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Sorption and diffusion of micropollutants on/in biofilms: experimental observations and a model-based interpretation

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ABSTRACT

In this study we investigated the diffusion and sorption of 22 pharmaceuticals in/on nitrifying biofilms of different thickness. Experimental observations were subject to model-based interpretation and the assessment of a sorption coefficient K_d and effective diffusivity coefficient *f*. Three biofilm depths were obtained by using Z-carriers (AnoxKaldnes) as support, which allows tight control of biofilm thickness. Biofilms of increasing thickness had increased porosity (and thus decreasing density). Sorption was significant for the positively charged compounds at experimental pH (with few exceptions) and K_d increased with biofilm thickness. The effective diffusivity *f* negatively correlated with biofilm density, suggesting that diffusion of micropollutants in thinner biofilms could be limited. Overall, this study elucidated how biofilm thickness can positively influence sorption of micropollutants on biofilm as well as how diffusion limitation is strongly impact by biofilm characteristics (density and porosity) and the specific chemical.

INTRODUCTION

Micropollutants are contaminants of emerging concern which are found in wastewater at trace level concentration (from ng L^{-1} to µg L^{-1}) and have been observed to have a potential ecotoxic impact on aquatic systems (Pomiès et al., 2013). In wastewater treatment systems, sorption to solid matrices is one of the general mechanisms leading to the removal of micropollutants present in the aqueous phase. Sorption depends typically on the specific substance, and is governed by its affinity for organic phase (hydrophobic partitioning) and/or to the occurrence of electrostatic and other similar interactions between ionized molecules and charged solid surfaces (non-hydrophobic partitioning) (Khunjar and Love, 2011; Ternes et al., 2004). While sorption has been characterized in activated sludge for a wide number of pharmaceuticals, fewer studies investigated sorption in biofilm systems (e.g., Alvarino et al., 2016; Wunder et al., 2011). Even though it has been considered as a comparably fast process, sorption is influenced by mass transfer limitation through diffusive boundary layers and in solid matrices, controlling the time needed to reach equilibrium between aqueous and sorbed concentrations. Biofilm characteristics (density, porosity) have been found to influence intra-biofilm diffusion of a number of organic and inorganic chemical species. This effect can be described by the coefficient *f*, indicating the reduced effective diffusivity in biofilms as compared to free aqueous media. However, no evidences currently exist for *f* on micropollutants in biofilms. In this study, we developed and calibrate a model that described diffusive transport and partitioning in biofilms with the aim to investigate the influence of biofilm thickness on (i) the extent of partitioning, described by K_d coefficients, and (ii) on molecular diffusion of organic micropollutants inside biofilm matrix, described by *f*. To do so, recently developed plastic carriers for Moving Bed Biofilm Reactor (MBBR) that allow controlling biofilm thickness (AnoxKaldnes-Z-carriers) were used in this study (Torresi et al., 2016).

MATERIAL AND METHODS

Experimental setup. Nitrifying biofilms were grown on plastic carriers as support, in continuous-flow operation of two MBBRs for approximately 1 year, by feeding the systems with effluent municipal wastewater spiked with ammonium (50 mg L^{-1}) and nutrients (Torresi et al., 2016). Z-carriers consisted a saddle shaped grid covered surface, which allowed the biofilm to growth only up to the height of the grid wall, which corresponded to the maximum biofilm thickness. Three types of Z-carriers were used in this study and that is Z50, Z200 and Z500, corresponding to biofilm of defined thickness of 50, 200, 500 µm respectively. Sorption batch experiments were performed in three 200-ml glass beakers (one for each type of carriers) using filtered effluent wastewater and an adjusted biomass concentration (same for each batch beakers) of 0.8 g L^{-1}. Biomass was inhibited by (i) addition of allylthiourea (ATU, 10 mg L-1, Khunjar and Love, 2011), and nitrogen sparging (Hamon et al., 2014) to inhibit nitryfing bacteria; and (ii) addition of sodium azide (0.5 g L-1; Khunjar and Love, 2011) to inhibit the fraction of heterotrophic bacteria. Twenty-two micropollutants (only pharmaceuticals) were spiked in all the beakers with an initial concentration of 1 µg L-1 except for X-ray contrast media (at 15 µg L-1) as previously reported in (Torresi et al., 2016). The batch experiments lasted 4 hours.

Modelling and parameters estimation

The diffusion-sorption model was implemented as one-dimensional biofilm model in Aquasim 2.1d (Reichert, 1994). Sorption and desorption processes were described by desorption rate k_{Des}, sorption coefficient K_d, dissolved micropollutant concentration in bulk C_{LI} and sorbed concentration to biofilm C_{SL} (Fig.1). The partitioning of organic micropollutants present in the aqueous phase to biofilms consisted of three consecutive steps (Joss et al., 2004): (1) diffusion of dissolved micropollutants from bulk aqueous phase, through the boundary layer, into the biofilm matrix; (2) diffusion of dissolved micropollutants through biofilm pores; (3) sorption to biofilm solid matrix (Fig. 1). Diffusivity of the chemicals in water ($D_{W,i}$, m^2 d^{-1}) mainly govern process 1, while due to the reduction given by the porosity and tortuosity inside the biofilm, the effective diffusivity of micropollutants within biofilms (D_{bf},i, m^2 d^{-1}) controls diffusion in the biofilm (2) and can be defined as:

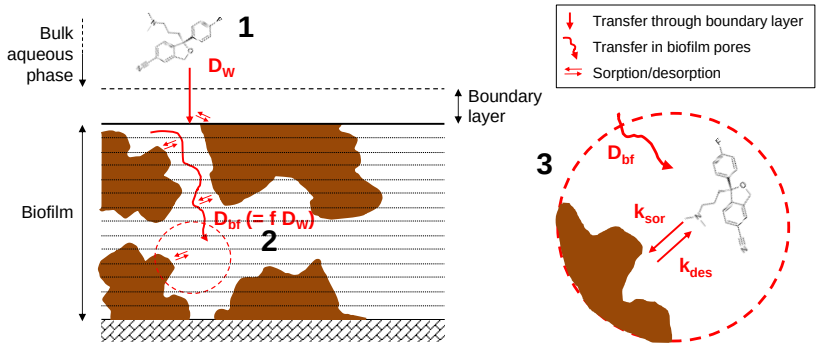
$$D_{bf,i} = f \cdot D_{w,i} \quad \text{(Eq1)}$$

Considering the assumptions of (i) biofilm as an homogenous medium and (ii) sorption into biomass (process 3) as an instantaneous process (by attributing an arbitrary high value to the desorption rate k_{Des}), processes 1 and 2 are the rate-limiting steps for sorption. Hence, it is possible to determine the factor *f* through the diffusion-sorption following two main steps: (i) calculation of the sorption solid-liquid partition coefficient K_d using Eq. 2 ($C_{LI,0}$ and $C_{LI,fin,}$ bulk aqueous initial and final concentration of micropollutant, $X_{biomass}$, biomass concentration, V_{bulk} (L) volume of the bulk liquid and V_{PW} (L) volume of the pore water in the biofilm matrix); and (ii) calibration of the model with experimental data and estimation of *f* for each micropollutant.

$$K_d = \frac{C_{LI,0} - C_{LI,fin}}{C_{LI,fin} X_{biomass}} \frac{V_{bulk}}{V_{bulk} + V_{PW}} \quad \text{(Eq2)}$$

Analytical methods. Samples for micropollutant analysis were collected (4 ml), prepared according to the procedure described by Escolà Casas et al. (2015) and analysed via direct injection using HPLC-MS/MS. Biomass concentration on Z-carriers was measured in two ways: (i) as attached biomass concentration (expressed as total solids, TS), calculated from the difference in weight of three dried carriers (105^{o}C for > 24 h) before and after biofilm removal (using 2M H2SO4 with subsequent brushing) and (ii) by scraping and dissolving the attached biofilm in tap water and measuring total suspended solids (TSS) and volatile suspended solids (VSS) according to APHA standard methods (Clesceri, 1989). Biofilm properties (density and porosity) were calculated

according to Tchobanoglous and Burton (1991) and Hu et al. (2013).



Process	Component C_{LI}	Component C_{SL}	Process rate
Desorption	1	-1	$k_{des}C_{SL}$
Sorption	-1	1	$k_{des}K_dC_{LI}X$

Figure 1. Conceptual model for diffusion and sorption of micropollutants into biofilms, including the consecutive steps required for partitioning onto biofilm solids (processes 1–3, see text).

RESULT AND DISCUSSION

Biofilm properties. Shortly, biofilm porosity among the different Z-carrier biofilms was found to increase with biofilm thickness with values ranged between 76% (Z50) to 93% (Z500). An approximate porosity of 80% is commonly assumed in one-dimensional biofilm models (Koch et al., 2000). Subsequently, biofilm wet density was found to decrease with thickness, from 51in Z50 to 16 kg m^{-3} in Z500.

Sorption coefficient. Sorption was shown to be significant (($C_{LI,0} - C_{LI,fin}$)/$C_{LI,0}$ > 10%) only for eight micropollutants over 22 (e.g., propranolol, citalopram, erythromycin), which mostly corresponded to micropollutants that were positively charged (>90% cationic fraction) at the experimental pH of 7.5. Fig. 2a shows the aqueous concentration profile of beta-blocker propranolol during batch experiments. We first observed different sorption behaviours between the three biofilms. The calculated K_d (L gTS^{-1}) for propranolol (Figure 2 b) were found to decrease with biofilm density (and thus increasing with biofilm thickness). This behaviour was also observed for the other 7 compounds which presented significant sorption, with K_d for Z500 up to 4-fold higher than Z50 for specific compounds (data not shown). We highlight that the sorption batch experiments were made at same biomass concentration (given by different total surface area for reactors, being higher for Z50). Thus, the observed increase of sorption with biofilm thickness could mainly derive from the different biofilm composition (i.e., biofilm density, porosity, microbial community composition as the relative fraction of autotrophic and heterotrophic organism,) and/or physical-related properties (i.e., diffusion limitation, available surface area). For example, higher porosity could have resulted in higher available surface area in biofilm, and thus sorption tendency (as for the case of Z500).

Effective diffusivity coefficient. We estimated effective diffusivity coefficients *f* for each compound depending on the calculated K_d and using the proposed model. For most of the compounds (90%), *f* was found to decrease with biofilm density and thus increase with biofilm thickness and porosity. This suggests that in thinner biofilms (≤ 50 µm), the transport of micropollutants could be significantly limited by the higher biomass density and the reduced porosity. Values of *f* for propranolol were reported in Fig. 2 b. A number of regressions to estimate the effective diffusivity of solutes in biofilms as a function of biofilm density or porosity have been previously developed (e.g.,Guimerà et al., 2016; Horn and Morgenroth, 2006; Zhang and Bishop, 1994), suggesting a negative correlation between *f* and density, as observed in this study. In general, *f* estimated for the targeted micropollutants were lower than the values estimated by the proposed models that were developed for compounds with lower molecular weight (< 100 mol-1) compared to the pharmaceuticals used in this study. A positive correlation was also found between *f* and the octanol-water partioning coefficient of the neutral species (*log* K_{OW}), which resulted in a formulation of a proposed empirical correlation between *f*, biofilm density (or thickness) and *log* K_{OW} (data not

shown). In Fig. 2 a, C_{LI} simulated in bulk (continuous lines) and in biofilm pores (dashed lines) were reported along with the measured data, suggesting solid-liquid partioning equilibrium (given by the converging of the two simulated profiles).

Prediction of sorption coefficient K_d. Finally, different physico-chemical descriptors were used to assess correlation with sorption coefficient K_d of the different micropollutants (e.g., molecular volume, dissociation constant(s) pKa, octanol-water partioning coefficient of ionized species (*log* K_D). While we observed a positive correlation (R^2=0.9) between K_d for Z50 and *log* K_{OW} and *log* K_D, weaker correlations were found for biofilm Z200, Z500, indicating that other descriptor may be more appropriate for sorption in thicker biofilms (e.g., molecular volume, R^2=0.8). However, it was not possible to identify physic-chemicals predictors' model for sorption of the targeted pharmaceuticals unique for the three biofilms, suggesting the complex sorption behaviour of positively charged compounds for which electrostatic interaction with the negatively charged surface of the biomass may play a major role.

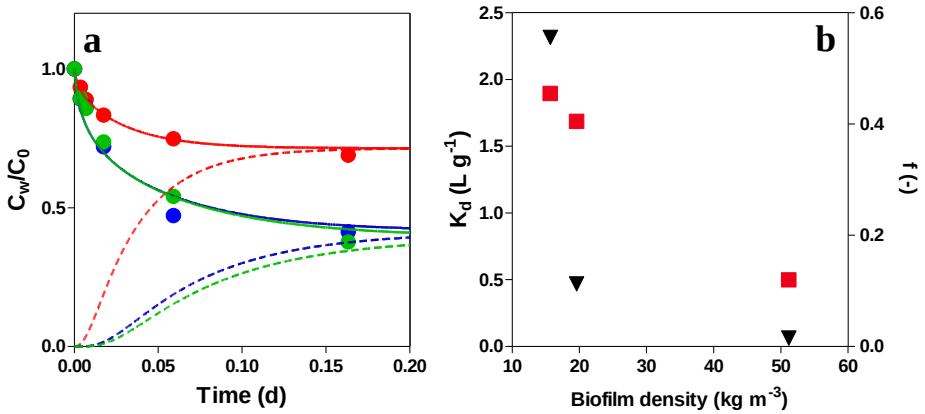


Figure 2. Conceptual model for diffusion and sorption of micropollutants into biofilms, including the consecutive steps required for partitioning onto biofilm solids (processes 1–3, see text).

REFERENCES

Alvarino, T., Nastold, P., Suarez, S., Omil, F., Corvini, P.F.X., Bouju, H., 2016. Role of biotransformation, sorption and mineralization of 14C-labelled sulfamethoxazole under different redox conditions. Sci. Total Environ. 542, 706–715. Beyenal, H., Lewandowski, Z., 2005. Modeling mass transport and microbial activity in stratified biofilms. Chem. Eng. Sci. 60, 4337–4348.

Clesceri, L.S., 1989. Standard methods for the examination of water and wastewater. American Public Health Association.

Fan, L.S., Leyva-Ramos, R., Wisecarver, K.D., Zehner, B.J., 1990. Diffusion of phenol through a biofilm grown on activated carbon particles in a draft-tube three-phase fluidized-bed bioreactor. Biotechnol. Bioeng. 35, 279–286.

Guimerà, X., Dorado, A.D., Bonsfills, A., Gabriel, G., Gabriel, D., Gamisans, X., 2016. Dynamic characterization of external and internal mass transport in heterotrophic biofilms from microsensors measurements. Water Res. 102, 551–560.

Hamon, P., Villain, M., Marrot, B., 2014. Determination of sorption properties of micropollutants: What is the most suitable activated sludge inhibition technique to preserve the biomass structure? Chem. Eng. J. 242, 260–268.

Horn, H., Morgenroth, E., 2006. Transport of oxygen, sodium chloride, and sodium nitrate in biofilms. Chem. Eng. Sci. 61, 1347–1356.

Hu, M., Zhang, T.C., Stansbury, J., Neal, J., Garboczi, E.J., 2013. Determination of Porosity and Thickness of Biofilm Attached on Irregular-Shaped Media. J. Environ. Eng. 139, 923–931. Joss, A., Andersen, H., Ternes, T., Richle, P.R., Siegrist, H., 2004. Removal of estrogens in municipal wastewater treatment under aerobic and anaerobic conditions: consequences for plant optimization. Appendix: Diffusive mass transfer across the boundary layer and inside the floc. Environ. Sci. Technol. 38, 3047–55.

Khunjar, W.O., Love, N.G., 2011. Sorption of carbamazepine, 17α-ethinylestradiol, iopromide and trimethoprim to biomass involves interactions with exocellular polymeric substances. Chemosphere 82, 917–922.

Koch, G., Egli, K., Van Der Meer, J.R., Siegrist, H., 2000. Mathematical modeling of autotrophic denitrification in a nitrifying biofilm of a rotating biological contactor. Water Sci. Technol. 41, 191–198.

Pomiès, M., Choubert, J.-M., Wisniewski, C., Coquery, M., 2013. Modelling of micropollutant removal in biological wastewater treatments: a review. Sci. Total Environ. 443, 733–48.

Reichert, P., 1994. Aquasim - a tool for simulation and data-analysis of aquatic systems. Water Sci. Technol. 30, 21–30.

Ternes, T.A., Herrmann, N., Bonerz, M., Knacker, T., Siegrist, H., Joss, A., 2004. A rapid method to measure the solid-water distribution coefficient (Kd) for pharmaceuticals and musk fragrances in sewage sludge. Water Res. 38, 4075–4084.

Torresi, E., Fowler, J.S., Polesel, F., Bester, K., Andersen, H.R., Smets, B.F., Plosz, B.G., Christensson, M., 2016. Biofilm thickness influences biodiversity in nitrifying MBBRs – Implications on micropollutant removal. Environ. Sci. Technol. 50, 9279–9288.

Wunder, D.B., Bosscher, V.A., Cok, R.C., Hozalski, R.M., 2011. Sorption of antibiotics to biofilm. Water Res. 45, 2270–2280.

Zhang, T.C., Bishop, P.L., 1994. Evaluation of turtuosity factors and effective diffusivities in biofilms. Water Res. 28, 2279–2287.