentration of this compound C (ng/L) was multiplied with the daily flow rate $Q_d$ (m/d) at the various sampling points. These values correspond to a daily load $B_d$ (mg/d). The proportion of a target compound $p_{Hospital}$, which originates from the hospital and would be discharged into the environment if there was not any on-site treatment with MBR, can be calculated as follows:

$$p_{Hospital} = \frac{B_{d,Hospital,Effluent}}{(B_{d,WWTP,Influent} + (B_{d,Hospital,Effluent} - B_{d,MBR,Effluent}))}$$

## Target compounds and analytical methods

A number of representative pharmaceuticals were chosen for the study on the basis of the most administered drugs in the hospital. A further selection criterion for the target compounds was their persistence in the environment, which is well documented in the literature. The substances should also be detectable in the hospital effluent, in the MBR effluent as well as in influent and effluent of the municipal WWTP of the investigated catchment area. The medical relevance of the active ingredient and its wide administration spectrum was also taken into consideration in the selection process. The selected target compounds are listed in Table 1.

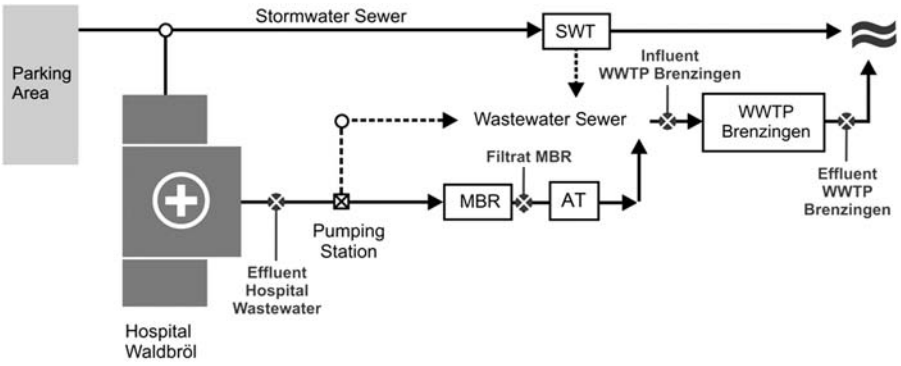
## Sampling and analytical methods for substance-specific detection

To obtain hospital wastewater, MBR and municipal WWTP effluent samples, all sampling points were used to collect 24 h composite samples at daily intervals. For the detection, identification and quantification of the non-volatile, polar pharmaceutical target compounds, liquid chromatography (LC) coupled with mass spectrometric (MS) detection (LC/MS) using a LTQ Orbitrap hybrid mass spectrometer (ThermoElectron, San Jose, CA, USA) was applied. As target drugs were different in polarity resulting in variations of ionization efficiencies, the selection of adequate adapted ionization interfaces was performed to obtain maximum response combined with low LOQs. LC-MS analyses were performed applying positive atmospheric pressure chemical ionization (APCI-MS (+)) or electrospray ionization (ESI-MS (+/−)) using both positive and negative ionization modes. For chromatographic separation prior to mass spectrometric detection, a Hypersil Gold aQ (150x2.1 mm) column (Thermo) was applied. Instrument control, data acquisition and data processing were performed using Xcalibur software (ThermoElectron). For coupling LC and MS, an APCI or an ESI

**Table 1** | Target compounds, their use as therapeutics and molecular weights

| Substance | Therapeutic use | mol. weight (g/mol) | Ionization method | LOQ (ng/L) |
|---|---|---|---|---|
| Bezafibrate | Lipid reducing drug | 361.819 | APCI pos | 10 |
| Bisoprolol | Beta blocker | 325.440 | APCI pos | 10 |
| Carbamazepine | Anticonvulsant and mood stabilising drug | 236.269 | APCI pos | 10 |
| Clarithromycin | Macrolide antibiotic | 747.953 | APCI pos | 30 |
| Ciprofloxacin | Antibiotic | 331.346 | ESI pos | 10 |
| Diclofenac | Non-steroidal anti-inflammatory drug | 296.148 | APCI pos | 10 |
| Ibuprofen | Non-steroidal anti-inflammatory drug | 206.280 | APCI neg | 20 |
| Metronidazole | Antibiotic | 171.150 | APCI pos | 10 |
| Moxifloxacin | Antibiotic | 401.431 | ESI pos | 10 |
| Tramadol | Non-opioid analgesic | 263.400 | APCI pos | 10 |

APCI: atmospheric pressure chemical ionization.
ESI: electrospray ionization.
LOQ: limit of quantification.




SWT: Stormwater tank.
WWTP: Wastewater Treatment Plant of the City Waldbröl-Brenzingen.
MBR: Membrane Bioreactor.
AT: Advanced Treatment.

**Figure 1** | Drainage plan.

interface (ThermoElectron, San Jose, USA) was applied. The detailed LC-MS conditions using the Orbitrap MS were reported by Gebhardt & Schröder (2007).

## Technical scheme

### Drainage plan

Figure 1 gives an overview of the drainage plan at the investigated site. The hospital wastewater is treated in a MBR before being discharged in the municipal sewer network. The choice of a MBR was driven by the small footprint of the system, which can easily be integrated in high density urban areas.

### Full scale MBR

The hospital wastewater is collected and treated in a full scale membrane bioreactor (Q = 130 m/d, 5 Kubota EK 400 flat sheet membrane modules). The MBR has been in stable operation since April 2007. The flow chart of the large scale MBR is shown in Figure 2.

## RESULTS AND DISCUSSION

### Mass balance

The results from the mass balance are presented in Table 2. The proportion of antibiotics found in the municipal wastewater, which originated from the hospital reaches 94% for Clarithromycin. According to Kümmerer (2009) up to 25% of the antibiotics administered in Germany are used in hospitals. Wastewaters generated in medical premises require particular attention because of their concentration in compounds not usually found in domestic wastewaters. Their discharge in the environment can have genotoxic and/or mutagenic effects (Panouilleres *et al.* 2007; Ferk *et al.* 2009). Furthermore, the

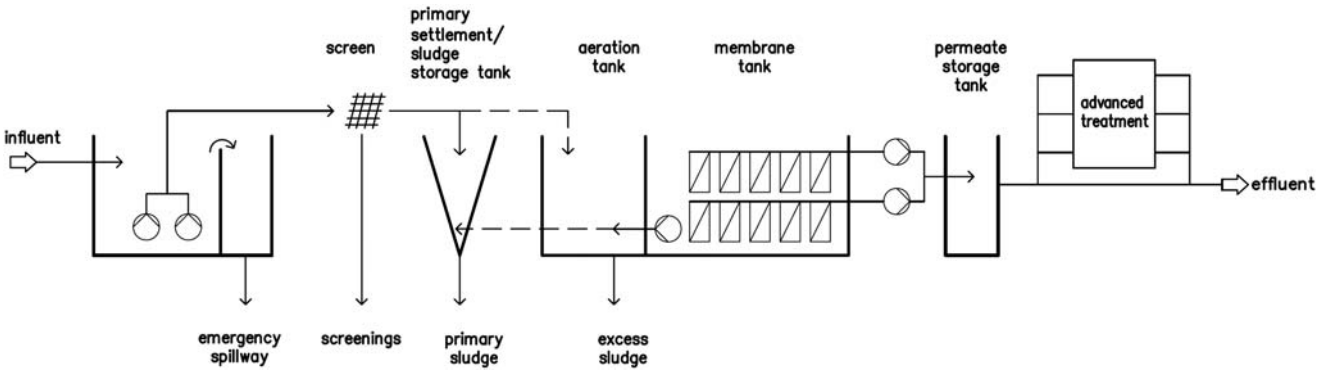



**Figure 2** | Flow chart of the large scale MBR at the hospital in Waldbröl, Germany.

**Table 2** | Proportion of pharmaceuticals originating from hospitals in the municipal wastewater

| Substance | Therapeutic use | Percentage originating from the hospital (%) |
|---|---|---|
| Bezafibrate | Lipid reducing drug | 27 |
| Bisoprolol | Beta blocker | 8–9 |
| Carbamazepine | Anticonvulsant and mood stabilising drug | 3–8 |
| Clarithromycin | Macrolide antibiotic | 61–94 |
| Ciprofloxacin | Antibiotic | 19–36 |
| Diclofenac | Non-steroidal anti-inflammatory drug | 7–9 |
| Ibuprofen | Non-steroidal anti-inflammatory drug | 3–7 |
| Metronidazole | Antibiotic | 84 |
| Moxifloxacin | Antibiotic | 34–42 |
| Tramadol | Non-opioid analgesic | 6–8 |

frequent discharge of antibiotics in waterways can lead to the development of resistant bacteria against antibiotics and consequently to ineffective treatment of human bacterial infections (Schwartz *et al.* 2003). For those reasons, hospital wastewaters should be classified as hazardeous material (Henninger & Kümmerer 2003). The separate treatment of hospital wastewater can reduce the level of antibiotics discharged in the environment and thus the development of resistant pathogens.

## Results of wastewater treatment in the MBR

Figure 3 illustrates the pharmaceutical concentrations in the hospital effluent and in the MBR effluent stream. The median values are presented as columns, together with the range of measured concentrations, defined by the minimum and maximum values (error bars). The degree of elimination achieved by mechanical and biological treatment in the MBR are shown with the black dots.

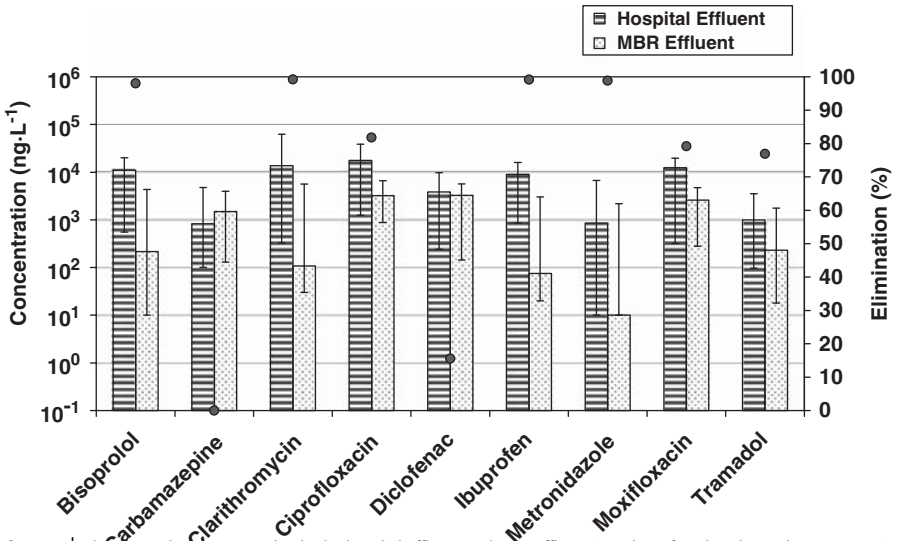



**Figure 3** | Pharmaceutical concentration in the hospital effluent and MBR effluent (Number of analysed samples: $n = 23–29$).

The substances Bisoprolol, Clarithromycin, Ibuprofen and Metronidazole were almost complitely removed by the MBR process (elimination close to 100%). A significant elimination ( >80%) was observed for the compounds Ciprofloxacin and Moxifloxacin. Because of the high concentration of the antibiotics Ciprofloxacin and Moxifloxacin in the hospital wastewater, the concentration of these compounds in the MBR effluent was still in the g $L^{-1}$ range. The concentration of Diclofenac und Carbamazepine was also in the g $L^{-1}$ range in the MBR effluent. A possible re-formation of the substance Carbamazepine can occur in the wastewater because of the presence of metabolites resulting from therapeutic treatment.

Table 3 summarised the elimination of the investigated pharmaceuticals by the MBR process, based on a comparison of the influent and effluent concentrations. To put the elimination degree into perspective, Table 3 also gives the percentage of MBR effluent samples analysed whose concentration exceeded 100 ng $L^{-1}$. The value of 100 ng $L^{-1}$ corresponds to target value set by the International Association of Waterworks in the Rhine catchment area (IAWR 2008) and its members, and also to the recommendation of the German Ministry for the environment (UBA 2008). It should be considered that the mentioned target value applies to water systems which are part of drinking water supplies. In the context of hospital wastewater treatment, this target value is of interest is the treated water is to be directly discharged into waterways, without going through the municipal WWTP.

**Table 3** | Elimination of selected pharmaceuticals in MBR (Number of analysed samples: $n = 23–29$)

| Elimination in % | Pharmaceutical name | Proportion of MBR effluent samples whose concentration exceeded the target value defined by AWR (2008) and UBA (2008) (%) |
|---|---|---|
| >80 | Bisoprolol | 74 |
| | Clarithromycin | 56 |
| | Ciprofloxacin | 100 |
| | Ibuprofen | 41 |
| | Metronidazole | 31 |
| 50–80 | Moxifloxacin | 100 |
| | Tramadol | 81 |
| 20–50 | – | – |
| <20 | Carbamazepine | 100 |
| | Diclofenac | 100 |

The measured eliminations correspond to a large extend to values cited in the litterature for membrane bioreactors (see Ternes 1998; Joss *et al.* 2006). The sludge age in the MBR treating hospital wastewater exceeded 100 days. The elimination of pharmaceuticals in the MBR is based on adsorption of the compounds on the activated sludge matrix and on biological degradation or transformation.

Considering that for many pharmaceutical compounds, the concentration in the MBR effluent is often higher than the target value of 100 ng $L^{-1}$, it is recommended to add an advanced treatment technology, such as activated carbon adsorption, ozone treatment or a further membrane step (nanofiltration or reverse osmosis) after the MBR process. Results on the efficiency of such advanced technologies for the treatment of hospital wastewaters can be found in Pinnekamp *et al.* (2009) and Beier *et al.* (2010).

### Design requirements for MBRs

Based on the operational experience gained at this site and on technical and economic optimisation, the following aspects should be considered in the design of MBR treating hospital wastewaters in high density urban areas:

- separate rainwater collection to reduce dilution effects
- where applicable, separation of water streams with low pharmaceutical concentrations (e.g. kitchen and laundry wastewaters)
- sludge age in the MBR >100 days to allow for biomass adaptation
- thermal treatment of the waste activated sludge and screenings for complete destruction of the adsorbed pharmaceuticals
- consideration of the special requirements on emission levels (noise and aerosols) for hospital patients with a weak immune system and/or needing a quiet environment as well as those of nearby residents.

## CONCLUSIONS AND OUTLOOK

The investigations presented in the paper confirm the appropriateness of MBR for the treatment of hospital wastewater in high density urban areas. Based on a mass balance in an appropriate large-scale case study, it was shown that the proportion of antibiotics found in municipal wastewaters originated to at least 34% from the hospital. Because the

pharmaceuticals concentration in the MBR effluent is often higher than the target value of 100 ng $L^{-1}$, it is recommended to add an advanced treatment technology, such as activated carbon adsorption, ozone treatment or a further membrane step (nanofiltration or reverse osmosis) after the MBR process. This also creates new opportunities for water reuse. It should be mentioned that the residual streams emerging from the treatment of hospital wastewater (such as sludges and screenings) require thermal disposal. In new hospital buildings, the streams containing pharmaceuticals should be segregated at the source and separately treated, for example in MBRs. This would avoid the discharge of these compounds in the sewer network and later on in the environment.

## ACKNOWLEDGEMENTS

We would like to thank the Ministry of the Environment and Conservation, Agriculture and Consumer Protection of the State of North Rhine-Westphalia for funding the project. Furthermore, the authors thank the county hospital of Waldbröl, the team of the R&D project Waldbröl, the operational staff of the Analytical Laboratory at ISA RWTH Aachen University and all student assistants.

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