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Treating emerging contaminants (pharmaceuticals) in wastewater and drinking water treatment plants

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Abstract. In this study the behaviour of several pharmaceuticals belonging to different therapeutic categories (analgesics and anti-inflammatory drugs, lipid regulators, antibiotics, etc.) was monitored during the treatment of wastewater in a laboratory-scale membrane bioreactor (MBR) and in a full-scale drinking water treatment plant (DWTP) using reverse osmosis (RO) and nanofiltration (NF). The results of MBR were compared with the removal of the target compounds in a conventional activated sludge (CAS) process in an existing wastewater treatment facility. The performance of an MBR was monitored during approximately two months in order to investigate a long-term operational stability of the system and a possible influence of solid retention time on the removal efficiencies of target compounds. The behaviour of the selected pharmaceutical residues facing an NF/RO membrane and evaluation of the performance of this kind of advanced treatment was studied under real conditions of a full-scale DWTP. Excellent overall performance of both NF and RO was noted, with high rejection percentages for almost all of the pharmaceutical residues investigated (>85%), while in wastewater treatment using an MBR the pharmaceutical compounds were generally removed to a higher extent than during CAS process.

Keywords. Pharmaceuticals – Membrane bioreactor (MBR) – Conventional activated sludge (CAS) – Nanofiltration (NF) – Reverse osmosis (RO).

Traitement des contaminants émergents (composés pharmaceutiques) dans les stations d'épuration des eaux usées et de traitement de l'eau potable

Résumé. *Le but de cette étude a été de suivre le comportement de plusieurs composés pharmaceutiques appartenant à diverses catégories thérapeutiques (médicaments analgésiques et anti-inflammatoires, régulateurs des lipides, antibiotiques, etc.) pendant le traitement des eaux usées dans un bioréacteur à membrane (BRM) à l'échelle de laboratoire et dans une station de traitement de l'eau potable (STEP) à grande échelle, utilisant le traitement par osmose inverse (OI) et par nanofiltration (NF). Les résultats du BRM ont été comparés avec ceux obtenus par l'évacuation des boues activées conventionnelles dans une usine de traitement des eaux usées. La performance du BRM a été évaluée pendant environ deux mois afin de déterminer la stabilité d'exploitation du système à long terme et l'influence possible du temps de rétention des solides sur l'efficience d'évacuation des composés cibles. Le comportement des résidus pharmaceutiques sélectionnés vis-à-vis d'une membrane de NF/OI et la performance de ce type de traitement avancé ont été étudiés dans les conditions réelles d'une station de traitement de l'eau potable à grande échelle. On a mis en évidence une performance générale excellente aussi bien dans le cas de la NF que dans le cas de l'OI, avec des pourcentages élevés de rejets pour la quasi-totalité des résidus pharmaceutiques considérés (>85%). Par ailleurs, dans le traitement des eaux usées, le BRM s'est avéré être plus performant que le système des boues activées conventionnelles pour l'élimination des composés pharmaceutiques.*

Mots-clés. *Composés pharmaceutiques – Bioréacteur à membrane (BRM) – Boues Activées Conventionnelles (CAS) – Nanofiltration (NF) – Osmose Inverse(OI).*

I – Introduction

Pharmaceuticals in their native form or as metabolites are continuously introduced to sewage waters mainly through excreta, disposal of unused or expired drugs or directly from pharmaceutical discharges. During the treatment at wastewater treatment plants (WWTP), they are either partially retained in the sludge, or metabolized to a more hydrophilic, but still persistent form that passes the wastewater treatment plant and ends up in the receiving waters. The removal of pharmaceuticals in WWTPs is variable and depending on the properties of the substance and process parameters (i.e. sludge retention time (SRT), hydraulic retention time (HRT), temperature) (Clara *et al.,* 2005; Vieno *et al.,* 2005). A large number of pharmaceuticals is hardly eliminated and therefore detected in WWTP effluents. The presence of pharmaceuticals in surface and drinking water is well documented in literature (Ternes, 1998; Heberer, 2002; Metcalfe *et al.,* 2003; Giger *et al.,* 2003; Castiglioni *et al.,* 2006; Gros *et al.,* 2007). Although present in low environmental concentrations, drugs can have adverse effects on aquatic organisms. These effects are rather chronicle than acute toxic effects, depending on the exposure factor (bioavailability), degradability and susceptibility of the compound in question (Jemba, 2006).

Therefore, in order to ensure compliance with future discharge requirements, an upgrading of existing wastewater treatment facilities and implementation of new technologies is required as a next step in the improvement of wastewater treatment. Membrane bioreactor (MBR) treatment is an emerging technology based on the use of membranes in combination with the traditional biological treatment. MBRs are considered as promising technologies to achieve further removal of micro-pollutants in comparison to conventional WWTP. This is due to two characteristics of MBRs, (a) the low sludge load in terms of biological oxygen demand (BOD) that can be expected to force bacteria to mineralize also poorly degradable organic compounds and (b) the high sludge age that gives bacteria the time to adapt to these substances (Ghyoot and Verstraete, 2000; Wei *et al.*, 2003).

Another advanced technique that has been gaining attention during the last few years is nanofiltration (NF) and reverse osmosis (RO) treatment. These two treatments seem to be able to effectively remove most organic and inorganic compounds and microorganisms from raw water (Chellam *et al.*, 1997; Gagliardo *et al.*, 1998) and have been widely applied to drinking water treatment and wastewater reclamation.

The objective of this work was twofold: (i) to assess the viability of MBR operating under anaerobic conditions in the treatment of pharmaceuticals in relatively low strength wastewaters in municipal applications and (ii) to evaluate the performance of full-scale NF and RO drinking water treatments in rejecting pharmaceutical residues from rather contaminated groundwater.

II – Methods

1. Conventional activated sludge (CAS) treatment at wastewater treatment plant (WWTP)

WWTP Rubí was designed for 125.550 equivalent inhabitants. During the sampling campaign WWTP was operating with an average daily flow of 22.000 m3 day-1. Treated wastewater is a mixture of municipal, hospital and industrial wastewater. The treatment consists of a pre-treatment, preliminary treatment, primary sedimentation unit and a secondary (biological) treatment. Pre-treated wastewater goes through a physical process of settling in a primary clarifier. Secondary treatment consists of a pre-denitrification (anaerobic) and nitrification (aerobic) tank, and two secondary clarifiers. Secondary sludge is being recirculated to a primary clarifier which improves settling characteristics of primary sludge and also increases sludge age. Mixture of primary and secondary (activated) sludge is being processed (thickening, dewatering) and anaerobically

digested, and biogas produced is being used for heating of a digester. Hydraulic retention time of CAS treatment in WWTP Rubí, calculated for an average daily flow, is approximately 12 h. During the performed sampling campaign, the plant was operating with SRT of approximately 3 days. WWTP effluent is being discharged into the river Riera de Rubí, which flows into the Mediterranean sea.

2. Membrane bioreactor (MBR)

A submerged MBR of approximately 21 l of active volume and equipped with 2 flat sheet membranes (A4 size, area 0.106 m2, pore size 0.4 μm) purchased from Kubota (Osaka, Japan) was installed in a municipal WWTP in Rubí (Barcelona, Spain). Although the nominal porosity of the membranes was 0.4 μm (microfiltration) a fouling layer formed on the surface of the membranes out of proteins and microorganisms brought up the effective porosity of 0.01 μm, which put the filtration type into the range of ultrafiltration. The biocenosis of the MBR was grown from the inoculated sludge from municipal WWTP (aeration basin) and cultivated over a period of approximately 1 month to reach steady state conditions. The hydraulic retention time was set to 14 hours by regulating the effluent flow, while SRT was infinite since there was no sludge discharged from the reactor. A laboratory-scale MBR was operated dynamically in an intermittent permeation mode: cycles of 8 minutes of permeation interrupted with 2 minutes of halt. Influent and permeate flows were controlled using flow meters and computer controlled pumps. A continuous aeration was provided by a sparger pipe situated at the bottom of the reaction vessel, keeping the oxygen concentration between 1 and 2 mg L-1. The temperature inside the reactor was 20º ± 2ºC during the whole sampling campaign. For more details see Radjenovic *et al.* 2007.

3. Nanofiltration and reverse osmosis waterworks

The sampled DWTP located in NE-Spain is able to treat 200 Ls-1 and supplies drinking water to around 50,000 inhabitants. The DWTP works with three treatment lines operating in parallel, one equipped with NF, and two lines equipped with RO membrane filtration racks (see Figure 1). All three lines are fed from groundwater wells.

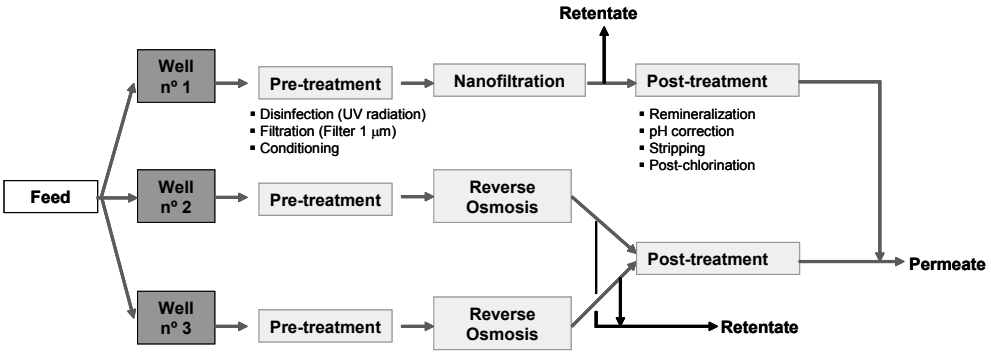

Figure 1. Scheme of nanofiltration and reverse osmosis treatment lines at the DWTP Besós.

The RO rack consists in two parallel stages, whereas the first has 40 membrane modules and the second one 20 (each one consists in 6 “loose” RO membranes type BW30LE-440, Dow-FilmTec). The NF line comprises also two stages, with 31 and 15 membrane modules, respectively, equipped with 6 “tight” NF membranes (NF90-400, Dow-FilmTec) each. The treatment consists in pre-treatment (UV radiation, filtration and conditioning), NF/RO filtration and post-treatment (remineralisation, pH correction, stripping by CO2 and post-chlorination). After the filtration stage, treated water from all three lines is being further processed before sending to water network in a

joint post-treatment step. During the pre-treatment, UV radiation is used to sterilize the entering water and to eliminate present organic matter before its entrance to the membrane's rack. Next, filtration is achieved by two cartridge filters (selectivity 1 µm; each filter has 180 cartridges) which are functioning alterably: when the filter in operation gets abrupt by impurities, the other one is set to function while the first one is being cleaned. Finally, water is conditioned with sodium hydrogen sulphate that prevents bacterial growth, eliminates organic matter, reduces free chlorine content (that can damage the membranes) and also water oxygen content (that causes corrosion), and lowers its pH. Moreover, a dispersant is added in order to lower water hardness.

4. Chemical analysis

All target compounds were extracted in one single extraction step, according to the previously published analytical method (Gros *et al.*, 2006) using Oasis HLB cartridges (200 mg, 6 ml) from Waters Corporation (Milford, MA). The elution was performed two times with 4 ml of methanol at a flow of 1 ml min-1. The extracts were then evaporated under a nitrogen stream and reconstituted with 1mL of methanol-water mixture (25:75, v/v).

LC analysis was performed using a Waters 2690 HPLC system (Milford, MA, USA) coupled to a Micromass Quattro (Manchester, UK) triple quadrupole mass spectrometer, equipped with a Z-spray electrospray interface. Chromatographic separation was achieved with a Purospher Star RP-18 endcapped column (125 x 2.0 mm, particle size 5µm) and a C18 guard column, both supplied by Merck (Darmstadt, Germany). Details of specific multi-residue analytical method applied for the analysis are published elsewhere (Gros *et al.*, 2006), with the addition of hydrochlorothiazide and glibenclamide. Recoveries of the method were determined as follows: groundwater samples were spiked in triplicate with a standard mixture of selected compounds to a final concentration of 1 µg L-1. Spiked samples together with a blank sample were analysed by the above mentioned method. Method detection limits (MDL) and method quantification limits (MQL) were calculated by a signal- to-noise ratio (S/N) of 3 and 10, respectively. Recoveries of the target pharmaceuticals were in the range 43.6% (mevastatin)-112.3% (glibenclamide), whereas for most of the compounds they were very satisfactory (>75%). Method detection limits (MDLs) were in the range 0.03 (azithromycin)-16.2 ng L-1 (lansoprazole).

III – Results and discussion

1. RO and NF

The sampling campaign was done in waterwork Besós (Barcelona, Spain) during September-December, 2006. In total 70 samples were analyzed, 45 samples from reverse osmosis (RO) pilot plant, and 25 samples from nanofiltration (NF) pilot plant. Compounds that were detected in feed stream (groundwater) of all five sampling campaigns and at relatively high concentrations (>100 ng L-1) were diuretic hydrochlorothiazide, analgesics and anti-inflammatory drugs ketoprofen, diclofenac and propyphenazone, lipid regulator pravastatin and antiepileptic drug carbamazepine. Excellent overall performance of both NF and RO was noted, with high rejection percentages for almost all of the pharmaceutical residues investigated. Pharmaceutical residues detected in all five sampling campaigns were analgesics and anti-inflammatory drugs ketoprofen, diclofenac, acetaminophen and propyphenazone, β-blockers sotalol and metoprolol, antiepileptic drug carbamazepine, antibiotic sulfamethoxazole, lipid regulator gemfibrozil and a diuretic hydrochlorothiazide. Highest concentrations in feed stream (groundwater) were found for a diuretic hydrochlorothiazide, analgesics and anti-inflammatory drugs ketoprofen, diclofenac and propyphenazone, lipid regulator pravastatin and antiepileptic drug carbamazepine (>100 ng L-1). No removal in either of the investigated processes was seen for psychiatric drug paroxetine and β-blocker propranolol (<20%). However, since these two pharmaceutical residues were detected

only in one or two sampling campaigns, this data cannot be taken as conclusive. Due to the high efficiency of NF and RO treatments, permeate concentrations of compounds detected in the feed water were below the limit of detection (bLOD) or below the limit of quantification (bLOQ) in most cases. The highest effluent concentrations were found for hydrochlorothiazide and gemfibrozil that had NF permeate concentrations of 73.0 and 60.0 ng L-1, whereas their RO permeate concentrations were slightly lower- 24.6 and 33.5 ng L-1, respectively (see Table 2). Removal rates of the detected pharmaceuticals were calculated and they are presented in Fig. 2.

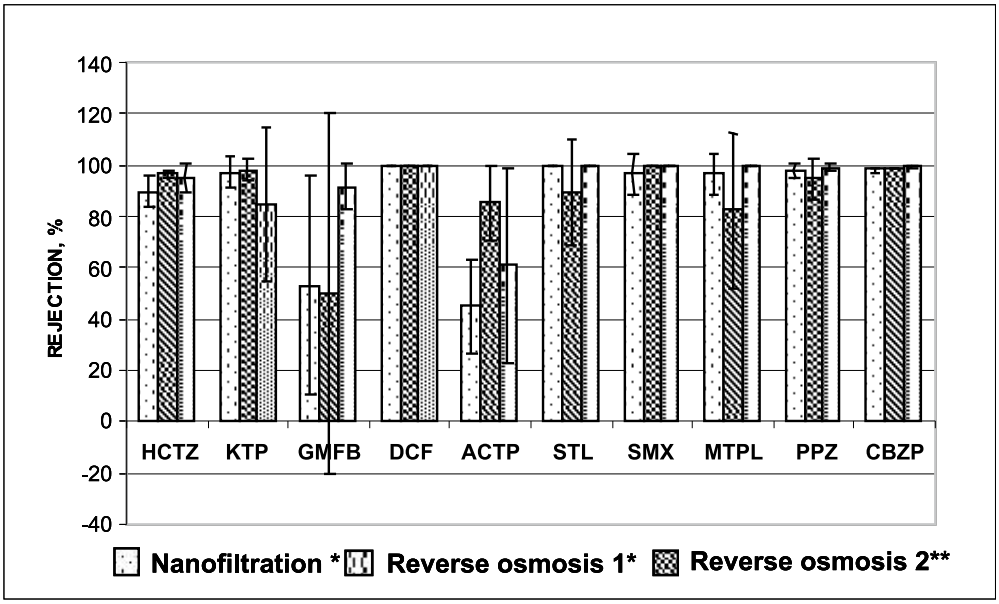

Figure 2. Rejection efficiencies in conditioning, UV, NF/RO stage of treatment are illustrated for frequently found pharmaceutical residues. Rejections are presented as mean values, with their corresponding RSDs for the NF and RO filtration stages (*N=5, **N=4). HCTZ-hydrochlorothiazide, KTP-ketoprofen, GMFB-gemfibrozil, DCF-diclofenac, ACTP-acetaminophen, STL-sotalol, SMX-sulfamethoxazole, MTPL-metoprolol, PPZ-propyphenazone, CBZP-carbamazepine.

Table 2. Concentrations ranges and frequencies of detection of compounds in permeate water of NF and two RO treatment lines of Besós waterworks.

Compounds	Frequency of detection in NF permeate (N=5)	NF permeate concentration (ng L^{-1})	Frequency of detection in RO permeate (N=9)	RO permeate Concentration (ng L^{-1})[a]
Hydrochlorothiazide	5	2.6-329.7 (73.0)	9	0.8-117 (24.6)
Ketoprofen	1	bLOD-37.3 (7.5)	2	bLOD-51.4 (8.0)
Gemfibrozil	3	bLOD-297.9 (60.0)	4	bLOD-288.3 (33.5)
Diclofenac	0	bLOD	0	bLOD
Acetaminophen	4	bLOD-9.3 (bLOQ)	5	bLOD-16.7 (bLOQ)
Sotalol	0	bLOD	1	bLOD-3.1 (bLOQ)
Sulfamethoxazole	1	bLOD-4.8 (bLOQ)	0	bLOD
Metoprolol	1	bLOD-8.1 (1.6)	2	bLOD-13.5 (2.6)
Propyphenazone	3	bLOD-7.9 (3.2)	4	bLOD-12.0 (2.4)
Carbamazepine	5	0.5-5.7 (2.3)	7	bLOD-1.8 (0.9)
Mefenamic acid	3	bLOD-19.9 (4.5)	4	bLOD-19.8 (4.7)
Glibenclamide	1	bLOD-2.9 (bLOQ)	2	bLOD-2.8 (bLOQ)
Propranolol	2	bLOD-57.8 (11.6)	2	bLOD-51.5 (10.3)
Ofloxacin	1	bLOD-7.0 (bLOD)	1	bLOD-11.5 (bLOQ)
Pravastatin	0	bLOD	0	bLOD
Erythromycin	0	bLOD	0	bLOD
Loratidine	0	bLOD	0	bLOD
Nifuroxazide	1	1.0	0	bLOD
Bezafibrate	1	bLOD-1.1 (bLOD)	2	bLOD
Atenolol	1	bLOD-0.3 (bLOD)	0	bLOD
Paroxetine	1	bLOD-3.9 (0.8)	2	bLOD-2.2 (0.8)

[a]Permeate water concentrations are presented as a range, with mean values inside the brackets.

2. MBR

The performance of an MBR was monitored during approximately two months in order to investigate a long-term operational stability of the system and a possible influence of solid retention time on the removal efficiencies of target compounds. In general pharmaceuticals were removed to a higher extent in the MBR integrated system than during CAS process. For most of the investigated compounds, MBR treatment had a better performance (removal rates>80%) and steadier effluent concentrations than the conventional system (e.g. diclofenac, ketoprofen, ranitidine, gemfibrozil, bezafibrate, pravastatin, ofloxacin) (see Table 1). In some cases the removal efficiencies were very similar and high for both treatments (e.g. ibuprofen, naproxen, acetaminophen, paroxetine, hydrochlorothiazide). The antiepileptic drug carbamazepine turned out to be the most persistent pharmaceutical as it passed both through MBR and CAS system untransformed. Since there was no washout of biomass from the reactor, high-quality effluent in

terms of chemical oxygen demand (COD), ammonium content (N-NH4), total suspended solids (TSS) and total organic carbon (TOC) was obtained.

Table 1. Mean removal of selected pharmaceuticals for MBR and CAS process

Compound	Elimination in MBR, %[a]	Elimination in CAS,%[b]
Naproxen	99.3 (1.52) *	85.1 (11.4)
Ketoprofen	91.9 (6.55)	51.5 (22.9)
Ibuprofen	99.8 (0.386)	82.5 (15.8)
Diclofenac	87.4 (14.1)	50.1 (20.1)
Indomethacin	46.6 (23.2)	23.4 (22.3)
Acetaminophen	99.6 (0.299)	98.4 (1.72)
Mefenamic acid	74.8 (20.1)	29.4 (32.3)
Propyphenazone	64.6 (13.3)	42.7 (19.0)
Ranitidine	95.0 (3.74)	42.2 (47.0)
Carbamazepine	no elimination**	no elimination
Paroxetine	89.7 (6.69)	90.6 (4.74)
Ofloxacin	94.0 (6.51)	23.8 (23.5)
Sulfamethoxazole	60.5 (33.9)	55.6 (35.4)
Erythromycin	67.3 (16.1)	23.8 (29.2)
Atenolol	65.5 (36.2)	no elimination
Metoprolol	58.7 (72.8)	no elimination
Hydrochlorothiazide	66.3 (7.79)	76.3 (6.85)
Glibenclamide	47.3 (20.1)	44.5 (19.1)
Gemfibrozil	89.6 (23.3)	38.8 (16.9)
Bezafibrate	95.8 (8.66)	48.4 (33.8)
Clofibric acid	71.8 (30.9)	27.7 (46.9)
Pravastatin	90.8 (13.2)	61.8 (23.6)

* values are presented as average with relative standard deviation (%) in brackets, for [a]N=10 and [b]N=8 samples.

**as to “no elimination” all cases with elimination efficiency below 10% were considered.

IV – Conclusions

For most of the investigated pharmaceuticals MBR effluent concentrations were significantly lower than in the effluent of a conventional treatment. Hydrochlorothiazide and paroxetine had slightly higher elimination percentages in CAS. Some substances were not removed neither in MBR nor in CAS process (e.g. carbamazepine). However, no relationship was found between the structures of target compounds and their removal during wastewater treatments. Furthermore, the range of variation of the removal rates of the MBR system was small for most of the compounds, while in the conventional treatment stronger fluctuations were observed and it turned out to be a lot more sensitive to changes in operational parameters (temperature, flow rate, etc).

NF and RO membranes investigated proved to be very efficient in eliminating the pharmaceuticals encountered, having different physico-chemical properties. The removal found for NF treatment was mostly over 85%, with the exception of gemfibrozil (50.2%), bezafibrate (71.8%), atenolol (66.6%), mefenamic acid (30.2%) and acetaminophen. The average removal from two RO treatment lines were slightly higher than for NF filtration (>90%). The only compounds with lower RRs in RO treatment were mefenamic acid (57.9%) and acetaminophen. Paroxetine and

propranolol were not eliminated in neither of the treatments, but since they were found only in one sampling campaign no conclusion can be drawn on their behaviour.

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