Review on the fate of organic micropollutants in wastewater treatment and water reuse with membranes

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ABSTRACT

A brief review of the fate of micropollutants in membrane-based wastewater treatment due to sorption, stripping, biological degradation/transformation and membrane separation is discussed, to give an overview of these technologies due to the growing importance for water reuse purposes. Compared with conventional activated sludge treatment (CAS) micropollutant removal in membrane bioreactor (MBR) is slightly improved due to complete suspended solids removal and increased sludge age. For discharge to sensitive receiving waters advanced treatment, such as post-ozonation or activated carbon adsorption, is recommended. In water reuse plants nanofiltration (NF) and reverse osmosis (RO) efficiently reject micropollutants due to size exclusions as well as electrostatic and hydrophobic effects reaching potable quality. To remove micropollutants fully, additionally post-ozone or the addition of powdered activated carbon (PAC) have to be applied, which in parallel also reduce NDMA precursors. The concentrate has to be treated if disposed to sensitive receiving waters due to its high micropollutant concentration and ecotoxicity potential. The present review summarizes principles and capabilities for the most important membrane-based applications for wastewater treatment, i.e. porous membranes in MBRs (micro- or ultrafiltration) and dense membrane applications (NF and RO) for water reuse.

Key words | biological degradation/transformation, MBR, NF, ozonation, PAC, RO, sorption, stripping

INTRODUCTION

Today more than 100,000 different chemicals are registered in the EU, of which some 30,000 are marketed in quantities in excess of one ton. During manufacturing, disposal and use of the substances, a portion will enter the environment. With today’s chemical analytical methods, compounds and their transformation products from chemical and biological degradation are increasingly being detected in water bodies and sewage sludge in the microgram to nanogram per liter range; these are designated micropolllutants. Amongst these are pesticides, food additives, industrial chemicals, pharmaceuticals and personal care products (PPCP). In addition, in the last two decades new environmental effects have been observed, such as feminization in fish, which is partly a result of the chronic exposure to endocrine disruptive compounds (EDC). These include, along with natural hormones, pharmaceutical substances, cleaning products and industrial chemicals.

The extent to which trace substances can be eliminated in today’s sewage treatment plant depends on the level of the biological treatment and the efficiency of the suspended solids separation methods. In the last 40 years, biological wastewater purification has been adapted step-by-step to the tightening effluent conditions for COD, total suspended solids (TSS) and nutrient removal. Recently, the requirement of additional treatment steps has been intensively discussed, with much attention on membrane technologies. The most important micropolllutant elimination processes in membrane bioreactor (MBR) and water reuse plants with membranes are:

- sorption to suspended solids in mechanical and biological treatment, which are removed by sedimentation and filtration, and in MBR sorption to the membrane surface and matrix (membrane sorption is exhausted if the sorbed concentration reaches equilibrium);
- decomposition of substances through bacteria in activated sludge, which may achieve biological mineralization but is mostly limited to compound transformation (Wick et al. 2010a);
stripping by aeration is rather negligible for the considered micropollutants as these are mostly large, hydrophilic and only partially uncharged compounds with low volatility;

- rejection by tight membranes (nanofiltration (NF) and reverse osmosis (RO)) due to size exclusion, hydrophobic and electrostatic effects and their concentration in the concentrate that has to be disposed or further treated.

The present brief review summarizes principles and capabilities of the most important membrane-based applications for wastewater treatment, i.e. porous membranes in MBRs (micro- or ultrafiltration) and dense membrane applications (NF and RO) for upgrading wastewater.

**FATE OF MICROPOLLUTANTS IN MEMBRANE BIOREACTORS WITH MICRO OR ULTRAfiltrATION**

MBR are normally operated at higher solid retention times than conventional activated sludge (CAS) systems, the effluent is free of suspended solids and higher airflow is required per volume of treated wastewater than in conventional wastewater treatment plant (WWTP) due to cross flow aeration.

For the sorption of organic trace substances, a distinction is made between:

- absorption: hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms and the fat fractions of the sludge (compounds with high octanol–water partition coefficients ($K_{OW}$), e.g. tonalide in Figure 1);

- adsorption: electrostatic interactions of positively charged groups of chemicals with the negatively charged surfaces of the microorganisms (see norflaxacin in Figure 1).

The sorbed concentration of a substance $C_{sorb}$ ($\mu g \ L^{-1}$), can be expressed by the Freundlich model or for wastewater suspended solids by a simplified linear model (Wick et al. 2011b). It is dependent upon the sorption constant $K_d$ ($L \ g_{TSS}^{-1}$), the concentration of TSS or the amount of sludge produced $(SP; g_{TSS} \ L^{-1})$ to which the substance can adhere and the dissolved substance concentration of the $C_{diss}$ ($\mu g \ L^{-1}$): $C_{sorb}=K_d SP \ C_{diss}$. For a fully mixed system removal efficiency is: $\eta_{sorb}=C_{sorb}/(C_{diss}+C_{sorb})=K_d SP/(1+K_d SP)$.

$K_d$ can be roughly estimated from the octanol–water distribution coefficient for non-polar compounds, for polar and charged compounds with electrostatic interactions, it must be determined by means of sorption trials. A substance with a low $K_{OW}$ that sorbs relatively well to suspended solids is the antibiotic norflaxacin. The sorption is based to a large extent on electrostatic interactions between the positively charged amino group of norflaxacin and the negatively charged surfaces of the microorganisms. In a study carried out in the Zurich sewage plant, Golet et al. (2005) confirmed that more than 80% norflaxacin of the primary effluent is sorbed to the secondary sludge (Figure 1) while removal in primary treatment is significantly lower. The reason for this is that microorganisms in the secondary sludge represent the greater proportion of the suspended solids, resulting in a relatively high sorption constant $K_d=35 \ L g_{TSS}^{-1}$. For the primary sludge, however, the sorption constant of norflaxacin is much lower ($K_d=2.5$), because in spite of having the same concentration of suspended solids, the primary sludge contains essentially fewer microorganisms but has instead a large fat fraction. Thus, only 27% norflaxacin is sorbed to the primary sludge. The hydrophobic musk fragrance tonalide sorbs more strongly to the lipophilic primary sludge than the secondary sludge (Figure 1). With other substances, such as the anti-inflammatory diclofenac and estrogens the proportion sorbed is significantly smaller (Figure 1). $K_d$ values for other pharmaceuticals, day care products and biocides are given in Joss et al. (2006) and Wick et al. (2011b).

For strongly sorbing compounds ($K_d>5 \ L g_{TSS}^{-1}$), e.g. many of the priority pollutants and heavy metals, the sorbed fraction in the effluent of a conventional WWTP with 10–20 $g_{TSS} \ m^{-3}$ is not negligible and a post-filter or a MBR is expected to strongly reduce effluent toxicity, for WWTP with significant influent load of strongly sorbing compounds. This can also be shown with life cycle assessment including ecotoxicity (Neptune report 4.3).

**Stripping** due to the aeration of the biology and membrane scouring (cross flow aeration) is mostly rather low because of the low volatility of the large and rather

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**Figure 1** Sorption of some compounds in raw wastewater, primary and secondary sludge based on the $K_d$ values given in Joss et al. (2006) assuming no biological degradation. The sorbed fraction is related to the inlet of the primary clarifier and the inlet to biology, respectively.
The elimination is thought to arise through the by-chance affinity of a trace substance with the bacterial enzymes in the activated sludge. The chance of transformation or decomposition increases with the sludge age due to the increasing diversity, as slower growing bacteria are better retained in the bioreactor at high sludge ages: the only slightly higher micropollutant removal of MBRs compared with CAS (Figure 2 right) is assumed to be due mainly to the higher sludge age in MBR. This is demonstrated by the contraceptive 17α-ethinylestradiol that requires nitrifying conditions for degradation (Andersen et al. 2003).

Due to the low concentrations of trace substances, the decomposition occurs mostly as a first-order reaction \( r_{\text{deg}} = k_{\text{deg}} X_{\text{TSS}} C_{\text{diss}} \) (Joss et al. 2006; Wick et al. 2009). In this case, a cascade type arrangement of the activated sludge volume is advantageous because this results in lower discharge concentrations than is the case with a single fully mixed tank.

Many micropollutants or their intermediates are polar substances, which are biologically degradable or transformed only to a small degree or not at all and sorption is also restricted (Wick et al. 2011a). Thus on passing through the sewage plant (incl. micro- and ultrafiltration), they are only partly eliminated and thus discharged to the water body with the plant effluent. Parallel to measures at the source, technical measures at the WWTP by advanced treatment methods are required to protect sensitive receiving waters and water resources as well as for water reuse. Powdered activated carbon (PAC) added directly to the MBR allows an efficient removal of micropollutants and might reduce biofouling of membranes but requires about three times more PAC (30–40 mg/L) than for an addition to the MBR effluent with recycling to the MBR and creates therefore higher sludge production and operation costs than post treatment, but requires no additional reactor system (Boehler et al. 2011). Ozonation of the MBR effluent, requiring 5–10 mgO₃/L, is an efficient and reasonable method to oxidize micropollutants, but produces oxidation by-products that should be degraded in a biofilm system, e.g. sand filter (Hollender et al. 2009; Zimmermann et al. 2011).
FATE OF MICROPOLLUTANTS IN NANOFILTRATION AND REVERSE OSMOSIS

The growing demand of potable water in regions with water scarcity has increased interest in water reuse. But of great concern is the rejection of organic micropollutants such as disinfection by-products, EDCs, pesticides, as well as PPCPs. Different research groups investigated, described and modeled the mechanisms of micropollutant rejection in NF and RO. The list of the following cited authors is far from complete.

Bellona & Drewes (2005) investigated the membrane surface charge of two commercial NF membranes at different pH values and feed water composition. Six different organic acids were selected for this study representing typical physico-chemical properties of emerging organic trace pollutants. Findings of this study indicated that the rejection of negatively charged organic acids is primarily driven by the surface charge of the membrane and correlated with the degree of ionization of the solute. Increasing feed water pH resulted in an increased negative surface charge, an increased percentage of solutes in the deprotonated state and an increased rejection through electrostatic repulsion. The rejection of the pharmaceutical residue ibuprofen, an organic acid with hydrophobic properties, was also pH dependent, at pH values below the pK_a ibuprofen partially adsorbs and its diffusion through the membrane is therefore reduced. At pH above the pK_a, adsorption of ibuprofen was minimal due to an increased solubility and the effect of electrostatic repulsion was dominant.

Kimura et al. (2004) studied a total of 11 compounds with a certain range of molecular weights and K_{OW}. With respect to membranes, two different materials (polyamide and cellulose acetate) were examined. Generally, the polyamide membrane exhibited a better rejection but the retention was still not complete (57–91%). It was found that salt rejection or molecular weight cut-off often used to characterize membrane rejection properties did not provide quantitative information in terms of EDCs and pharmaceutical rejection by NF/RO membranes. Size exclusion dominated the retention by the polyamide membrane, while polarity was better able to describe the retention trend by the cellulose acetate membrane. The results obtained in this study imply that each membrane polymer material for NF/RO, including those newly developed, would exhibit different trends in terms of rejection of micropollutants, which is determined by physico-chemical compound properties.

The study of Xu et al. (2006) indicate that membrane fouling significantly affects the rejection of organic solute by cellulose triacetate RO (CTA), commercial polyamide NF, and ultra-low pressure RO (ULPRO) membranes while it is less important for thin-film composite RO membranes. Due to foulant precipitation and cake-layer formation, membrane surface characteristics changed considerably in hydrophobicity, surface charge, and surface morphology, which potentially affected transport of contaminants as compared with new membranes. The transport of ionic organic micro-pollutants was hindered as a result of improved electrostatic repulsion likely due to a more negative surface charge. Membrane fouling also resulted in an increased adsorption capacity and reduced mass transport through partitioning and diffusion of solutes across the membrane. These effects led to an increase in rejection of hydrophobic non-ionic solutes (e.g. disinfection by-products and chlorinated solvents) by fouled membranes. However, the increasing surface charge has the potential to result in a larger molecular weight cut-off of a fouled membrane due to membrane swelling, which can lead to lower rejection for hydrophilic non-ionic solutes, especially for NF membranes with larger molecular weight cut-off. Membrane fouling facilitated the transport of hydrophobic and hydrophilic organic contaminants through CTA membranes resulting in elevated concentrations of target solutes in the permeate.
Radjenovic et al. (2008) observed for most of the pharmaceuticals analyzed more than 85% rejection for NF and RO applied in full-scale drinking water treatment with the exception of acetaminophen gemfibrozil and mfenamic acid that are removed only by 30–70%. Thompson et al. (2011) observed in RO of a water reuse plant after MBR or conventional activated sludge treatment followed by ultrafiltration (CAS/UF) more than 95% removal of perfluor-octane sulfonate and perfluoro-octanoic acid (PFOS and PFAO) below the detection limits of about 1 ng/L. Snyder et al. (2006) evaluated the fate of a suite of structurally diverse target compounds based largely upon occurrence and molecular structure. NF and RO were capable of significant rejection of nearly all target compounds, although compounds were detectable at trace levels in permeates.

Despite significant molecular differences between the selected micropollutants Sahar et al. (2012) found high removal rates by the RO stage (99% for macrolides, pharmaceuticals, cholesterol, and BPA, 95% for diclofenac, and 93% removal of sulfonamides). However, low antibiotics concentrations and 28–223 ng/L residuals of ibuprofen, diclofenac, salicylic acid, cholesterol, and BPA in the MBR/RO and CAS-UF/RO permeates showed that although RO is an efficient removal solution, it cannot serve as an absolute barrier. Therefore, additional treatment techniques such as ozonation (Joss et al. 2011; Pisarenko et al. 2012), PAC addition (Kazner et al. 2008), and GAC filtration (Snyder et al. 2006) could be combined with RO or NF to ensure complete removal of such substances in the permeate.

Joss et al. (2011) show that most organic micropollutants are degraded and retained to below the limit of detection (≤10 ng/L) in an MBR plant followed by RO, except for small and polar compounds such as the anticorrosive benzo-triazoles, as well as the rather persistent pharmaceuticals propanolol, diclofenac and carbamazepine. The comparison of the concentrations in the concentrate and the permeate shows that the high retention is achieved by the RO. All measurable concentrations are further reduced by inserting an ozonation step in the concentrate stream before recycling it back to the MBR. As the DOC is elevated in the concentrate (20 mg/L), relatively high ozone dose is required to achieve good elimination. However, elimination rates obtained were comparable with results from ozonation experiments of treated municipal wastewater for similar concentrations of ozone relative to DOC (Hollender et al. 2009). An ozone dose of 0.85 gO₂/gDOC effectively eliminates the micropollutants and reduces the discharged amount in the concentrate.

Kazner et al. (2008) tested a direct capillary NF also in combination with an upstream powdered activated carbon treatment 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 concentrations of 1 to 2 μg/L to evaluate the process performance. In direct NF the net removal of the micropollutants was between 5 and 40%. Adsorption to the membrane played a major role leading to an apparent 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 95–99.9% depending on the PAC type and dose. The cytostatics showed a very high removal already in direct NF due to unspecified losses. The PAC/NF process provided a consistently high permeate quality with respect to bulk and trace organics.

The concentrate of water reuse plant with its high content of micropollutants is of major concern for sensitive receiving waters (river, lake, groundwater, estuary) and should therefore be further treated, e.g. by ozonation (Benner et al. 2008; Joss et al. 2011).

N-nitrosodimethylamine (NDMA) formation is of major concern among wastewater recycling utilities practicing disinfection and biofouling control of RO membranes with chloramines (Farre et al. 2011). NDMA stems from precursors in raw water and can be generated during treatment. Generally removal of precursors is more achievable than the removal of NDMA itself. For example, the potent NDMA precursor dimethylamine is rapidly removed in biological pretreatment, while many other precursor amines are more persistent. Ozonation has also been shown to produce NDMA in treatment (Schmidt & Brauch 2008; Krauss et al. 2010). Ozonation combined with UV is the preferred method for removal of NDMA in water treatment, although RO membranes are possible alternatives if effective retention can be achieved (Schäfer et al. 2010). The NDMA formation potential (FP) test is a simple and straightforward method to evaluate NDMA precursor concentrations in treated wastewaters. The biological step of nutrient removal plant can degrade NDMA precursor by more than 80% reaching effluent concentration of several 100 ng/L (Krauss et al. 2010). RO removed more than 98% of NDMA precursor from biology effluent (Krauss et al. 2010; Farre et al. 2011). This drastically reduces the potential for reformation of NDMA after the RO stage even if chloramines may be present (or added) there.

Although Joss et al. (2011) observed an increase of NDMA by a factor of four after addition of 10–15 mg/L...
chloramine to MBR effluent, more than 95% was rejected in RO to concentration around 7 ng/L, thus still complying with US EPA drinking water standards. NDMA concentration decreased to about 4 ng L\(^{-1}\) by the ozonation of the recycled rejected water, presumably due to degradation of NDMA precursors during ozonation and biological treatment. After chloramination, Pisarenko et al. (2012) also observed a significant decrease of NDMA formation by ozone and ozone/peroxide pretreatment and are recommending a DOC adapted dosage of ozone (optimal dosage in the range of O\(_3/\text{DOC} \sim 0.5\)) preventing significant bromate formation.

**Gadolinium (Gd)** complexes have been used as paramagnetic contrast agents for magnetic resonance imaging (MRI) for over 20 years, and have recently been identified as environmental contaminants. As the rare earth elements (REE), which include Gd, are able to be measured accurately at very low concentrations using inductively coupled plasma mass spectrometry (ICP-MS), it is possible to determine the fate of this class of compounds during the production of purified recycled water from WWTP effluent. Coagulation and microfiltration have negligible removal, with the major removal step occurring across the RO membrane where anthropogenic Gd (the amount of Gd attributable to MRI contrast agents) is reduced by 99.85% from 390 to 0.59 pmol/kg (1 pmol=10\(^{-12}\) mol). The increased concentration in the RO concentrate (2.6 nmol Gd/kg) may allow further development of anthropogenic Gd as a tracer evaluation the fate of the RO concentrate in the environment (Lawrence et al. 2010). Anthropogenic Gd is expected to co-occur with any wastewater sourced micropollutant. Anthropogenic Gd could therefore be utilized as a cheap, sensitive, and rapid tracer to assess the distribution of other more environmentally damaging micropollutants. The detection of anthropogenic Gd in water supply dams would be an indicator of contamination; most likely from the addition of WWTP effluent upstream of the dams, but potentially also due to system failure within wastewater recycling plants. Carbamazepine and sucralose are other inert tracer compounds being used to detect wastewater pollution in water bodies (Clara et al. 2004; Lubick 2009).

**CONCLUSIONS**

The elimination of micropollutants in MBR by sorption, stripping and biological degradation is slightly improved compared with CAS treatment due to complete removal of the suspended solids, higher specific airflow and the higher sludge age operated. However, a lot of micropollutants are not or only partly eliminated or transformed and parallel to measures at the source, technical measure by advanced treatment methods (e.g. ozone or PAC) are required for sensitive receiving waters, water reuse and to protect water resources.

The rejection efficiency of micropollutants in NF and RO depends strongly on solute composition, membrane characteristics, biofouling, and operating conditions. With increasing feed water concentration rejection efficiency increases, suggesting the need to conduct experiments at typical concentration. Currently micropollutant rejection is specific for each membrane type and no generally suitable prediction method has been identified. Although NF and RO is an efficient removal solution, it cannot serve as an absolute barrier and additional treatment techniques such as ozonation or activated carbon adsorption could be combined with RO or NF to ensure complete removal of such substances in the permeate. The concentrate of water reuse plants with its high content of micropollutants is of major concern for sensitive receiving waters (river, lake, groundwater, estuary) and should therefore be treated further, e.g. by ozonation. The formation of NDMA is of major concern among water recycling utilities practicing disinfection and biofouling control of RO membranes with chloramines. RO removed more than 98% of NDMA precursor from biology effluent, which drastically reduces any potential for re-formation of NDMA after the RO stage even if chloramines may be present (or added) there. Stable Gd complexes are used as paramagnetic contrast agents and can be measured accurately at very low concentrations using ICP-MS. Gd is retained by more than 99.8% in RO of water reuse plants. Since it is expected to co-occur with any wastewater sourced micropollutants, Gd could be a wastewater tracer to assess the distribution of other more environmentally damaging micropollutants.

**REFERENCES**

Andersen, H., Siegrist, H. & Halling-Sorensen, Ternes, T. 2005 *Fate of estrogens in a municipal sewage treatment plant*. *Environmental Science and Technology* 37, 4021–4026.


Kimura, K., Yoshima, S., Amy, G. & Watanabe, Y. 2004 Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes. *Journal of Membrane Science* 245, 71–78.


Lubick, N. 2009 Artificial sweetener makes ideal tracer. *Environmental Science and Technology* 43 (12), 4220.


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