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# Can those organic micro-pollutants that are recalcitrant in activated sludge treatment be removed from wastewater by biofilm reactors (slow sand filters)?

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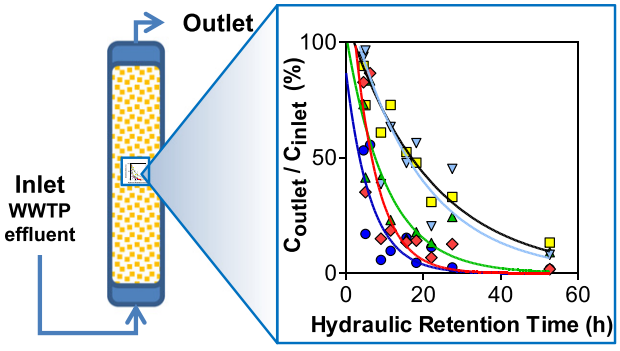
## HIGHLIGHTS

- A biofilm reactor (biofilter) can remove micro-pollutants from WWTP effluent.
- Sorption could be excluded as the dominant removal mechanism.
- Biodegradation was responsible for removing seven compounds.
- The removal efficiency was usually proportional to the hydraulic residence-time.
- Single first-order removal rates apply for most compounds

## GRAPHICAL ABSTRACT

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## ABSTRACT

The degradation of seven compounds which are usually recalcitrant in classical activated sludge treatment (e.g., diclofenac, propranolol, iopromide, iohexol, iomeprol tebuconazole and propiconazole) was studied in a biofilm reactor (slow sand filtration). This reactor was used to treat real effluent-wastewater at different flow rates (hydraulic loadings) under aerobic conditions so removal and degradation kinetics of these recalcitrant compounds were calculated. With the hydraulic loading rate of 0.012 $m^3$ $m^{-2}$ $h^{-1}$ the reactor removed 41, 94, 58, 57 and 85% of diclofenac, propranolol, iopromide, iohexol and iomeprol respectively. For these compounds the removal efficiency was dependent on hydraulic residence-times. Only 59 and 21% of the incoming tebuconazole and propiconazole respectively were removed but their removal did not depend on hydraulic residence time. Biofilm reactors are thus efficient in removing micro-pollutants and could be considered as an option for advanced treatment in small wastewater treatment plants.



## 1. Introduction

A multitude of xenobiotics (pharmaceuticals, biocides etc.) are present in current Wastewater Treatment Plant (WWTPs) effluents (Joss et al., 2006; Kormos et al., 2011; Ternes et al., 2007). Some exceed the environmental target concentrations (European Parliament, 2000,

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2013). To improve effluent quality, different processes such as activated carbon treatment, reverse osmosis and Advanced Oxidation Processes (AOPs) can be added to the conventional activated sludge treatment. Activated carbon and reverse osmosis are techniques that reach satisfactory removal rates but they are phase-transfer processes so they do not destroy the compounds in question (Choubert et al., 2011). On the other hand, AOPs can efficiently oxidize micro-pollutants, but they require intensive process control, have high operating costs and can produce by-products (Choubert et al., 2011; Lee et al., 2013; Prieto-Rodríguez et al., 2013; Reungoat et al., 2011, 2012; Stalter et al., 2010). Alternatively, biological processes such as biofilm reactors can also remove micro-pollutants (Bester and Schafer, 2009; Falås et al., 2012; Joss et al., 2008) and do not require as much process control as AOPs. Ideally, the microorganisms use the organic micro-pollutants to build up biomass or for gaining energy. Biofilm reactors can be implemented in biofilter systems (Banzhaf et al., 2012; Bester and Schafer, 2009; Bester et al., 2011; Janzen et al., 2009). Multiple studies focused on biofilm reactors for removing organic micro-pollutants from raw drinking water by using underground passage, bank filtration etc. which are somewhat similar, but usually not designed but grown in natural conditions (Andresen and Bester, 2006; Benner et al., 2013; Gray and Sedlak, 2005; Heberer et al., 2004; Laws et al., 2011; Scheytt et al., 2004, 2006; Ternes et al., 2007; Zearley and Summers, 2012).

Only a very limited amount of studies use porous media biofilm processes to remove organic micro-pollutants from wastewater (Bester and Schafer, 2009; Bester et al., 2011; Janzen et al., 2009; Matamoros et al., 2007, 2009; Reungoat et al., 2011).

It is known that the effectiveness of biofilm reactors depends on the hydraulic residence-time (HRT), the compound residence time and the biofilm surface area. Aerobic processes appeared to be the most efficient for the removal of many organic micro-pollutants, albeit a few compounds degrade better under anoxic conditions (Hijosa-Valsero et al., 2011; Matamoros et al., 2009; Rittmann, 1985). Apart from that, the most efficient configuration for the biodegradation of organic micro-pollutants is unknown and the mechanisms involved are unclear.

Usually there are two mechanisms relevant for porous media biofilm systems: biodegradation and sorption. Scheytt et al., 2004 demonstrated the influence of sorption even for a hydrophilic compound like diclofenac in a water-saturated sandy-sediment column in the laboratory. In that study, diclofenac was not biodegraded but sorbed to/retained by the soil. Thus it is important to discriminate the two processes: sorption and degradation.

This study focuses on the biodegradation of seven representative micro-pollutants that are commonly recalcitrant after activated sludge treatment: diclofenac, propranolol, iopromide, iohexol, iomeprol, propiconazole and tebuconazole (S1). Diclofenac and propranolol have been detected in WWTPs in the range 0.1–1 μg $L^{-1}$ (Scheurer et al., 2010; Thomas et al., 2007). Iopromide, iohexol and iomeprol are found in wastewater with concentrations of 1–100 μg $L^{-1}$ (Hirsch et al., 2000; Ternes and Hirsch, 2000). Propiconazole and tebuconazole are used as biocides present in wood and coatings, and therefore can be detected in WWTP in the range of 0.01–0.1 μg $L^{-1}$ (Bollmann et al., 2014; Kahle et al., 2008). All the selected compounds were present in the wastewater effluent used for the study, thus no additional spiking was conducted (Table 1).

This study aims to answer whether built porous media biofilm reactors can be considered as a solution to remove and degrade micro-pollutants in wastewater effluents from small WWTPs.

## 2. Materials and methods

### 2.1. Biofilm reactor set-up

The biofilm reactor was built using a glass column (500 mm length and 25 mm ID) from LCTech (Dorfen, Germany). The column was filled with quartz sand (50–70 mesh (i.e. 0.210–0.297 mm particle size)) from Sigma-Aldrich up to 29 cm (142 mL volume).

To achieve a faster establishment of biofilms, 3 mL of activated sludge (performing BOD removal as well as nitrification and denitrification) from Bjergmarken WWTP (Roskilde, Denmark) was placed at the start of the column. Fig. 1 shows the column set-up. Effluent wastewater saturated with oxygen from the same WWTP was pumped through the column using a Reglo-CPF digital pump from Ismatec (Wertheim, Germany). The water was pumped against gravity to facilitate the removal of air-bubbles and thus achieve a water-saturated flow, which allowed an easy control of hydraulics. To protect the pump from clogging, a glass-fiber filter (Grade GF/C: 1.2 μm) was installed at the inlet tube, to reject particles. The feed water tank was refrigerated to 4 °C. Considering a maximum flow rate of 0.2 mL $min^{-1}$, it is assumed that the feed warms up to room temperature (20 °C) in the feedline and in the pump, thus the reactor itself is at room temperature as well. This assumption has been verified in later experiments. The tubing and the biofilm reactor were covered with aluminum foil to prevent algae growth. The system was acclimatized and thus adapted to the respective water for three months and showed stable removal rates after that conditioning time.

### 2.2. Materials

Analytical standards of diclofenac, propranolol, iopromide, iohexol, iomeprol tebuconazole and propiconazole were obtained from Dr. Ehrensdorfer GmbH (Augsburg, Germany). Formic acid and gradient grade methanol were obtained from Merck (Darmstadt, Germany); water was from an in-house Millipore apparatus.

**Table 1**
Average concentration of the compounds in the reactor feed during the experimental period, elution volumes of the target compounds from the biofilm reactor, reaction rate constants ($k$) and percentage removal of the target compounds at minimum, intermediate and maximum flows.

| Target compound | Feed concentration (mean ± SD) (n = 18) | Elution volume | Reaction rate constant ($k$) | Removal 1 (mean ± SD) (n = 4) | Removal 2 (mean ± SD) (n = 5) | Removal 3 (mean ± SD) (n = 5) |
|---|---|---|---|---|---|---|
| Flow [μL $min^{-1}$] | | | | 17 | 98 | 196 |
| | [μg $L^{-1}$] | [mL] | [$h^{-1}$] | [%] | [%] | [%] |
| Propranolol | 0.055 ± 0.015 | 78.4 | 0.143 | 98 ± 1 | 94 ± 2 | 45 ± 14 |
| Diclofenac | 0.24 ± 0.047 | 54 | 0.040 | 82 ± 1 | 41 ± 2 | 0 |
| Propiconazole | 0.11 ± 0.059 | 62.4 | – | 21 ± 22 | 17 ± 3 | 0 |
| Tebuconazole | 0.022 ± 0.006 | 65.6 | – | 59 ± 20 | 58 ± 4 | 0 |
| Iohexol | 3.28 ± 1.3 | 53.2 | 0.101 | 91 ± 8 | 57 ± 3 | 25 ± 18 |
| Iomeprol | 20.8 ± 11 | 53.2 | 0.090 | 93 ± 10 | 85 ± 0.2 | 17 ± 12 |
| Iopromide | 2.9 ± 0.83 | 53.2 | 0.046 | 91 ± 6 | 58 ± 0.3 | 0 |
| Tracer (NaBr) | | 54.8 | | | | |