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Removal of trace organics by anaerobic membrane bioreactors

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ABSTRACT

The biological removal of 38 trace organics (pharmaceuticals, endocrine disruptors, personal care products and pesticides) was studied in an anaerobic membrane bioreactor (AnMBR). This work presents complete information on the different removal mechanisms involved in the removal of trace organics in this process. In particular, it is focused on advanced characterization of the relative amount of TO accumulated within the fouling layers formed on the membranes. The results show that only 9 out of 38 compounds were removed by more than 90% while 23 compounds were removed by less than 50%. These compounds are therefore removed in an AnMBR biologically and partially adsorbed and retained by flocs and the deposition developed on the membranes, respectively. A total amount of 288 mg of trace organics was retained per m^2 of membrane, which were distributed along the different fouling layers. Among the trace organics analyzed, 17α-ethynylestradiol, estrone, octylphenol and bisphenol A were the most retained by the fouling layers. Among the fouling layers deposited on the membranes, the non-readily detachable layer has been identified as the main barrier for trace organics.

1. Introduction

There is an increasing concern about the presence of trace organics (TO), such as pharmaceutically active compounds (PhACs), personal care products (PCPs), endocrine disrupting compounds (EDCs) and pesticides in water bodies worldwide. It is reasonable to surmise that the occurrence of TO in the environment is not a newly emerging phenomenon but, it has become more widely evident thanks to the recent improvements of the chemical analysis methodologies and the lower detection limits for a wide spectrum of trace xenobiotics in environmental samples. The analysis of the TO cycle in nature reveals the important role that wastewater treatment plants (WWTP) play on the control of their occurrence in the environment (Daughton and Ternes, 1999). Conventional WWTP and septic systems have not been specifically designed to remove xenobiotic organics present at trace levels, hardly

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biodegradable compounds or highly polar micropollutants like PhACs (Bendz et al., 2005). In fact, TO have been detected in numerous effluents resulted from conventional WWTP (Petrović and Barceló, 2007). Moreover, combined sewer overflows may release directly raw wastewater with TO in case of heavy rain (Tamtam et al., 2011). In this scenario, the absence of complete removal leads to the distribution of xenobiotics in two phases: the resulting aqueous effluents and the sewage sludge, causing an even wider spread in the environment, when effluents are discharged and biosolids are used for soils amendment.

There are significant differences on the biological removal efficiencies of these compounds, depending on the TO nature, and the operating conditions of the various treatment systems used (Radjenović et al., 2007). For example, the removal efficiencies for PhACs of various therapeutic categories (ibuprofen, acetaminophen, dipyrone, diclofenac, carbamazepine and codeine), pesticides (chlorfenvinfos and permethrin), caffeine, triclosan and bisphenol A, in a municipal wastewater treatment plant consisting in a pre-treatment for solids removal, a primary sedimentation, an activated sludge biological treatment and a final clarification, varied from 20 to 99% (for carbamazepine and acetaminophen, respectively) (Gómez et al., 2007).

Anaerobic high rate bioreactors are adopted in order to provide a treatment process which is both technologically and economically viable with the dual goals of resource recovery and compliance with current legislation for effluent discharge (Chan et al., 2009). However, anaerobic biological treatment of domestic wastewater is constrained by the low organic strength of the wastewater, the quality of the available carbon and the high half velocity constant (K_s) value associated with the anaerobic communities which impair the bacterial growth and an effective treatment. Thus, implementation of new technologies (e.g. membrane bioreactors) are highly demanded for an increased efficiency (Suárez et al., 2008). Recently, the potential for using membranes as a method of biomass retention has been discussed (Martin et al., 2011). In particular, benefit has been reported from their high solids retention, even at low temperatures, and the rejection of high molecular weight organics, which are further degraded, which would otherwise be lost in the effluent. Translating the concept to municipal wastewater treatment, the adoption of anaerobic membrane bioreactors (AnMBRs) results in a reduction both in energy usage and in sludge production. Recent reviews on AnMBRs have reported the impact of operational factors on biological performance (Liao et al., 2006) and those parameters affecting membrane flux (Martin-Garcia et al., 2011).

A number of comparative studies on the fate of TO in the aqueous phase of MBRs are available and have shown promising results (Clara et al., 2005). It is apparent that anaerobic digestion reduces the concentrations of PhACs, PCPs (Carballa et al., 2008), and EDCs (Paterakis et al., 2012). For most of the investigated PhACs, the concentrations detected in MBR effluents were usually significantly lower than levels reported for the effluents from conventional systems. Thus, it would therefore be expected to confer a high degree of protection against exposure and transfer to the receiving/re-use environment.

The efficiency of MBR technology and the removal mechanisms of TO pollutants remain unclear (Qu et al., 2009). Removal efficiency of micropollutants is thought to be governed to a large extent by their physicochemical properties, such as molecular structure, hydrophobicity, size and charge (Kimura et al., 2005). Although the main removal pathway is biodegradation, abiotic loses may also be important (volatilization and sorption onto waste sludge). There is a need to further expand the understanding of the fate of micropollutants during their treatment and the mechanisms relevant for their removal by MBR in the presence of a fouling layer on the surface of the membrane. This study therefore aims to analyze the sorption of TO on fouling layers created over the membrane during the wastewater treatment by AnMBR, in accordance with the physicochemical properties of the TO and the components of the foulants.

2. Materials and methods

2.1. *Experimental setup for continuous runs*

A 30 L membrane upflow anaerobic sludge blanket reactor was fed by synthetic low-strength wastewater from the bottom. The reactor was inoculated with 130 g VS of granular sludge from a full scale UASB reactor treating brewery wastewater. The sludge was characterized by a VS to TS ratio of 0.80 and an average granule diameter of 1–2 mm. The hydraulic retention time (HRT) was kept constant at 6 h, the sludge retention time (SRT) at 30 d, the working temperature at $30 \pm 1\ ^{\circ}\mathrm{C}$ and the pH at 7.5. Membranes were installed after the stabilization of the anaerobic bioreactor to avoid the deposition of non-granulated material present in the inoculum over the membranes during the start-up. The reactor is constituted of two parts: sludge bed (8 L) and supernatant (12 L) as described elsewhere (Tran et al., 2013). Membrane module consisted of 20 fibres of hollow-fibre membrane (Siemens Water Technologies, pore size of 0.04 μm and total area of $0.0245\ \mathrm{m}^2$), were submerged in the supernatant area and driven by a peristaltic pump. Transmembrane pressure (TMP) and flux (J) were measured by pressure transmitter and balance, respectively, which both were connected to a computer for data acquisition (LabView, National Instruments). Membranes were operated at a constant permeate flux of $10\ \mathrm{L\ m^{-2}\ h^{-1}}$. The membrane module was continuously aerated at a flow rate of $500\ \mathrm{mL\ min^{-1}}$.

2.2. *Membrane cleaning protocol*

The foulant layers were removed sequentially via a four-step procedure, whereby an increasing amount of strength was applied to detach four foulant layers, i.e. external, cake, residual and irreversible, from the membrane surface and thus assess preferential deposition of organics on the membrane surface. This protocol was not primarily aimed to replicate cleaning strategies applied in the industry, but to obtain three fouling layers in a well controlled environment for further characterization by analytical tools. Although this is not a standardized method, this protocol has been used to provide further insights into fouling layers properties (Henderson et al., 2011; Tran et al., 2013; Wu et al., 2008). The membrane modules were submerged in 400 mL MilliQ water and shaken manually for 2 min to remove the weakly adsorbed fraction.