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Removal characteristics of pharmaceuticals and personal care products: Comparison between membrane bioreactor and various biological treatment processes

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HIGHLIGHTS

- Removal of 57 PPCPs in MBR and various biological treatment systems was investigated.
- The majority of PPCPs were efficiently eliminated in MBR.
- Adsorption capability between MBR and other processes did not vary significantly.
- Enhanced biodegradation in MBR was the dominant removal mechanism for most PPCPs.

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ABSTRACT

We investigated the concentrations of 57 target compounds in the different treatment units of various biological treatment processes in South Korea, including modified biological nutrient removal (BNR), anaerobic-anoxic-aerobic (A2O), and membrane bioreactor (MBR) systems, to elucidate the occurrence and removal fates of PPCPs in WWTPs. Biological treatment processes appeared to be most effective in eliminating most PPCPs, whereas some PPCPs were additionally removed by post-treatment. With the exception of the MBR process, the A2O system was effective for PPCPs removal. As a result, removal mechanisms were evaluated by calculating the mass balances in A2O and a lab-scale MBR process. The comparative study demonstrated that biodegradation was largely responsible for the improved removal performance found in lab-scale MBR (e.g., in removing bezafibrate, ketoprofen, and atenolol). Triclocarban, ciprofloxacin, levofloxacin and tetracycline were adsorbed in large amounts to MBR sludge. Increased biodegradability was also observed in lab-scale MBR, despite the highly adsorbable characteristics. The enhanced biodegradation potential seen in the MBR process thus likely plays a key role in eliminating highly adsorbable compounds as well as non-degradable or persistent PPCPs in other biological treatment processes.

1. Introduction

Recently, one of the key issues in wastewater reclamation has been the emerging problem of micropollutants such as pharmaceuticals and personal care products (PPCPs), which can have negative effects on human health and aquatic ecosystems (Jones et al., 2004). Some researchers have pointed out that certain PPCPs present in trace concentrations, ranging from a few ng/L to several μg/L, can have adverse impacts on the environment (Behera et al., 2011; Gabet-Giraud et al., 2010; Gros et al., 2010; Han et al., 2006; Tewari et al., 2013). The main source of these compounds is effluent from wastewater treatment plants (WWTPs) (Gómez et al., 2007; Gracia-Lor et al., 2012; Joss et al., 2006; Miège et al., 2009; Verlicchi et al., 2012; Vieno et al., 2007): current WWTPs generally use conventional activated sludge (CAS) system and are designed to remove only organic matter and nutrients, without considering

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PPCPs. Thus most of these compounds are not completely eliminated.

In the last 2 decades, the membrane bioreactor (MBR) process has become an alternative to CAS processes in terms of the removal of PPCPs as well as conventional pollutants such as organic matter and nutrients during wastewater treatment. Its PPCPs removal performance has been well documented, and it has been found to be superior to CAS systems (Hu et al., 2007; Kimura et al., 2007; Reif et al., 2008; Sipma et al., 2010). The fates of several antibiotics, such as macrolide and sulfonamide, at WWTPs were investigated by Sahar et al. (2011), who reported that the antibiotics removal efficiency in the MBR process was 15–42% greater than in the CAS process. Similarly, in a recent study by Tran et al. (2016), the MBR process showed greater removal efficiencies than the CAS process, for lincomycin (62% in MBR vs. 42% in CAS), azithromycin (91% vs. 78%), sulfamethazine (88% vs. 80%), tetracycline (92% vs. 67%), oxytetracycline (93% vs. 80%), trimethoprim (69% vs. 33%), and triclocarban (80% vs. 70%). There were, however, no significant differences in the respective removal efficiencies of CAS and MBR in the case of some PPCPs, including sulfamethoxazole, trimethoprim, and erythromycin (Radjenović et al., 2009). Clara et al. (2005) investigated the removal of pharmaceuticals, polycyclic musk fragrances, and endocrine disrupting chemicals, and found comparable removal efficiencies for tonalide, galaxolide, bezafibrate, and ibuprofen in the CAS and MBR systems.

Elimination of PPCPs during wastewater treatment using MBR occurs mainly through biodegradation, sorption to sludge, photodegradation, and volatilization. However, the latter two pathways are not considered important in WWTPs. In general, removal of PPCPs with Henry values smaller than 10^{-5} is not affected by volatilization (Stevens-Garmon et al., 2011; Ternes et al., 2004a,b). Also, photodegradation in bioreactors can be negligible because of the high turbidity of mixed liquor. Consequently, biodegradation and sorption are assumed to be the primary mechanisms for the removal of target compounds (Gao et al., 2012; Guerra et al., 2014; Trinh et al., 2016). This is because, first, the higher mixed liquor suspended solids (MLSS) concentration usually developed in MBR by the long solids retention time (SRT) can improve the biodegradation potential (Clara et al., 2005; Sipma et al., 2010), and second, sorption tendency can be maximized by the smaller floc size and large surface area in the MBR process (Fernandez-Fontaina et al., 2013). However, although many studies have focused on the removal of PPCPs, there is still little comprehensive knowledge on the occurrence and fate of PPCPs at WWTPs located in South Korea. Furthermore, there have been few comparative studies of whether MBR is more effective than other biological treatment systems in removing PPCPs.

Therefore, our objective here was to investigate the occurrence, fate and removal of 57 selected PPCPs including both the solid phase of sludge and liquid samples in the different treatment units (primary, secondary, and post-treatment) of various biological treatment processes. To better understand the role of biodegradation and sorption in terms of removal of PPCPs, the comparative evaluation was also performed by calculating mass balances in A2O and a lab-scale MBR process.

2. Materials and methods

2.1. Chemicals and standards

We selected a total 57 compounds (e.g., non-steroidal anti-inflammatory drugs (NSAIDs), analgesics, antibiotics, and antibacterials) as targets (Table 1). The specific categories and classes of the selected compounds are shown in Table S1 of the supplementary information section. The stock solutions of the PPCPs, which had concentrations ranging from about 100 to 1000 mg/L, had isotopic purity greater than 98%. The solutions were prepared with methanol and then stored at −30 °C in the dark.

2.2. Sample preparation and analytical methods

For pretreatment, liquid samples (200 mL) were filtered through a glass fiber filter (Whatman GF/B, 1 μm). EDTA-2Na at 1 g/L and a mixture of surrogate standard were added after filtration. We then applied solid-phase extraction (SPE) with Oasis HLB sorbent (Waters, 200 mg, 6 cc); the cartridges were conditioned with 3 mL of methanol and 3 mL of distilled water. After loading of the cartridges, the product was eluted with 6 mL of methanol and evaporated under a gentle stream of nitrogen (Okuda et al., 2008). Solid samples (1 g wet) were pretreated simultaneously at three pH levels (twice at pH 7; once at pH 2; twice at pH 11), to extract individual PPCPs adsorbed to sludge, and mixed in methanol in a 9:1 (v/v) ratio. Then, ultrasonication (ASU-20D, As One) for 10 min at 40 °C and centrifuging (Centrifuge 4000, Kubota) for 10 min at 2500 rpm were repetitively used to collect the supernatants of the solid samples. They were then evaporated to dryness and dissolved in 1 mL of a mixture of formic acid and methanol. We used a 1 mL final extract for LC-MS/MS (UPLC (AQUITY, Waters) and MS/MS (Quattro micro API, Waters). Recovery correction was calculated from the difference between two aliquots from one sample with and without the addition of the target PPCPs mixture (Kim et al., 2012). The internal standard method with appropriate surrogate standards was used to quantify the samples, except for sulpiride, lincomycin, and ethenzamide, which were quantified by absolute calibration (Narumiya et al., 2013). Detailed information on corresponding surrogate and relative recoveries of samples is shown in Table 1.

In addition to analyzing the PPCPs, we analyzed the water quality at WWTPs, including biochemical oxygen demand (BOD_5), chemical oxygen demand (COD_{cr}), total nitrogen (TN), and total phosphorus (TP) in accordance with standard methods (APHA, 2005). MLSS or mixed liquor volatile suspended solids (MLVSS) concentrations were measured under aerobic conditions at all the surveyed WWTPs. Operating parameters such as dissolved oxygen (DO), pH, temperature, and oxidation-reduction potential were measured with a portable meter (D-50 and 55, Horiba).

2.3. Specification of WWTPs and sampling points

Sampling was performed at four WWTPs located close to Seoul, South Korea, from June 2014 to May 2015. Fig. S1 gives simplified flow diagrams and sampling points of the WWTPs; composite liquid samples (over 24 h) and grab samples of mixed liquor were collected. Details of the main processes, influent sources, population served and inflow rates are summarized in Table 2.

WWTP-A consisted of two main streams, namely domestic treatment (Fig. S1(a), henceforth WWTP-A (D)) and industrial treatment (Fig. S1(b), henceforth WWTP-A (I)); these two processes were similar, except for the disinfection system. A combination of chlorine-based disinfectants and biological fixed film (BFF) was used for disinfection and sterilization in WWTP-A (D), whereas a micro-media disk filter (MDF) made of polyester was used in WWTP-A (I). The Main process of WWTP-A is SymBio technology, an emerging strategy for biological nitrogen removal that allows nitrification and denitrification to occur simultaneously in the same reactor (Spellman, 2013). It measures the intracellular pool of reduced nicotinamide adenine dinucleotide to assess the real-time biological activity in activated sludge systems. This information is used to control the air supply in the aeration tank to maintain DO at