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Influence of humic acid addition on the degradation of pharmaceuticals by biofilms in effluent wastewater

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ABSTRACT

The degradation of organic micropollutants in wastewater treatment is suspected to depend on co-degradation i.e. be dependent on concentrations of substrate. This complicates predicting and modelling their fate. The effect of humic acid, as a model for complex organic substrate, was investigated in relation to the biodegradation of pharmaceuticals by suspended biofilm carriers adapted to polishing effluent water from a tertiary sewage treatment plant. Twelve out of 22 investigated pharmaceuticals were significantly biodegradable. The biodegradation rate constants of ten of those compounds were increasing with increased humic acid concentrations. At the highest humic acid concentration (30 mgC/L), the biodegradation rate constants were four times higher than the biodegradation rate constants without added humic acid. This shows that the presence of complex substrate stimulates degradation via a co-metabolism-like mechanism and competitive inhibition does not occur. Increases of rate constant per mgC/L are tentatively calculated.

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1. Introduction

Effluents from municipal wastewater treatment plants (WWTPs) contain pharmaceuticals (typically μg/L), as many of these compounds are not removed in traditional wastewater treatment processes (Falås et al., 2012a; Wang et al., 2015). As pharmaceuticals are designed to have biological effects, it is inevitable that they can potentially have effects on aquatic life, and thus regulation authorities increasingly develop water quality criteria for pharmaceuticals in the ng/L and μg/L ranges, which are not achievable with currently used wastewater treatment methods (Álvarez-Muñoz et al., 2015). Therefore, there is an increasing interest to understand the mechanisms of the removal of pharmaceuticals in the wastewater treatment processes and to identify technologies that can achieve better removal.

Besides chemical methods for polishing pharmaceuticals in wastewater effluents such as ozonation (Hansen et al., 2016), biofilm methods are being investigated as methods to improve removal of pharmaceuticals from wastewater (Escolà Casas et al., 2015; Falås et al., 2013, 2012b; Joss et al., 2004). The moving bed biofilm reactor (MBBR) consists of a wastewater reactor containing suspended plastic carriers that serve as support to biofilm growth, making it possible to utilise the whole tank volume for biomass growth (Ødegaard, 2006). Over the past decades, MBBR have been used successfully to treat different types of wastewater containing organic chemicals of concern (Borghei and Hosseini, 2004; Chen et al., 2007; Escolà Casas et al., 2015). Previous studies have already demonstrated that MBBR reactors achieve similar or better biodegradation efficiencies for micropollutants compared to activated sludge treatment (Escolà Casas et al., 2015; Falås et al., 2012b; Mazioti et al., 2015).

Biomass communities found in wastewater treatment facilities are related to the conditions under which they grow (Cydzik-Kwiatkowska and Zielińska, 2016). An important parameter for these conditions is the type and concentration of carbon in wastewater. However, there is a lack of knowledge on how this parameter affects biofilm activity. Biodegradation of micropollutants may interact with organic matter by two types of mechanisms: co-metabolism and competitive inhibition. The terms 'co-metabolism' and 'competitive inhibition' will be used in this article as defined below because they were found to be the most suitable. It is important to notice that such terms do not exactly correspond to their definition in biochemistry.

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Co-metabolism involves the transformation of a non-growth substrate (e.g. pharmaceutical) in the obligate presence of a substrate that is utilised by the biomass for growth. Non-growth substrate refers to compounds that are unable to support cell replication at the given concentrations (Dalton et al., 1982), such as micropollutants in realistic wastewater conditions. Namely, the obligatory presence of a growth substrate or another utilisable compound is essential to the main biomass and induces enzymes for assimilation or co-factors for biodegradation (Arp et al., 2001). Some relevant studies in the literature have found that phenol and glucose act as primary growth substrates and enhance the biodegradation of 4-chlorophenol, which is considered a non-growth substrate at low concentrations (Tobajas et al., 2012). Essentially under such conditions the higher the substrate concentration, the faster the degradation of the pollutant.

Competitive inhibition proposes that, a pollutant and the usual grow substrate compete for active sites (e.g. of enzymes) for being processed. Thus the higher the substrate concentration the slower the degradation of the pollutant (Chang and Alvarez-Cohen, 1995). To minimise and optimise the discrepancy between the observed removal and estimated removal of micropollutants, previous studies in the literature demonstrate that the ability of the model used to predict micro-pollutant degradation improved after the addition of an parameter regarding competitive inhibition (Plósz et al., 2010). Experimentally, Joss et al. (2004) found that differences in the removal rates of oestrogens, between the batch experiment and the corresponding compartment of full-scale plants, could be interpreted in terms of the competitive inhibition of oestrogen degradation by the substrate. This was explained because the batch experiments were run without adding a primary effluent, while the full-scale plants were operated under regular conditions (Joss et al., 2004).

According to the descriptions above, co-metabolism and competitive inhibition thus make opposite predictions on the effect of substrate on pollutant removal.

The aim of this study was to investigate the effect of additional carbon sources on the removal of micropollutants by biofilms. Specifically, laboratory-scale MBBRs were used to mimic a potential treatment for effluent wastewater from a CAS treatment plant. In this test, humic acid (HA) was chosen to simulate different concentrations of complex carbon (i.e. not easily biodegradable carbon) as a carbon source (feed) to induce biological activity. This way it was tested whether enhanced carbon loads are beneficial or detrimental to degradation of recalcitrant compounds (meaning whether the effect of co-metabolism or competitive inhibition by additional carbon is predominant).

2. Methods

2.1. Chemicals

The investigated micropollutants include antibiotics (azithromycin, ciprofloxacin, sulfadiazine, sulfamethizole, sulfamethoxazole, trimethoprim and the sulfadiazine metabolite acetyl-sulfadiazine), beta-blockers (atenolol, metoprolol, propranolol and sotalol), antindepressants/antiepileptics (venlafaxine and carbamazepine), analgesics (diclofenac, ibuprofen, phenazone and tramadol) and X-ray contrast media (iopromide, iohexol and iopamidol). The investigated compounds were obtained from different suppliers, as described in the supplementary information (SI; Table S1). Formic acid and gradient-grade methanol were obtained from Merck (Darmstadt, Germany). Humic acid sodium salt was purchased from Sigma-Aldrich (Steinheim, Germany), and water of a gradient grade came from Sigma-Aldrich (Munich, Germany).

2.2. Instruments

The HPLC was equipped with a dual low-pressure mixing ternary gradient system, namely Ultimate 3000, from Dionex. This system consisted of a pump, a column oven and a degasser, which were all 3000 series, and a 3000 TSL autosampler (WPS 3000 TSL). The mass spectrometer was an API 4000 (ABSciex, Framingham, MA, USA). The HPLC–MS/MS conditions are the same as the supplementary information (S2) in Escolà Casas et al. (2015).

2.3. Wastewater and the growth of biofilm carriers

The effluent wastewater used for the growth of the biofilm carriers and for the experiment was collected from Bjergmarken WWTP in Roskilde, Denmark. Bjergmarken WWTP is a classical activated sludge plant, with nitrification and denitrification as well as biological phosphorus removal. The wastewater was stored at 4 °C and before starting the experiment it was allowed to reach room temperature. The characteristics of the wastewater in this experiment are presented in Table S2.

To grow the biofilm on the carriers, 150 new MBBR-carriers K5 (800 m^2/m^3 specific surface area) from AnoxKaldnes™ (AnoxKaldnes, Lund, Sweden) were incubated in a beaker containing 1500 mL of the described effluent wastewater. The carriers were stirred with a magnetic stir-bar and the wastewater was fully changed three times a week. No additional aeration was performed, as oxygen consumption in the system was very low. These conditions were maintained for four months. At that time, the carriers were ready for the batch experiment.

2.4. Experimental design and procedure

The experiment consisted in testing the degradation of spiked pharmaceuticals in secondary treated wastewater in the presence of three defined concentrations of humic acid (all in triplicates). Humic acid sodium salt was used in this experiment, as it is easier to solubilise than natural, isolated humic acid. To prepare solutions of humic acid 4.9, 7.4 or 24.7 mg humic acid sodium salt were added into 200 mL volumetric flasks which were filled with effluent from Bjergmarken WWTP.

For the spiking, 10 μL of a stock solution containing pharmaceuticals in methanol were transferred to 100 mL Erlenmeyer flasks. After the methanol had evaporated, 40 mL of the humic acid sodium salt solutions in effluent water were introduced into the respective flasks. This gave initial concentrations of the pharmaceuticals ranging between 1.2 and 14.6 μg/L.

When the flasks were prepared, three carriers with biofilm were placed into each of them. This resulted in a filling ratio of 23%, corresponding to 104 m^2/m^3 surface area, which was kept constant (maximum variations of ±3%) by adjusting the number of carriers to the remaining water at certain time-points after sampling. The experiment was optimised for gaining comparable and stable results rather than working at optimal filling ratio. The Erlenmeyer flasks were placed on a mechanical shaker (120 rpm) for a period of two weeks. The design of the experiment is shown in Table S3.

2.5. Quantification and analysis

2.5.1. General parameters

Dissolved oxygen and pH were measured with a multi-parameter meter (Multi 3420, WTW), while dissolved organic carbon (DOC) concentration was analysed by a total organic carbon analyser (Shimadzu, TOC-V wp with ASI-V, Japan). COD and other parameters mentioned for wastewater in the effluent from Bjergmarken WWTP (Table S2) were measured following Danish Standard Methods (http://www.ds.dk/en, accessed June 2015).

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