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REVIEW PAPER

Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR)

Magdalena Cirja · Pavel Ivashechkin · Andreas Schäffer · Philippe F. X. Corvini

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Abstract As a consequence of insufficient removal during treatment of wastewater released from industry and households, different classes of organic micropollutants are nowadays detected in surface and drinking water. Among these micropollutants, bioactive substances, e.g., endocrine disrupting compounds and pharmaceuticals, have been incriminated in negative effects on living organisms in aquatic biotope. Much research was done in the last years on the fate and removal of those compounds from wastewater. An important point it is to understand the role of applied treatment conditions (sludge retention time (SRT), biomass concentration, temperature, pH value, dominant class of micropollutants, etc.) for the efficiency of conventional treatment plants (CTP) and membrane bioreactors (MBR) concerning the removal of micropollutants such as pharmaceuticals, steroid- and xeno-estrogens. Nevertheless, the removal rates differ even from one compound to the other and are related to the physico-chemical characteristics of the xenobiotics.

Keywords Organic micropollutants · Sorption · Biodegradation · Wastewater · Conventional wastewater treatment · Membrane bioreactor

M. Cirja · A. Schäffer
Institute of Environmental Research – Environmental Biology and Chemodynamics (BioV), RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany

P. Ivashechkin
Institute of Environmental Engineering (ISA), RWTH Aachen University, Mies-van-der-Rohe-Str. 1, 52074 Aachen, Germany

A. Schäffer
IME Fraunhofer Institute, Auf dem Aberg 1, 57392 Schmallenberg, Germany

P. F. X. Corvini (✉)
Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences Northwestern Switzerland (FHNW), 40 Gründenstrasse, 4132 Muttenz, Switzerland
e-mail: philippe.corvini@fhnw.ch

1 Introduction

Environmental pollution by organic micropollutants is nowadays of great concern, especially, when it affects the aquatic environment. For many years, quantification of water pollution was restricted to monitoring biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrates, phosphates and total suspended solids (Metcalf and Eddy 2003; EN-ISO-9887 1994). Paralleling the bio/analytical progresses, the focus on macropollutants related to extensive industrial and agricultural activities is being enlarged to micropollutants belonging to diverse classes of chemicals such as pesticides, pharmaceuticals and personal care products (PPCP), and industrial chemicals, which are detected in trace amounts (Daughton and Ternes 1999).

Raising the micropollutants, e.g., pharmaceuticals and personal care products (PPCP), endocrine disrupting compounds (EDCs), and natural estrogens, as topic of interest, analytical chemistry technology improved the ability to detect concentrations of ng/l in aqueous media over the last decades. Mass spectrometric methods and techniques combining two chromatographic separation steps such as GC-MS(MS) and LC-MS(MS) (Marcomini et al. 1987; Jeannot et al. 2000; Li et al. 2000; Reemtsma et al. 2002; Braun et al. 2003; Clara et al. 2004a; Kloepfer et al. 2004b; Stehmann and Schröeder 2004; Einchorn et al. 2005; Huber et al. 2005; Weber et al. 2005; Moeder et al. 2006; Ternes 1998; Rychlowska et al. 2003; Luthje et al. 2004) and the use of radiolabelled tracers (Ingerslev et al. 2001; Doi et al. 2002; Lalah et al. 2003; Corvini et al. 2004; Liebig et al. 2005) are only few examples of analytical techniques to identify and analyse organic micropollutants and their degradation products occurring in wastewater. In parallel, the importance of detecting micropollutants was emphasized through the development of biotests (e.g., specialized to identify compounds with endocrine disrupting properties), which pointed out to the high biological activity of some class of micropollutants. For instance, the ubiquitous distribution in the environment of EDCs and their harmful potential was emphasized through the development of very sensitive biological tests based on immunological techniques such as ELISA or on endocrine functions such as yeast estrogen screen (YES) (Huang and Sedlak 2001; Aerni et al. 2003; Bringolf and Summerfelt 2003; Matsunaga et al. 2003) E-SCREEN assay (Soto et al. 1995), EROD activity assay (Ma et al. 2005) or combination of bioassays (Oh et al. 2006). Part of these studies concluded that some of these compounds [e.g., alkylphenol ethoxylates, bisphenol A (BPA), estrone (E1), 17β-estradiol (E2), 17α-ethinylestradiol (EE2)] can have high (specific biological) estrogenic activity even at extremely low concentration (Purdom et al. 1994; Jobling et al. 1998). Depending on the dose exposure, the EDCs are responsible for a wide range of adverse effects on aquatic organisms, e.g., feminization of male fish, masculinization of snails (Desbrow et al. 1998; Körner et al. 2000, 2001; Rajapakse et al. 2002), growth inhibition (Halling-Sørensen 2000; Cleuvers 2005), immobility (Cleuvers 2004), mutagenicity, mortality (Robinson et al. 2005), and changes in population density (Shull and Pennington 1993). Micropollutants are detected in river water world-wide (Ternes 1998; Kolpin et al. 2002) and wastewater is identified as substantial release route. Besides, further contamination occurs via leaching from solid waste sites, deposition from the air, etc. Micropollutants are not sufficiently removed in conventional sewage treatment plants and in order to prevent the spreading of contamination to groundwater and soils, the emission of some micropollutants, which are considered to be priority compounds, is regulated through the Water Framework Directive (2000/60/EC). The removal of micropollutants from wastewater during the treatment occurs through abiotic transformation, biological degradation and/or sorption. Among these mechanisms, sorption to suspended solids and biodegradation were reported to play predominant roles. Nevertheless, mechanisms of removal do not follow a general rule since their relative contribution depends on the physico-chemical properties of the micropollutant, the origin and composition of the wastewater, and the operational parameters of the wastewater treatment facility.

This article provides an overview on the fate of representative classes of organic micropollutants, i.e., PPCP and EDCs, during the wastewater treatment. Conventional treatment process (CTP) and membrane bioreactor (MBR) are in the focus of this review since CTP is still nowadays the most common wastewater treatment process, while MBR is a new promising technology for municipal wastewater treatment as well as for industrial one. Due to the lack of information on MBR and CTP comparative studies, important classes of micropollutants such as pesticides were left out of discussion in the present paper.

CTP and MBR are presented in parallel with respect to their performance for the removal of micropollutants. After a short overview on the fate of micropollutants in CTP and MBR in terms of bioavailability, sorption, biodegradation, and abiotic phenomena, the main factors affecting the removal of organic micropollutants during wastewater treatment are presented. These factors are linked to the chemical properties of pharmaceuticals and estrogenic compounds and the operational parameters of wastewater treatment process including sludge retention time, biomass concentration, pH value and temperature of wastewater.

2 Wastewater treatment plant (WWTP)

The treatment of wastewater aims at the removal of bulk organic matter (proteins, carbohydrates, etc.) and nutrients (Clara et al. 2005a). In CTP and MBR processes, sorption and biological degradation of organics and assimilation of inorganics by activated sludge, take place. In both systems, activated sludge consists mainly of flocculating microorganisms held in suspension and contact with wastewater in mixed aerated tanks. In CTP, the wastewater influent is first submitted to a mechanical treatment where large particles are removed from water. After a primary sedimentation stage, where the water flows slowly through large tanks, wastewater is send to the biological activated sludge tank. Finally, one additional separation step is achieved by gravity sedimentation in an external clarifier. In MBR process, the mechanical treatment and primary sedimentation tanks are not carried out. The main difference between CTP and MBR is the sludge–liquid separation step. The activated sludge tank includes a filtration step through micro or nanofiltration membrane, which retains the solid particles in the aeration tank. The biomass separation technique considerably influences the quality of wastewater effluent (Clara et al. 2005b). Generally, CTPs are operated at 1–5 g/l mixed liquor suspended solids (MLSS), while in MBR this concentration is considerably higher, ranging from 8 to 25 g/l or even more (Stephenson et al. 2000; Galil et al. 2003; Ivasheckin et al. 2004a). MBR technology allows sewage treatment at high MLSS concentration due to the membrane separation step and is not limited by the sedimentation capacity of the secondary clarifier. As biomass continuously grows, excess sludge has to be removed from the system in order to maintain a constant concentration of microorganisms in the tank. One of the main parameters of activated sludge systems is the sludge retention time (SRT), which is controlled via the removal of excess sludge. High SRTs generally correlate with high performance of the wastewater treatment concerning COD removal. Usually, SRT up to 25 or 80 days are applied in MBR, while typical values for a CTP vary from 8 to 25 days (Winnen et al. 1996; Cote et al. 1997; Cicek et al. 1999; Stephenson et al. 2000; Clara et al. 2004a; Johnson and Williams 2004; Joss et al. 2005). Due to the high SRT values and complete retention of solids inside of MBR, biodiversity of the microorganisms is favoured and even slowly growing and free living bacteria remain in the system (Clara et al. 2005b; Pollice and Laera 2005; Howell et al. 2003). Furthermore, the adaptation of some microorganisms for the degradation of persistent compounds contained in sewage, e.g., nonylphenol (NP) and further estrogens, is assumed to be more likely in MBR than in CTP (De Wever et al. 2004; Ivasheckin et al. 2004a; Siegrist et al. 2004).

Recognized advantages of MBR are high effluent quality in terms of COD, nitrogen, phosphorus, ammonia, retention of suspended solids and microorganisms, reliable biomass concentration, efficient treatment of complex waste streams and compactness of the installation (Cicek et al. 1999; Abegglen and Siegrist 2006; Cornel and Krause 2006). At the opposite, the high MLSS concentration used in MBR leads to problems concerning oxygen supply of the microorganisms and the membranes require frequent cleaning (Cicek et al. 2001; Cornel and Krause 2006).

3 Fate of micropollutants in CTP and MBR

The fate of micropollutants during CTP or MBR treatment depends on physico-chemical properties of the compound, operational parameters (biomass concentration, sludge retention time, hydraulic retention time, temperature and pH) of wastewater to be treated. In the literature, sorption and biodegradation are reported to be two of the most important removal processes of micropollutants from wastewater and both processes are correlated with the availability of the substrate to the degrading microorganisms (Clara et al. 2004a; Ivashechkin et al. 2004a; Clara et al. 2005a; Joss et al. 2005).

3.1 Bioavailability

As biodegradation is the primary removal pathway for organics in the activated sludge treatment, the degree of bioavailability of a micropollutant is important (Vinken et al. 2004; Burgess et al. 2005). In wastewater treatment plants, the accessibility of micropollutants to the population of the activated sludge can be defined in terms of external and internal bioavailability. External bioavailability rather defines the accessibility of the substance to microorganisms, while internal bioavailability is limited to the uptake of the compounds into the internal cell compartment. In general, bioavailability consists of the combination of physico-chemical aspects related to phase distribution and mass transfer, and of physiological aspects related to microorganisms such as the permeability of their membranes, the presence of active uptake systems, their enzymatic equipment and ability to excrete enzymes and biosurfactants (Wallberg et al. 2001; Cavret and Feidt 2005; Del Vento and Dachs 2002; Ehlers and Loibner 2006). Higher bioavailability and thus potential for biological degradation of pollutants depend mostly on the solubility of these compounds in aqueous medium.

3.2 Sorption

Sorption mainly occurs via absorption and adsorption mechanisms. Absorption involves hydrophobic interactions of the aliphatic and aromatic groups of compounds with the lipophilic cell membrane of some microorganisms and the fat fractions of the sludge. Adsorption takes place due to electrostatic interactions of positively charged groups (e.g., amino groups) with the negative charges at the surface of the microorganisms' membrane. The quantity of a substance sorbed C_{sorbed} (g/l), is usually modelled with a simplified linear equation (1) (Siegrist et al. 2004).

$$C_{\mathrm{sorbed}} = K_{\mathrm{d}} \cdot \mathrm{SS} \cdot C_{\mathrm{dissolved}} \tag{1}$$

K_{d} is the sorption constant (l/g), which is defined as the partitioning of a compound between the sludge and the water phase. SS (g/l) represents the concentration of suspended solids in the activated sludge tank, and $C_{\mathrm{dissolved}}$ (g/l) is the dissolved concentration of the substance.

3.3 Biodegradation

Biodegradation defines the reaction processes mediated by microbial activity (biotic reaction). In aerobic processes, microorganisms can transform organic molecules via the succession of oxidation reactions to simpler products for instance other organic molecules or mineralized to CO_2 (Siegrist et al. 2004; van der Meer et al. 2006). At low concentration, the kinetics of decomposition of micropollutants occurs mostly according to a first order reaction (see Eq. 2, Siegrist et al. (2004).

$$R_{\mathrm{degradation}} = K_{\mathrm{degradation}} \cdot \mathrm{SS} \cdot C_{\mathrm{micropollutant}} \tag{2}$$

$R_{\mathrm{degradation}}$ is the degradation rate, $K_{\mathrm{degradation}}$ is the degradation constant, SS (g/l) is the concentration of suspended solids and $C_{\mathrm{micropollutants}}$ (mg/l) is the concentration of micropollutants in influent supposed to be degraded.

The degradation rates are strongly dependent upon environmental conditions, such as the redox potential of the systems and the microbial populations present. The acclimatization of microorganisms to the substrate requires time and the affinity of the bacterial enzymes for the micropollutant in the activated sludge influences the pollutant transformation or decomposition (Spain et al. 1980; Matsumura 1989).

3.4 Abiotic degradation and volatilization

Abiotic degradation comprises the degradation of organic chemicals via chemical (e.g., hydrolysis, oxidation) or physical (e.g., photolysis) reactions (Acher 1985; Doll and Frimmel 2003; Bouillon and Miller 2005; Iesce et al. 2006). Abiotic processes are not mediated by bacteria and have been found to be of fairly limited importance in wastewater compared to the biodegradation of micropollutants (Stangroom et al. 2000; Lalah et al. 2003; Ivashechkin et al. 2004a; Katsoyinnis and Samara 2005; Soares et al. 2006). The removal of micropollutants by volatilization during the activated sludge process depends on vapour pressure (Henry's constant) and octanol water partition coefficient (K_{ow}) of the analysed micropollutant, and becomes significant when the Henry's law constant (H) ranges from 10^{-2} to 10^{-3} (Stenstrom et al. 1989). At very low H/K_{ow} ratio, the compound tends to be retained by particles (Galassi et al. 1997; Roger 1996). The rate of volatilization is also affected by gas flow rate and therefore, high efficiency submerged aeration systems such as fine bubble diffusers should be used to minimize volatilization rates in wastewater treatment plants (Stenstrom et al. 1989).

4 Factors affecting the removal of micropollutants during wastewater treatment

4.1 Chemical properties of micropollutants

4.1.1 Hydrophobicity and hydrophilicity

Hydrophobicity refers to the physical property of a molecule that is repelled from a mass of water. Many of the organic micropollutants found in wastewater are hydrophobic compounds. Hydrophobicity is the main property, which leads to sorption to the sludge, fat and particulate matter during the wastewater treatment (Garcia et al. 2002; Ilani et al. 2005; Yu and Huang 2005). Micropollutants can sorb to suspended solids and subsequently be removed via the withdrawal of the excess sludge during the wastewater treatment. Sorption of micropollutants to the solid phase can be estimated using the K_{ow} values, which reflects the equilibrium of partitioning the organic solute between the organic phase, i.e., octanol and the water phase (Lion et al. 1990; Stangroom et al. 2000; Yoon et al. 2004). High K_{ow} is characteristic for hydrophobic compounds, poor hydrosolubility and high tendency to sorb on organic material of the sludge matrix (Lion et al. 1990; Stangroom et al. 2000; Yoon et al. 2004). For compounds with log $K_{ow} < 2.5$, the sorption to activated sludge is not expected to contribute significantly to the removal of the pollutants via excess sludge withdrawal. Between log K_{ow} 2.5 and 4 moderate sorption is expected and values higher than 4.0 are synonyms to high sorption potential (Rogers 1996).

4.1.1.1 The influence of hydrophobicity on the removal of pharmaceuticals in wastewater treatment Despite the presence of ionic charges on antibiotic molecules and their low K_{ow}, the fate of these compounds in wastewater treatment systems can be influenced by hydrophobic interactions with the sludge matrix. For instance, oxytetracycline can sorb to the sludge even if they are present in the form of zwitterion (Kulshrestha et al. 2004). Sorption to sewage sludge of antibiotics in a CTP led to 80–90% removal of ciprofloxacin and norfloxacin (Giger et al. 2003). In another study, approximately 80% of norfloxacin and ciprofloxacin which entered into the CTP was sorbed to particles in the raw sewage water (Lindberg et al. 2006). Sorption kinetics of oxytetracycline to the sludge in a lab scale study was studied by Kim et al. (2005). At 3.6 g/l MLSS concentration, 95% of oxytetracycline was removed from water phase within only 1 h and the concentration at equilibrium remained unchanged over 24 h.

In sewage treatment plant, the removal of some pharmaceuticals (e.g., diazepam, diclofenac, ibuprofen, naproxen, sulfamethoxazole) was mainly due to adsorption of those compounds to sludge present in the biological reactor (aeration tank) (Carballa et al. 2004). At the end of this experiment, the removal efficiency varied between 40 and 60% for the anti-inflammatory compounds and reached approximately 60% for sulfamethoxazole. The sorption was even evident during the primary treatment aiming at fat separation, whereby the liphophilic properties of organic pollutants led to removal rates ranging from 20 to 50%. In another study, Carballa and collaborators (2005) studied the behaviour of micropollutants with high hydrophobicity (galaxolide, tonalide) during different steps of wastewater treatment and compared the results with the behaviour of more polar compounds (e.g., ibuprofen, naproxen, diclofenac, diazepam, carbamazepine). Once more, it was concluded that the high sorption properties of tested compounds with hydrophobic character led to up to 70% removal. At the opposite side, no removal of carbamazepine and ibuprofen was observed.

4.1.1.2 The influence of hydrophobicity on the removal of steroid- and xeno-estrogens in wastewater treatment The estrogenic compounds are generally characterized by relatively medium hydrophobicity (see Table 1). Andersen et al. (2003) carried out a series of sorption experiments using artificial wastewater and activated sludge from municipal CTPs in order to determine the minimal equilibrium time between water and solid phases for estrone (E1), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2). Within half an hour 87–97% of the estrogens were associated with sludge particles and after 2 h the equilibrium was approached. Sorption was estimated to 42.9% (E2), 39.1% (EE2), 47.4 (E3), 46.2% (octylphenol, OP), 34.7% (Bisphenol A, BPA) and 61.8% (nonylphenol, NP) (Yamamoto et al. 2003). The authors of this study demonstrated that the fate of these compounds is highly correlated to increasing or decreasing log K_{ow} value. Experiments carried out with ^{14}C-labelled EE2 indicated that 80% of the compound was bound to the sludge and removed from the liquid phase in this way (Layton et al. 2000).

A significant amount of the NP entering the CTP with the influent was accumulated in the sludge (93.5%), while the percentage discharged through effluent varied from 4.8% up to 51.5% (Keller et al. 2003). Esperanza and collaborators (2004) found that approximately 60% of the NPnEO surfactants were associated with the solids in the aeration tank and increased concentration of all targeted compounds was observed in the effluent in comparison to raw influent due to a slow desorption process. Approximately 80% of NP was eliminated in a pilot scale MBR treating dumpsite leachate (Wintgens et al. 2003). These authors assumed

Table 1 Physico-chemical properties (e.g., Log K_{ow} and vapour pressure) of a selection of pharmaceuticals, steroids and xeno-estrogens discussed in present article for determining the fate in CTP and MBR systems

Class of compounds	Name of compound	Log K_{ow}	Vapour pressure (mmHg)
Pharmaceuticals	Acetylsalicylic acid[a]	1.19	2.02E-05
	Benzafibrate[d]	4.25	n.a.
	Carbamazepine[a]	2.45	1.84E-07
	Ciprofloxacin[d]	0.4	n.a.
	Clofibric acid[d]	2.84	8.96E-07
	Diclofenac[d]	4.02	4.73E-12
	Ibuprofen[a]	3.95	1.86E-04
	Ketoprofen[a]	3.12	3.72E-07
	Mefenamic acid[a]	5.12	4.63E-07
	Naproxen[d]	3.18	1.89E-06
	Norfloxacin[a]	–1.0	n.a.
	Oxytetracycline[d]	0.90	3.9E-25
	Phenazone[d]	0.38	n.a.
	Sulfamethoxazole[d]	0.89	n.a.
	Tetracycline[d]	–1.30	3.60E-25
	Trimethoprim[c]	0.2891	1.082E-17
Steroid- and xeno-estrogens	Bisphenol A (BPA)[a]	3.32	3.91E-07
	17α-ethinylestradiol (EE2)[b]	3.67	7.94E-12
	17α-estradiol (E2)[a]	4.01	1.26E-08
	Estrone (E1)[a]	3.13	1.42E-07
	Estriol (E3)[a]	2.45	1.97E-10
	Octylphenol (OP)[a]	4.12	4.78E-04
	Nonylphenol (NP)[a]	4.48	2.36E-05

[a] Nakada et al. (2006)
[b] Hansch et al. (1995)
[c] Takacsnovak et al. (1992)
[d] Predicted by WSKOW v1.41 and HENRYWIN v3.10 (EPI Suite, USEPA)

that the adsorption of the compound on suspended matter in the bioreactor and the subsequent withdrawal with the excess sludge was the main removal pathway of investigated compound. The sorption and removal of micropollutants in CTP or MBR is strongly dependent on the K_{ow} value of micropollutant. Highly hydrophobic compounds reaching the treatment plant will be adsorbed and removed from wastewater while, very polar compounds will be poorly eliminated through sorption process.

4.1.2 Chemical structure

Another chemical property important in evaluating the removal potential of organic micropollutants is the chemical structure. Chemical structure and the elementary composition of a compound can influence the removal rates from wastewater during CTP or MBR treatment.

4.1.2.1 Influence of chemical structure on the removal of pharmaceuticals in wastewater treatment Pharmaceuticals are complex molecules and are most notably characterized by their ionic nature. Compounds having a complex chemical structure such as the pharmaceuticals ketoprofen and naproxen were not eliminated during CTP process but were by MBR (Kimura et al. 2005). It was assumed that the poor removal in CTP is due to the presence of complex structure with two aromatic rings making the compound more resistant to degradation process. Compounds like clofibric acid and diclofenac are small molecules harbouring chlorine groups and were not efficiently removed by both CTP and MBR. Therefore, these authors attributed the recalcitrance of these PPCP to the presence of halogen groups. Nevertheless, this theory requires further verification. On basis of the removal extent and the chemical structure the same authors proposed a classification of PPCP into compounds, which are easily removed by both CTP and MBR (i.e., ibuprofen), not efficiently removed in both systems (i.e., clofibric acid, dichlofenac), and not satisfactory removed by CTP but well removed by MBR (i.e., ketoprofen, mefenamic acid and naproxen). According to other authors, increasing amounts of nitro- and chlorine-groups in aromatic compounds result in a decreasing degradation rate (Andreozzi et al. 2006).

4.1.2.2 The influence of chemical structure on steroid- and xeno-estrogens in wastewater treatment The removal efficacy of polar compounds such as naphthalene sulphonates (anionic surfactants) during MBR treatment depends strongly on their respective molecular structure (Reemtsma et al. 2002). The removal of the naphthalene monosulphonates was almost complete, while the removal of naphthalene disulfonates was limited to about 40%. Degradation and partitioning behaviour have also been reported to be a function of the polar-to-non polar group ratio of the molecule (Rutherford et al. 1992), the presence of aromatic moieties (Chiou et al. 1998), and the organic carbon content (Yamamoto et al. 2003) which characterize the molecule. Linear alkylbenzene sulphonates (LAS) with long alkyl chain were preferentially adsorbed to the sludge matrix, while the short homologues of this anionic surfactant were found in the effluent in a comparative study in CTP and MBR (Terzic et al. 2005).

The chemical structure of alkyl chain of NP and LAS is responsible for completely different biodegradation pathways. For instance, branched isomers of NP are very recalcitrant and resulting metabolites posses incomplete degraded alkyl chain while ultimate degradation of linear NP isomers is faster (Cirja et al. 2006; Corvini et al. 2006).

The removal rate is influenced by the chemical structure of steroids. 17β-estradiol and 17α-ethinylestradiol have basically the same chemical structure, except the ethinyl group present in EE2, which leads to drastic differences in biodegradability. In wastewater treatment systems, microorganisms are able to degrade quite easily E2, while EE2 is very recalcitrant (Ternes et al. 1999).

On the whole, chemical structure of an organic pollutant does not only provide information concerning the class to which the compounds belong, but also indicates degradability or persistence of xenobiotics reaching the aquatic environment. A compound with simple chemical structure (e.g., absence of branched alkyl chain) will be prone to removal via degradation during the wastewater treatment. Compounds with complex structure or chemicals bearing toxic groups are likely to persist as parent compounds or incompletely degraded metabolites in sewage water (either in dissolved state or sorbed to the sludge particles).

4.2 Process parameters of CTP and MBR

4.2.1 Sludge retention time (SRT) and biomass concentration

Influence of SRT. Sludge retention time (SRT) is the mean residence time of microorganisms in CTP and MBR systems. Many studies state that sufficient high SRT is essential for the removal and degradation of micropollutants from wastewater and allow for the enrichment of slowly growing bacteria and also the establishment of a more diverse biocoenosis able to degrade a large number of micropollutants. It was demonstrated that at short SRTs (<8 d) those bacteria are removed from the system and in this case, the biodegradation is less significant and adsorption to sludge will be more important (Jacobsen et al. 1993). A diversified microbiocoenosis can develop at SRT higher than 8 d, including also nitrifying bacteria. Nitrification leads to the conversion of ammonia to nitrate and this process is mediated by endogeneous microorganisms in aerated tanks. Complete nitrification was demonstrated in MBRs at sludge ages of 5–72 d and organic loading rate of 0.05–0.66 kg BOD m^{-3} d^{-1}(Fan et al. 2000). The Byrns model (Byrns 2001) concerning xenobiotics degradation shows that at low SRTs, most of the compounds are removed through sludge discharge. As the SRT increases, the proportion of sludge wasted from system decreases and higher amount of less polar micropollutants remain in the system for further degradation.

Influence of biomass characteristics. The biomass characteristics are important factors for biodegradation and differ between CTP and MBR treatment (Brindle and Stephenson 1996). The possibility for genetic mutation and adaptation of microorganisms to assimilate persistent organic compounds increases at higher STP (Cicek et al. 2001). Furthermore, some enzymatic activities increase proportionally to the higher specific surface area of MLSS, which is directly related to the floc-structure. The activated sludge composition varies both with the influent composition and operating conditions adapted to the wastewater treatment system (Chang and Judd 2003). Comparing the MBR and CTP systems, Cicek and collaborators (1999) showed that the biomass in the MBR has higher viable fraction than in the CTP. This phenomenon can be attributed to improved mass-transfer conditions in the MBR favoured by smaller flocs and the presence of many free-living bacteria. The size of bacterial flocs contained in the activated sludge can be another factor causing the difference between CTP and MBR wastewater treatment processes. In MBR it varies between 10 and 100 μm, and in the CTP between 100 and 500 μm (Zhang et al. 1997). The same authors reported that specific flocs surface per unit reactor volume was ten times higher in MBR than in CTP systems. The small size of microorganisms and the flocs surface implies short distances to be overcome by the substrate during the diffusion into the flocs.

4.2.1.1 Influence of SRT on removal of pharmaceuticals from wastewater In order to remove pharmaceuticals from wastewater through the treatment in CTP or MBR, SRT is one of the factors easy to modify and improve the process efficiency. Two MBRs operated at high SRT of 26 d showed removal efficacy of 43% for benzothiazoles (Kloepfer et al. 2004a). By varying the SRT in MBRs, Lesjean et al. (2005) noticed that the removal of pharmaceuticals residues increased with a high sludge age of 26 d and inversely decreased at lower SRT of 8 d. SRT values between 5 and 15 d are required for biological transformation of some pharmaceuticals, i.e., benzafibrate, sulfamethoxazole, ibuprofen, and acetylsalicylic acid (Ternes et al. 2004). Nevertheless, the application of high SRT is not automatically leading to the removal of all pollutants. For SRT of 2 d, Clara et al. (2005) found out that none of investigated pharmaceuticals, e.g., ibuprofen, benzothiazole, dichlorofenac and carbamazepine was eliminated, while applying SRT of 82 d in MBR and 550 d in CTP removal rate >80% were obtained. Nevertheless, removal rate of carbamazepine remained below 20%, for all applied SRTs. The same results were reported also by Ternes et al. (2004) were carbamazepine and diazepam is not degradable even at SRT over 20 d. In MBR containing acclimatized sludge, the removal of diclofenac ranged from 44 to 85% at SRT of 190–212 d (Gonzáles et al. 2006).

The biodegradability of trimethoprim was studied during different sewage treatment steps using batch systems (Perez et al. 2005). The main outcome of this study was that the activated sludge treatment comprising nitrification process was the only treatment capable to eliminate trimethoprim. The capacity of nitrifying bacteria (growing at SRT >8 d) to break down trimethoprim was quite unexpected, because a precedent study reported that this xenobiotic cannot be degraded by microorganisms (Junker et al. 2006).

In a lab scale MBR with high sludge concentration ranging between 20 and 30 g/l and a SRT of 37 d, degradation of selected pharmaceuticals were tested (Quintana et al. 2005). Bezafibrate was transformed (60%) but not mineralized and the metabolites were tentatively identified. The naproxen was degraded over a period of 28 d. Ibuprofen degradation started after 5 d and was complete after 22 d.

The antibiotics tetracyclines were highly sorbed to the sludge and the sorption correlated well with the SRT during adsorption test in batch system (Sithole and Guy 1987). The adsorption kinetics for tetracyclines was determined at various biomass concentrations in sequencing batch reactors at different SRT and HRT (Kim et al. 2005). Between 75 and 95% of applied tetracyclines was adsorbed onto the sludge after 1 h. At long SRT (10 d) the removal of tetracyclines was 85–86%, while the decrease of SRT to 3 d gave a lower removal (78%). The lower degradation rates were assigned to the reduced biomass concentration once the SRT was shortened.

4.2.1.2 Influence of SRT on removal of steroid- and xeno-estrogens from wastewater Johnson and his collaborators (2005) operated many CTPs in order to evaluate the removal of NP and E1, E2, EE2 from wastewater. Satisfying degradation of investigated compounds was registered at high SRT of 30 d. In the same study it was shown that no significant difference is observed between the MBR and CTP in term of degradation performances. Similar observation on the removal of NP and BPA was described by Ivashechkin et al. (2004a) during the operation of MBR and CTP processes at SRTs of 12 and 25 d. The high removal efficiency (95%) associated to the operation of high SRT in MBR was confirmed as well by Terzic et al (2005) concerning the removal of NPnEO from wastewater. Joss et al. (2004) studied the E1, E2, EE2 degradation in batch experiment using sludge from CTP with SRT of 11 d and MBR with 30 d. For the natural estrogens E1 and E2, degradation activity seemed to be higher in MBR than in CTP by a factor of 2–3 with the respect to the applied SRT. Clara et al. (2005b) confirmed the good removal (80%) of BPA, E1, E2, E3 in CTPs or MBR. For SRT higher than 10 d, no significant difference was observed between the various wastewater treatment systems; the removal rates ranged between 90 and 95% for E1, E2 and EE2 in CTP and MBR. The good performance of the treatment was attributed to the high age of the biofilm sludge. Using SRT of 12–15 d, both of the treatment systems were adapted to nitrification denitrification process. In a full-scale municipal plant including a nitrification step, degradation rates of estrogens ranged between 79 and 95% and the extended biodegradation was mainly attributed to the nitrifying activity (Vader et al. 2000). When the sludge was adapted to the nitrification process, the degradation of EE2 reached satisfying rate of removal (half-life of approximately 28 h). On the contrary, the degradation of EE2 stopped when the sludge lost the nitrification capacity due to the low temperature. The correlation between the efficacy of biological treatment to remove micropollutants and the nitrogen removal is supported by other studies where good removal rates are reached in installations designed for the optimal treatment of nitrogen from effluents (Clara et al. 2005b). Apparently, WWTP designed for nitrogen removal achieved also a high removal of EDC.

Concerning the removal of micropollutants, SRT is a key parameter of the wastewater treatment in CTP and MBR. At longer SRT in the treatment system the contact time, the diffusion into the flocs, and the adaptation of microorganisms to the substrate are improved. From these studies, it can be concluded that SRTs ranging between 10 and 30 d allow for sufficient removal rates concerning most of the investigated micropollutants. The SRT of CTP and MBR has to be chosen according to the persistence of micropollutants to be eliminated. In relation to SRT, the biomass concentration is very important. Sorption of micropollutants is favoured by the high biomass content, which is especially characteristic for MBR and additionally, the sludge composition plays an important role concerning the micropollutants degradation.

4.3 pH value

The acidity or alkalinity of an aqueous environment can influence the removal of organic micropollutants from wastewater by influencing both the physiology of microorganisms (pH optima of microbial enzyme activities) and the solubility of micropollutants present in wastewater.

4.3.1 Influence of pH value on the removal of pharmaceuticals during wastewater treatment

Depending on their pK_a values, pharmaceuticals can exist in various protonation states as a consequence of pH variation in the aquatic environment. At pH 6–7 tetracyclines are not charged and therefore, adsorption sludge becomes an important removal mechanism (Kim et al. 2005). It was also demonstrated that the hydrophobicity of norfloxacin varies with the pH values, being very low at pH < 4 and pH > 10 and the maximal hydrophobic value was reached at pH of 7.5 (Advanced Chemistry Development, ACD Labs). Another study identified the pH value as critical parameter affecting the removal of micropollutants during the MBR treatment, pH value varied from neutral to acidic as nitrification became significant in the MBR (Urase et al. 2005). At pH lower than 6, high removal rate (up to 90%) was observed for ibuprofen. Ketoprofen was removed from MBR up to 70% when the pH dropped down below 5.

4.3.2 Influence of pH value on the removal of steroid- and xeno-estrogens

The sorption of E1 and E2 to the organic matrix was reported to be strongly dependent on the pH value (Jensen and Schaefer 2001). In these studies, 23% of the steroid estrogens were sorbed to the activated sludge at pH value of 8, while this proportion increased up to 55% when pH value was maintained at 2 and it was shown that increasing pH values up to pK_a (pH > 9) lead to an increased desorption of steroids. The same behaviour was observed in the study of Clara and collaborators (2004a, b), where solubility of E2 and EE2 increased at pH of 7–12. During the sludge treatment like sludge dewatering and conditioning with lime, the pH is increasing over 9 and the micropollutants can be desorbed from sludge solids. For instance, the recovery of BPA in aqueous phase, took place at pH > 12 and desorption was attributed to the increased hydrosolubility of the deprotonated form of BPA (Clara et al. 2004b; Ivashechkin et al. 2004b). The consequence of such high release was a high backloading of CTP via the recycling of the process water.

In another study, the sludge–water partition coefficients (K_p) of investigated estrogens in activated sludge from a CTP were increased with the decrease of pH value for almost all the investigated compounds (BPA, E2, EE2) (Kikuta 2004). In the case of compounds harbouring one carboxyl group, the K_p values at pH = 5.6 were 2.5–30 times higher than those at pH = 6.7, while for compounds having phenol groups such as E1, EE2, BPA the increase of partition coefficient varied to a lower extent within this range of pH values.

The better removal rate of deprotonable micropollutants from wastewater can be achieved at low pH value, the protonation state influencing both sorption and degradation processes. On the one hand, acidic conditions are not usual in CTP or MBR, but could be adapted for systems treating wastewater from highly contaminated sites or industrial wastewater in order to increase degradation rates. On the other hand, since the dissolution of a compound can be controlled by varying the pH value, one can use this advantage in order to avoid further contamination. A possible application would be the alkalinization of sludge to be used for soil amendment in agricultural applications.

4.4 Temperature during the wastewater treatment

Temperature is influencing the microbial activity in both CTP and MBR as microbial growth rate strongly varies according to the applied temperature conditions (Price and Sowers 2004). With increasing temperatures, adsorption equilibriums are reached earlier and degradation rate and bacterial growth are faster (ten Hulscher and Cornelissen 1996).

4.4.1 Influence of temperature on the removal of pharmaceuticals during wastewater treatment

In a recent study, the removal of pharmaceuticals, i.e., ibuprofen, benzafibrate, diclofenac, naproxen and ketoprofen was reported to increase during the summer time when the temperature reached 17°C in comparison to the winter season when the water temperature was around 7°C (Vieno et al. 2005). A temperature of 20°C was beneficial for the removal of pharmaceuticals in CTP and MBR and for instance more than 90% bezafibrate was eliminated (Clara et al. 2004a). At low temperature during winter season, the degradation rates decreased. In the case of diclofenac, naproxen, and ibuprofen, better performances of removal are reached when the systems are operated at 25°C than at 12°C (Carballa et al. 2005). In another study, comparing the removal of pharmaceuticals (phenazone, carbamazepime and metabolites) during CTP and MBR process, the performance of the CTP process remained relatively constant over time despite the winter/summer changes of temperature (10–25°C), while in MBR removal rates were strongly affected by the seasonal changes (Lesjean et al. 2005). The higher temperature registered in summer in MBR and the long sludge age (26 d) improved the removal rates at 80–100%. The same study states that the extent of removal in MBR units was up to 99% for pharmaceuticals and up to 80% for the steroids initially present in the incoming wastewater during the summer period. The adsorption of antibiotics fluoroquinolone to the particles in the raw water is influenced by the temperature. Lindberg et al. (2006) stated that at 12°C the adsorption was 80%, while Golet et al. (2003) showed an adsorption of 33% when the temperature was higher. Studies on the influence of high temperature on the removal of COD from wastewater of pharmaceutical industry led to the conclusion that temperature serves as pressure of selection for the bacterial community development during aerobic biological wastewater treatment (La Para et al. 2001). In the same time, it stimulates higher degradation rates of pharmaceuticals.

4.4.2 The influence of temperature on the removal of steroid- and xeno-estrogens during wastewater treatment

Temperature was reported to influence also the mineralization of E2 (Layton et al. 2000). An increase of 10°C leads to a duplication of microbial activity (from Arrhenius equation) and mineralization rate and changes of approximately 15°C had statistically significant effect on the mineralization rate of E2 present in the aqueous phase. Concerning EE2, other authors carried out investigations in both systems and reported that over the sampling period (May–July) the removal varied from 60 to 70% in both CTP and MBR (Clara et al. 2004a). In December, the EE2 removal in the CTP was 60%, while as a consequence of temperature decrease this compound was not removed in MBR, although removal of EE2 should at least have occurred through sorption. Another study on the fate of estrogens led to the conclusion that biomass was less active concerning the removal of steroids during the winter and high concentration was observed in the effluent (Desbrow et al. 1998).

The removal of NPnEO and LAS from municipal wastewater was investigated (Terzic et al. 2005). The results of this study showed removal efficiency up to 95% and the efficacy was in fact improved when the temperature in the treatment system varied from 3 to 30°C. In the case of NP it was stated that at 10–15°C, which are typical values for Europe, the compound is preferentially distributed into the sludge fraction (Brunner et al. 1988; Tanghe et al. 1998). The degradation of NP in a packed bed bioreactor containing cold adapted bacteria, (Soares et al. 2006) showed optimal biodegradation rate at temperature of 10°C. By decreasing the temperature from 10 to 5.5°C a negative effect on the bioreactor efficiency was observed. The explanation was based on the lower diffusion of organic pollutants (limited solubility), which decreases with the temperature.

On the whole, the temperature influences the solubility and further physico-chemical properties of micropollutants present in the wastewater treatment systems and also the structure of the bacterial community. Concerning the removal of micropollutants, it seems that CTP shows better stability than MBR during seasonal temperature variations. The larger surface of CTP than MBR would attenuate the variations of temperature, protecting bacterial activity against temperature shock produced in the system. The temperature-induced increase in microbial activity favours a higher biodegradation rate of micropollutants. Besides, as the MBR system are more compact, operation at high constant temperature required for the degradation of persistent organic micropollutants represents a solution for a satisfying removal of micropollutants.

5 Conclusions

From the general overview of the factors influencing the removal of organic micropollutants from wastewater, it can be concluded that sorption and biodegradation are the dominant removal processes in CTP and in MBR, which are influenced by operation conditions. Operation parameters of both treatment systems seem to play substantial/important role on the biodegradation rates and pathways for the removal of pharmaceuticals and estrogenic compounds. Sewage treatment conditions represent in fact the key for the optimization of different processes for efficient removal of xenobiotics and macropollutants before releasing the effluent into the environment. Most of the studies related in the present article concerned adapted systems, which were operated under different conditions. This fact must be taken into account in order to interpret the results and compare the values retrieved from various studies. The operation mode and the scale of the process are important and data obtained from studies carried out at real scale can drastically differ from those resulting from batch experiments. However, the latter can supply qualitative information on the fate of the investigated compound, which may be extrapolated to the real scale for modelling applications. The removal rates differ from one compound to the other, even if physico-chemical properties such as K_{ow}, pK_a, and chemical structure are similar.

Concerning the factors determinant for the removal of micropollutants from wastewater, which have been discussed in the present work, some general rules can be derived as follows:

(1) Hydrophobic compounds (NP, EE2, etc.) can be removed from the influent via adsorption to the sludge particles present in the system.
(2) Chemical structure: compounds containing complex structure (e.g., alkyl chain branching) and toxic groups (e.g., halogens and nitro group) show higher resistance to biodegradation processes.
(3) When SRT in the wastewater treatment system is high enough (at least 8 d) the removal of organic compounds through biodegradation processes is enhanced.
(4) The temperature of wastewater treatment seems to play an important role; WWTP in countries with average temperature of 15–20°C may better eliminate micropollutants as in cold countries with a temperature mostly under 10°C. The seasonal temperature changes between summer and winter influences the biodegradation and removal of micropollutant.

(5) The pH value influences the removal of micropollutants from wastewater. Although few studies focused on this parameter, the control of pH value might be a solution for the removal of micropollutants in WWTP. The pH of industrial wastewater is often subject to variations and may also negatively influence the removal of the micropollutants. One solution would be the adjustment of the pH of the influent before the biological treatment step. Furthermore, modifying the protonation state of some compounds represents a solution for increasing their removal via adsorption to the sludge.

By comparing CTP and MBR, it can be concluded that there is no real difference between the two investigated systems concerning the removal of different classes of micropollutants. Nevertheless, the removal rates differ from one compound to the other and the rates of removal depend on the physico-chemical characteristics of the xenobiotic, e.g., hydrophobicity, chemical structure, pK_a, etc. Hydrophobic compounds are removed from the liquid phase via adsorption, and possibly through biodegradation processes when the SRT is high enough.

Although the research on the fate and removal of micropollutants from wastewater has made consequent progress, one can still notice a lack of studies at full scale, especially for MBR process. Additionally to the compactness of MBR plant and the high organic load that can be applied, this process is promising concerning the removal of micropollutants, which are eliminated at high SRT and biomass concentration.

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