Active Biomass and Sludge Retention Time as Determining Factors to Biodegradation Kinetics of Pharmaceuticals

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Abstract

Biodegradation rates of pharmaceutical active compounds (PhACs) in activated sludge systems are usually determined in lab-scale experiments where biomass is a key parameter. The latter is often addressed by lumped parameters such as total suspended solids (*TSS*). However, only active microorganisms mediate PhAC breakdown. In this context, this study focused on **active heterotrophs (X_{bh})** that govern COD removal suggesting a potential determining factor for biological PhAC removal as well. The biodegradation of five polar PhACs was investigated in two Luxembourg wastewater treatment plants (WWTP Mamer, Boevange) that differed clearly in size, operation and **sludge retention time (SRT)**.

Results showed that fractions of X_{bh} / *TSS* varied significantly between the two sludges indicating that *TSS* does not reveal information about heterotrophic activity. Moreover, PhAC removal was clearly faster in presence of high amounts of heterotrophs and a low SRT. Pseudo first-order kinetics modified with X_{bh} was used to describe decreasing PhAC elimination with increasing SRT.

Active Heterotrophic Biomass

The amount of active heterotrophic biomass was estimated by respirometry batch tests and modeling simulations (Plattes *et al.* 2006; Vanrolleghem *et al.*, 1999) while autotrophs were inhibited.

Significant different fractions f_{at} of X_{bh} / *TSS* reveal that large fractions of the suspended solids consist of inactive materials leading to biased estimates when used in rate calculations, as often done in modeling approaches. The formation of different fractions of active biomass is most likely due to available biodegradable substrates present in incoming wastewater .

	Population Equivalents	SRT [d]	TSS [g L^{-1}]	X_{bh} [g L^{-1}]	Fraction f_{at} [%]
WWTP Mamer	20'300	6	2.4 ± 0.3	1.5 ± 0.1	62.9 ± 5.8
WWTP Boevange	2'700	54	2.5 ± 0.1	0.6 ± 0.1	25.2 ± 6.3

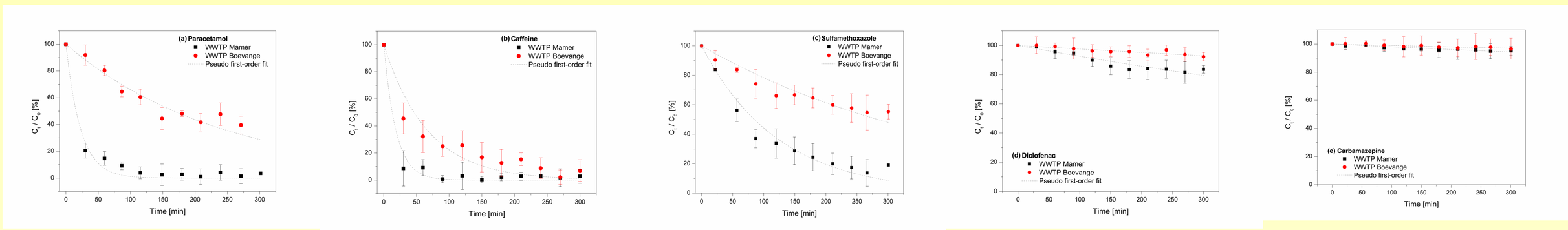
Biodegradation Kinetics

Pseudo-first order reaction kinetics was applied to describe pharmaceutical removal in batch tests. Thereby, degradation kinetics was assumed to depend on the degradation rate constant k_{biol} and the amount of active heterotrophic biomass that is expected to be constant over the duration of the experiment. The biodegradation rate constant k_{biol} is derived from fitting the kinetics to the measured data (n=11):

Eq. 1

$$\frac{\Delta C_t}{\Delta t} = -k_{biol} \cdot X_{bh} \cdot C_s$$

where ΔC_t / Δt is the reaction rate [ng L^{-1} h^{-1}], C_t is the pharmaceutical concentration at time t [ng L^{-1}], t is the time [h], k_{biol} is the degradation rate constant [L gX_{bh}^{-1} h^{-1}], X_{bh} is the amount of active heterotrophic biomass [g L^{-1}] and C_0 is the initial dissolved pharmaceutical concentration [ng L^{-1}].



It can be observed that the degradation of paracetamol, caffeine, sulfamethoxazole and diclofenac was significantly enhanced in batch tests with activated sludge from WWTP Mamer compared to sludge from WWTP Boevange for identical experimental conditions whereas carbamazepine was not affected.

Suggesting heterotrophs to be governing the removal, the k_{biol} of pseudo first-order kinetics would result in identical values in both sludges and hence in a ratio of 1 since k_{biol} is directly proportional to X_{bh} (Eq. 1). As it can be seen from the table below, the differences in xenobiotic degradation efficiency can be largely explained by X_{bh} for 4 of the 5 substances considered.

	Degradation rate constant [L gX_{bh}^{-1} h^{-1}]				**Ratio [-]**
	WWTP Mamer	r^2	WWTP Boevange	r^2	
Carbamazepine	0.007 ± 0.001[a]	0.81	0.010 ± 0.001[a]	0.78	**0.7 ± 0.2**
Diclofenac	0.029 ± 0.002	0.87	0.025 ± 0.002	0.82	**1.2 ± 0.2**
Sulfamethoxazole	0.307 ± 0.022	0.94	0.245 ± 0.014	0.89	**1.3 ± 0.1**
Paracetamol	1.654 ± 0.181	0.97	0.415 ± 0.034	0.89	**4.0 ± 0.8**
Caffeine	2.030 ± 0.185	0.98	1.500 ± 0.147	0.92	**1.4 ± 0.2**

Heterotrophic PhAC Biodegradation and Sludge Retention Time

The SRT is a process parameter that is inherently related to microbial growth activity. The latter increases with increasing biodegradable COD available in incoming wastewater. By definition, the SRT decreases with increasing sludge production and therefore high active fractions of X_{bh} are usually found at low SRTs. The relation between the active heterotrophic fraction f_{at} and SRT has been mathematically described by Ekama & Wentzel (2008).

Results suggested heterotrophs to be a governing factor for the removal of the selected PhACs since autotrophs were inhibited during the experiments. Increased degradation rates of the selected PhACs were observed in the sludge with the lower SRT and higher fractions of X_{bh} except for persistent carbamazepine. This is consistent with the fact that increasing heterotrophic biomass fractions are linked to decreasing SRTs and thus highest active fractions of X_{bh} occur at low SRTs.

The SRT does not give any direct information about the microbial or enzyme spectrum but can be used as an indicator for heterotrophic active fractions. It can be expected that the selected compounds may follow similar breakdown pathways as dominant substrates present in wastewater (Stasinakis *et al.*, 2010) and may therefore be subjected to non-specific enzyme cleavage.

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