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Comparative study of emerging micropollutants removal by aerobic activated sludge of large laboratory-scale membrane bioreactors and sequencing batch reactors under low-temperature conditions

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HIGHLIGHTS

- Removal of ibuprofen, diclofenac, estrone and 17α-ethinylestradiol is studied.
- Collection of micropollutants in solid phase (cells) of activated sludge was shown.
- Membrane bioreactor with long SRT favours biological removal of micropollutants.
- Increasing SRT to 90 days improves emerging micropollutants removal at 8 °C.

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ABSTRACT

Four emerging micropollutants ibuprofen, diclofenac, estrone (E1) and 17α-ethinylestradiol (EE2) were studied in large laboratory-scale wastewater treatment plants (WWTPs) with high nitrifying activity. Activated sludge (AS) with sludge retention times (SRTs) of 12 days and 14 days in sequencing batch reactors (SBRs) and 30 days, 60 days and 90 days in membrane bioreactors (MBRs) were examined at 8 °C and 12 °C. Concentrations of pharmaceuticals and their main metabolites were analysed in liquid phase and solid phase of AS by liquid chromatography–tandem mass spectrometry (LC–MS/MS). A remarkable amount of contaminants were detected in solids of AS, meaning the accumulation of micropollutants in bacterial cells. The biodegradation rate constants (K_{biol}) were affected by SRT and temperature. MBR with a 90-day SRT showed the best results of removal. Conventional SBR process was inefficient at 8 °C showing K_{biol} values lower than 0.5 l gSS^{-1} d^{-1} for studied micropollutants.

1. Introduction

The potential danger of emerging micropollutants constantly discharged from municipal wastewater treatment plants (WWTPs) is now under active evaluation among researchers. Non-steroidal anti-inflammatory drugs (NSAIDs) and hormones are two groups of contaminants with an already proven potential risk for environmental organisms and humans. In particular, the ecotoxicological impact of the popular NSAIDs ibuprofen and diclofenac, frequently detected in wastewaters and natural waters, was described in many studies (Ericson et al., 2010; Fent et al., 2006; Lindqvist et al., 2005). The hormonal compounds natural estrogen estrone (E1) and synthetic contraceptive 17α-ethinylestradiol (EE2) have been commonly found in treated wastewater and showed high endocrine-disrupting activity already at concentrations as low as the ng l^{-1} level (Hamid and Eskicioglu, 2012; Silva et al., 2012). Moreover, during winter seasons in cold regions higher concentrations of micropollutants have been detected due to low temperature conditions (Vieno et al., 2005; Wang et al., 2011). Studying the removal efficiency and the fate of these compounds during wastewater treatment is essential in order to determine the incoming load of dangerous micropollutants to the environment.

Aerobic biological removal is considered an effective mechanism to eliminate these micropollutants during wastewater treatment. AS with higher nitrifying activity can according to several studies improve and speed up the removal of NSAIDs and endocrine disruptors due to sufficiently long SRT (Vieno and Sillanpää, 2014; Silva et al., 2012). Despite the fact that in some studies

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seasonal temperature changes are considered insignificant for micropollutant removal rates, in general, low temperature conditions inhibit biochemical reactions and thus the biodegradation activity of bacteria (Luo et al., 2014). During the winter season in Finland, the temperature of water in WWTPs decreases down to 7 °C or even colder. The activity of nitrifies and other specialist-degrading bacteria at this temperature is very poor. According to Vieno et al. (2005) the wastewater temperatures in Finland remain lower than 13 °C until May which can cause low removal of micropollutants most of the year.

Biological removal of ibuprofen in WWTPs is commonly higher than 75% and the average reported removal of E1 is 83% and EE2 removal is higher than 44% (Hamid and Eskicioglu, 2012; Luo et al., 2014). The removal of diclofenac is less efficient (<25%) and extremely variable, including cases in which the concentration in the influent is exceeded due to transformation of the metabolite conjugates back to the parent compound. Also formation of nitro-diclofenac (NO_2-DCF) in AS could falsify the diclofenac analyses (Luo et al., 2014; Vieno and Sillanpää, 2014). In all, significant variations in biodegradation rates can be found in different studies for all four compounds and pseudo-first order biodegradation kinetic constants (K_{biol}) can vary from 10 up to 100 times due to different operational conditions and wastewater treatment process variations. However, the information about the operational conditions in most of the studies is very limited and the temperature of the process is mostly not reported or is in the range of 16–26 °C (Pomiés et al., 2013). For these reasons, it is hard to apply the published data to the conditions of cold regions and use for WWTP design.

In addition to the lack of operational conditions, there is no information about the fate of the micropollutants inside the AS cells. In most of the studies, the removal rates of compounds have been determined only by comparing the influent and effluent concentrations in filtered samples or in the liquid phase of the AS samples (Estrada-Arriaga and Mijaylova, 2010; Hai et al., 2011; Smook et al., 2008; Vieno and Sillanpää, 2014). However, the first phase of the biological removal process is biosorption followed by the uptake of substances via the bacterial cell (Siegrist et al., 2005; Silva et al., 2012). If some part of the contaminant remains unchanged by the bacterial cells, it can easily return to wastewater through the desorption process, cell over-saturation or death. Thereby, in order to assess the biodegradation (K_{biol} values and removal efficiencies) the measurements of micropollutants' concentrations from the solid phase of AS should be taken into consideration.

Using the MBR process in wastewater treatment according to recent studies could enhance the removal of emerging micropollutants, including NSAIDs and hormones (Luo et al., 2014; Silva et al., 2012; Vieno and Sillanpää, 2014). Hai et al. (2011) claimed that short-term temperature shifts between 10 and 35 °C do not affect the removal of discussed micropollutants by the MBR process, however long-term removal studies with AS adapted to a certain temperature regimes are crucial to conduct. One of the key parameters for the higher removal efficiency of MBR is longer SRT resulting in the appearance of slowly growing specialist-degrading bacteria (Silva et al., 2012; Luo et al., 2014). However, even though higher removal rates were described for MBRs when compared to conventional AS, limited mineralisation of NSAIDs can take place in both treatment technologies. Therefore, biological transformation products (metabolites) such as NO_2-DCF, hydroxy-ibuprofen (4′-OH-IBU) and carboxy-ibuprofen (CBX-IBU) could enter the effluents (Kimura et al., 2010; Lee et al., 2012; Quintana et al., 2005; Pérez and Barceló, 2008).

The objectives of the research were: (1) to compare the fates of four emerging micropollutants in conventional and MBR aerobic AS and to find the beneficial process parameters for enhancing AS removal potential in cold climate conditions; (2) to study the significance of the micropollutant content in the solid phase (cells) of AS. With this purpose, concentrations of ibuprofen, its metabolites 2′-OH-IBU and CBX-IBU, diclofenac, 4′-NO_2-DCF, E1 and EE2 were measured over the course of 24 h in the liquid phase and solid phase of AS and K_{biol} values were calculated.

2. Material and methods

2.1. Chemicals and synthetic wastewater

Ibuprofen, diclofenac, E1 and EE2 for operating MBRs and SBRs as well as dansyl chloride for LC–MS/MS analysis were purchased from Sigma–Aldrich. Stock solutions of ibuprofen and diclofenac were prepared according to Kruglova et al. (2014). Stock solutions of E1 and EE2 were prepared by diluting 50 mg of compound in 100 ml of ethanol and then 900 ml ultrapure water each month for synthetic wastewater preparation and one day before each experiment for spiking. Stock solutions were stored in the dark at 4 °C.

Internal standards (IBU-d3, DCF-d4 and 2-OH-IBU-d6, E1-d4 and EE2-d7), CBX-IBU and 2-OH-IBU, E1 and EE2 for LC–MS/MS analysis were purchased from Toronto Research Chemicals (North York, ON, Canada). The chemical purities of deuterated standards were 98% and isotopic purities were 99%. 4′-NO_2-DCF was synthesized at Åbo Akademi University. Standard solutions of 1 mg ml^{-1} were prepared in methanol and stored at −18 °C. From these, working solutions for LC–MS/MS analysis were prepared in methanol.

Synthetic wastewater containing 130.8 mg l^{-1} of CH_3COOH, 209.7 mg l^{-1} of yeast extract, 184.68 mg l^{-1} of peptone, 38.2 mg l^{-1} of NH_4Cl, 35.1 mg l^{-1} of KH_2PO_4, 70 mg l^{-1} of $CaCl_2$*$2H_2O$, 60.9 mg l^{-1} of $MgSO_4$*$7H_2O$ and solution of micronutrients were prepared for both MBRs and SBRs twice a week as described by Kruglova et al. (2014). $NaHCO_3$ was added in order to keep the alkalinity in the reactors in the range of pH = 7.5 ± 0.2. Micropollutants were added to synthetic wastewater in the concentrations presented in Table 1.

2.2. MBR reactors

Two equal glass MBRs with an operational volume of 15 l were installed and operated in parallel in a temperature-controlled chamber. Each MBR contained one flat-sheet submerged membrane with 0.11 m^2 of membrane surface made of chlorinated polyethylene with pore size 0.4 μm. Feeding with synthetic wastewater and permeate control were done by peristaltic pumps with a flow rate of 15 l d^{-1} (and an operational flux of 0.14 m d^{-1}). Fine bubble aerators were placed in the bottom of the reactors for constant aeration (5.0 l min^{-1}) to keep the membrane surface clean during filtering as well as provide AS with dissolved oxygen (DO = 6 ± 1 mg l^{-1}). Excess AS was wasted manually three times per week during operation with 30-day SRT and once a week during operation with 60-day and 90-day SRT. Temperature in the chamber was maintained at 12 °C or 8 °C according to the experimental setup as presented in Table 1.

2.3. SBR reactors

Two equal glass SBRs with 12 l operational volume were built and run automatically as described by Kruglova et al. (2014) with 8-h cycles (5.8 h react time) and organic loading rate 0.17 kg BOD_7 m^{-3} d^{-1} since this conditions showed higher removal efficiency. Feeding with synthetic wastewater (6 l d^{-1}) and permeate control were done by peristaltic pumps, aeration was provided by ceramic