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Characterization of soluble microbial products (SMPs) in a membrane bioreactor (MBR) treating synthetic wastewater containing pharmaceutical compounds

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ABSTRACT

This study investigated the behaviour and characteristics of soluble microbial products (SMP) in two anoxic-aerobic membrane bioreactors (MBRs): $MBR_{control}$ and MBR_{pharma}, for treating municipal wastewater. Both protein and polysaccharides measured exhibited higher concentrations in the MBR_{pharma} than the $MBR_{control}$. Molecular weight (MW) distribution analysis revealed that the presence of pharmaceuticals enhanced the accumulation of SMPs with macro- (13,091 kDa and 1587 kDa) and intermediate-MW (189 kDa) compounds in the anoxic MBR_{pharma}, while a substantial decrease was observed in both MBR effluents. Excitation emission matrix (EEM) fluorescence contours indicated that the exposure to pharmaceuticals seemed to stimulate the production of aromatic proteins containing tyrosine (10.1–32.6%) and tryptophan (14.7–43.1%), compared to $MBR_{control}$ (9.9–29.1% for tyrosine; 11.8–42.5% for tryptophan). Gas chromatography–mass spectrometry (GC-MS) analysis revealed aromatics, long-chain alkanes and esters were the predominant SMPs in the MBRs. More peaks were present in the aerobic MBR_{pharma} (196) than anoxic MBR_{pharma} (133). The SMPs identified exhibited both biodegradability and recalcitrance in the MBR treatment processes. Only 8 compounds in the MBR_{pharma} were the same as in the $MBR_{control}$. Alkanes were the most dominant SMPs (51%) in the $MBR_{control}$, while aromatics were dominant (40%) in the MBR_{pharma}. A significant decrease in aromatics (from 16 to 7) in the MBR_{pharma} permeate was observed, compared to the aerobic MBR_{pharma}. Approximately 21% of compounds in the aerobic $MBR_{control}$ were rejected by membrane filtration, while this increased to 28% in the MBR_{pharma}.

1. Introduction

Pharmaceutical and personal care products (PPCPs) are considered as "emerging contaminants" and many of them are frequently detected in wastewater treatment plant (WWTP) effluents, and surface water and drinking water due to their hydrophilic character and persistence in the aquatic environment (Verlicchi and Zambello, 2015). Although the presence of these compounds in the environment corresponds to low concentration levels (from parts per trillion to parts per billion), their continuous release from WWTPs may pose a potential long-term threat to aquatic and terrestrial ecosystems (Carballa et al., 2004; Kimura et al., 2007).

Soluble microbial products (SMP) are organic compounds biologically derived from wastewater treatment processes (Rosenberger et al., 2006; Drews et al., 2007; Liang et al., 2007). Previous studies have reported considerable variability in the production of SMPs in response to environmental stresses imposed on the microorganisms, such as the presence of toxic compounds (Avella et al., 2010; Han et al., 2013; Wu et al., 2015). Han et al.

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(2013) investigated the effects of continuous Zn (II) exposure on SMP production, and found that the SMP content in the activated sludge increased slightly at below 400 mg/L of Zn (II), but rose sharply at 600 and 800 mg/L Zn. Wang and Zhang (2010) characterized SMPs under stressed conditions and revealed that microorganisms exposed to 50 ppm $CrCl_3$ increased their generation of low MW hydrophilic protein-like materials. In a recent study on the effect of continuous Ni(II) exposure on the organic degradation and SMP formation in anaerobic reactors, Wu et al. (2015) indicated that more protein than polysaccharide was produced, suggesting the prominent function of protein when reacting to the negative effect of toxic metals. Although a number of studies on the characteristics and fate of SMPs in different bioreactors for the treatment of municipal and industrial wastewater and landfill leachate have been carried out (Trzcinski and Stuckey, 2010; Wu and Zhou, 2010; Juang et al., 2013), little information is available with regards to the effects of pharmaceuticals on SMP formation and characterization.

To date, research on SMP production and characterization has been limited to studies focused on several major components such as proteins, polysaccharides, humic substances, and fulvic acid (Barker and Stuckey, 1999; Dignac et al., 2000), and their precise composition remains unclear (Liang et al., 2007). Furthermore, SMPs have a broad spectrum of molecular weights (MW) ranging from greater than 100 kDa to less than 1 kDa (Shin and Kang, 2003; Jarusutthirak and Amy, 2006), and low-MW SMPs are commonly predominant in secondary wastewater effluents (Aquino and Stuckey, 2002). In a previous study on the identification of primary compounds using gas chromatography - mass spectrometry (GC-MS), Aquino and Stuckey (2004) detected long-chain alkenes and alkanes, as well as some aromatic compounds in significant concentrations (low mg/L). More recently, Trzcinski and Stuckey (2009) demonstrated that a number of aliphatic molecules were degraded in the submerged anaerobic MBR, while some aromatic recalcitrants such as Bis (2-ethylhexy) phthalate were retained in the MBR permeate. Nevertheless, only a few researchers have focused on the chemical identification of low-MW SMPs using sophisticated instruments, e.g., GC-MS (Kunacheva and Stuckey, 2014). Therefore, in order to better understand the fundamental mechanisms of secretion, fate and biodegradability of individual SMPs in biological wastewater treatment processes, as well as how to reduce the levels of these compounds in the effluent, more work needs to be done to specifically identify SMP composition and characteristics.

Many reported studies indicated that membrane bioreactors (MBRs) are more effective than conventional activated sludge (CAS) for the removal of pharmaceuticals, due to long sludge retention times (SRTs), high mixed liquor concentrations, minimal sludge production, and high biomass diversity (Joss et al., 2005; Kümmerer, 2009). SMP/extracellular polymeric substance (EPS) which accumulate in MBR systems have been shown to be a consequence of high membrane rejection and low biodegradability. Their formation, composition and behaviour may become even more complex in MBR systems compared to conventional CAS due to the MBRs retaining biomass at high cell retention times (Wang and Waite, 2009; Shen et al., 2010). Furthermore, under environmental stress, the cells may produce more EPS and SMPs as a result of metabolic changes in order to survive, possibly even resulting in cell rupture (Aquino and Stuckey, 2004). Therefore, changes in SMP quantity and composition may reveal the response and resistance of activated sludge in an MBR to the exposure to pharmaceuticals. However, changes in SMP concentration and composition have rarely been examined, and a greater understanding of the role SMPs plays in the resistance of CAS to pharmaceutical exposure is needed.

In this study, the occurrence and characteristics of SMPs in MBRs treating municipal wastewater containing pharmaceutical compounds was investigated. The main objectives were to i) characterize the SMP MW distribution using high performance liquid chromatography (HPLC) - size exclusion chromatography (SEC); ii) investigate the chemical composition of SMPs using three-dimensional fluorescence excitation emission matrix (EEM); and iii) identify low-MW SMPs in the biological treatment processes using GC-MS.

2. Materials and methodologies

2.1. Pharmaceuticals

Eight pharmaceuticals (carbamazepine, ibuprofen, naproxen, diclofenac, caffeine, ketoprofen, salicylic acid, and clofibric acid) were selected because they are frequently detected in the aquatic environment (Verlicchi and Zambello, 2015). They were purchased from Sigma-Aldrich (Singapore) with purity > 99%, and their chemical structures and physicochemical properties are given in Supplementary Table 1.

2.2. Lab-scale MBR

Two identical lab-scale MBR systems, i.e., $MBR_{control}$ and MBR_{pharma}, consisting of an anoxic compartment (3 L) and an aeration compartment (7 L), were operated in parallel (Fig. 1). A hollow fiber ultrafiltration (UF) membrane (ZeeWeed 500, GE Singapore), made of polyvinylidene fluoride, was submerged inside the aerobic compartment, and its effective membrane surface area was 565 cm^2 with a nominal pore size of 0.04 μm. To control the MBR process, 3 min of filtration followed by 1 min of relaxation was achieved using fully automated SCADA software (IFIX).

The MBRs were inoculated with biomass obtained from Ulu Pandan Wastewater Reclamation Plant (WRP), Singapore. Synthetic wastewater was used in this study to simulate domestic sewage, and its chemical composition is given in Table 1. The influent for $MBR_{control}$ and MBR_{pharma} was prepared in two 70-L glass tanks (maintained at 4 °C). The selected pharmaceuticals were spiked into the influent of the MBR_{pharma} resulting in a final concentration of 25 μg/L for each pharmaceutical. The concentration of mixed liquor suspended solid (MLSS) in the aeration tank was maintained at around 3–6 g/L with an average sludge retention time (SRT) of 25 d for each MBR. The hydraulic retention time (HRT) was approximately 10 h, and a permeate flux of 13–15 L/m^2 h (LMH) was maintained. Level sensors were installed in the two MBRs to control the feeding of influents and production of membrane permeates. Both MBRs were fitted with a gas diffuser located on the bottom of the aeration tank to maintain the dissolved oxygen (DO) concentration in the sludge at about 3–4 mg/L for biological oxidation and to achieve membrane scouring. The TMP was monitored automatically using a digital pressure gauge (Ashcroft). General parameters, such as membrane flux, pH, DO, and temperature were automatically recorded using a data logger. After 60 days of acclimatisation, the activated sludge in both MBRs reached a steady state; thereafter, the two MBRs were operated continuously for a period of 6 months.

2.3. Analytical methods

2.3.1. Detection of water quality parameters and pharmaceutical concentrations

Influents, anoxic mixed liquors, aerobic mixed liquors, and membrane effluents were collected twice a week from the two MBRs for measurement of conventional parameters and pharmaceutical concentration. The measurement of MLSS, mixed liquor