# Investigation on the removal mechanisms of organic micropollutants in activated sludge processes

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This paper investigates the removal mechanisms of 10 selected organic micropollutants (xenobiotics), chosen among the priority pollutants listed in the Decision 2455/2001/EC of the European Union, in activated sludge processes. The removal mechanisms of the micropollutants have been assessed both with unacclimated and acclimated biomass. The biodegradation rates and the biomass-water partition coefficients of the considered substances were measured through batch tests. The unacclimated biomass was able to biodegrade only phenol, whereas the acclimated biomass was also able to biodegrade 1,3,5-trichlorobenzene, naphthalene and pentachlorophenol. For most of the considered substances, adsorption was an important removal mechanism with both biomasses.

### **1. Introduction**

The presence in waters of organic micropollutants (among which polycyclic aromatic hydrocarbons, polychlorinated biphenyls, surfactants, pharmaceuticals) is causing increasing concern (European Directive 2000/60/EC and the following decision 2455/2001/EC). Micropollutants are often found in industrial or municipal wastewaters, e.g. in refinery wastewaters polycyclic aromatic hydrocarbons, chlorinated phenols and polychlorinated biphenyls can be present at concentrations up to dozens of mg/L (Al Zarooni and Elshorbagy, 2006); in municipal wastewaters anionic and nonionic surfactants can be present at mg/L levels (Mezzanotte et al., 2000). These substances are considered toxic for the environment and for human life, therefore they have to be removed from contaminated wastewaters to the highest possible extent. Being activated sludges the most used wastewater treatment processes, the removal of micropollutants in such processes is of particular interest. Micropollutants in activated sludge processes can be removed through different mechanisms (biotic or abiotic) (Byrns, 2001; Dionisi et al., 2006): biodegradation, volatilisation, air stripping or adsorption on activated sludge flocs. There is however little knowledge on the relative role of these different mechanisms in the overall removal of micropollutants.

This study describes xenobiotics removal by activated sludges cultured in two parallel sequencing batch reactors (SBRs), operated under the same experimental conditions, the only difference being feed composition: the feed of both reactors contained readily biodegradable substrates, but one (SBR1) was operated without micropollutants, whereas the other one (SBR2) contained also a mixture of 10 organic micropollutants. In SBR2, the concentration of micropollutants in the liquid phase during the cycle was analitically determined, allowing to calculate the removal of each substance. The role of biodegradation and adsorption as potential removal mechanisms was evaluated through batch tests. Comparing biodegradation ability of unacclimated and acclimated biomass, the role of biomass acclimation was also evaluated.

# 2. Materials and methods

### 2.1 Operation of the SBRs

Two parallel sequencing batch reactors were operated. The operating conditions of both reactors were the same and were typical of nitrogen removal SBRs (Wilderer et al., 2001): cycle length 6 h (unaerated feed 1.5 min, unaerated phase 57 min, aerated phase 246 min, sludge withdrawal 0.5 min, settling 45 min, effluent withdrawal 10 min). The volume of the filled reactors was 1.2 L, the volume at the end of the cycle before the new feed was 0.6 L (this corresponds to a volumetric exchange ratio of 0.5). The organic load rate was 1 gCOD/L/d and sludge age was in the range 10-12 days. The only difference between the two reactors was feed composition: both were fed with readily biodgeradable substrates but only SBR2 feed included a mixture of micropollutants. Complete feed compostion is reported in a previous paper (Dionisi et al., in press).

SBR2 was regularly sampled for analytical determinations of organic xenobiotics at the end of unaerated and aerated phases. In this way, by comparison with the concentrations in the feed, the removal of each substance during the unaerated and aerated phase was calculated.

Analytical procedures for xenobiotic measurement have been previously reported (Dionisi et al., 2006).

#### 2.2 Batch tests

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Biomasses from the two reactors were used for batch tests in order to evaluate biodegradation rates and adsorption equilibria of the considered xenobiotics. For each biomass, two parallel tests were carried out: with active biomass and with inhibited biomass. Biomass inhibition was obtained through addition of formaldehyde (1.9%). In the test with inactivated biomass, being biodegradation inhibited, the removal of the substances was due only to adsorption. All the tests were carried out in closed glass bottles (working volume 300 mL). The bottle with oxygen supply was connected to an automatic respirometer (COMPUT-OX, N-CON Systems Co, Inc.) which allowed oxygen supply without air bubbling in the liquid phase. In this way the possible removal mechanism of air stripping was excluded. Moreover, preliminary tests without biomass showed that also the removal by volatilisation (due to water gas partitioning into the closed bottles) was negligible. In each bottle, half of liquid volume (150 mL) was due to the solution of xenobiotics, 120 mL were due to activated sludge and 30 mL to the nutrient solution. The tests were replicated two times.

#### 2.3 Measurement of biodegradation and adsorption coefficents

From the profiles of each substance in batch tests, two parameters were determined: the specific biodegradation rate (K<sub>biod</sub>, day<sup>-1</sup>) and the biomass-water partition coefficient (K<sub>P</sub>, L/gVSS). The two parameters were defined according to the following relationships:

$$r_{biod} = K_{biod} \cdot X \tag{1}$$

$$q_{ads} = K_P \cdot C \tag{2}$$

where r<sub>biod</sub> is the biodegradation rate measured in batch tests (mg xenobiotic/L/day), X is biomass concentration in the batch test (mgVSS/L), q<sub>ads</sub> is the amount of substance adsorbed on the biomass (mg xenobiotic/g VSS) and C is the xenobiotic concentration in the liquid phase in equilibrium with  $q_{ads}$ . The parameters  $K_{biod}$  and  $K_P$  were not determined for 4-nonylphenol, benzene and for decachlorobiphenyl because their strong sorption to biomass immediately decreased their concentrations below detection limits.

# 3. Results and discussion

### 3.1 Removal of xenobiotics in SBR2

Average data of xenobiotics concentration at the end of unaerated and aerated phases, compared with feed concentrations, allowed to calculate the removal of each substance. Figure 1 summarises the removal from the liquid phase of the organic xenobiotics present in SBR2 feed, showing the contribution of the unaerated and aerated phase to the overall removal. To this regard, it is important to observe that, due to nitrification inhibition caused by xenobiotics, virtually no oxidised nitrogen (nitrate or nitrite) was present in SBR2 in the unaerated phase. This phase was therefore anaerobic. Thus, no biodegradation could occur during the unaerated phase; the only mechanisms which could act during the unaerated phase were therefore adsorption and volatilisation. In the aerated phase, on the other hand, biodegradation and stripping could be important.

The organic xenobiotics were removed from the liquid phase to a great extent, more than 80%, the only exception being 4-dodecylbenzenesulfonic acid, whose removal was only approx. 20%. Most of the substances were completely, or almost completely, removed during the unaerated phase. In particular no role of the aerated phase was observed for the removal of pyrene, benzene and decachlorobiphenyl. The only substances which were mostly removed during the aerated phase were phenol, naphthalene, and pentachlorophenol. The observed high removal of the considered substance from the liquid phase is well in agreement with other literature studies on activaed sludge processes: e.g., Melcer et al. (1995) observed more than 90% removal of polycyclic aromatic hydrocarbons in a municipal wastewater treatment plant; high removal of many aromatic substances has also been observed by Kempton et al. (1983). In order to have a deeper insight into the removal mechanisms of xenobiotics in our system, the relevance of adsorption and biodegradation as possible mechanisms of xenobiotics removal was evaluated through batch tests.



Figure 1. Removal of the organic xenobiotics in SBR2 (gray: removal during the unaerated phase; black: removal during the aerated phase)

#### 3.2 Batch tests – Evaluation of adsorption and biodegradation.

Batch tests were carried out both with unacclimated (from SBR1) and acclimated (from SBR2) biomass. Figure 2 shows a typical example of xenobiotic profile during batch tests with active and inactivated biomass (biomass from SBR2). The figure also shows how experimental data were used to calculate  $K_{biod}$  and  $K_p$  (according to equations (1) and (2) in the Materials and Methods section). The summary of the parameters obtained for the two biomasses is reported in Table 1. With regard to the biodegradation potential, important difference can be observed between the two biomasses. Unacclimated biomass was able to biodegrade only phenol, whereas acclimated biomass was able to biodegrade phenol, naphthalene, 1,3,5 trichlorobenzene and pentachlorophenol. Moreover, phenol biodegradation rate of SBR2 biomass was much higher than that of SBR1 biomass (0.115 vs. 0.011 day<sup>-1</sup>, respectively). These data indicate that acclimation was very important in increasing the biodegradation potential of SBR2 sludge.

Similarly to what observed with SBR1 biomass, in a previous study on the same substances (Dionisi et al., 2006) it was shown that an unacclimated activated sludge from a municipal wastewater treatment plant was able to biodegrade only phenol. With regard to the substances which were not biodegraded by SBR2 biomass (i.e. pyrene, 2,4-dichlorobiphenyl and 4-dodecylbenzenesulfonic acid), evidences of biodegradation have been obtained for pyrene, as well as for other polycyclic aromatic compounds, (Bamforth and Singleton, 2005) and for linear alkylbenzenesulfonates (Temmink and Klapwijk, 2004). On the other hand, aerobic biodegradation of polychlorinated biphenyls is usually reported to occur only under co-metabolic conditions (Pieper, 2005).

With regard to adsorption, both biomasses were able to adsorb the considered substances, with the exception of phenol. It is interesting to observe that partitition coefficients obtained for unacclimated biomass are usually higher than corresponding coefficients for acclimated biomass. It can be hypothesysed that the long-term exposure to micropollutants modified the floc surface decreasing the adsorption capacity of the biomass.

#### 3.3 Role of the different mechanisms in xenobiotics removal

By combining the data on xenobiotics removal obtained during SBR2 run (Figure 1), with the values of the biodegradation and adsorption coefficients (Table 1) a preliminary evaluation of the contribution of biodegradation and adsorption to the overall removal of the substances in SBR2 can be made. For those substances, i.e. phenol, pentachlorophenol, 1,3,5 trichlorobenzene and naphthalene, which can be biodegradation is likely an important removal mechanism. For the other substances in SBR2 feed, on the other hand, the removal mainly occurs during the unaerated phase. In this case, being these substances not biodegradable by SBR2 biomass, it is likely that adsoprtion plays an important role. The role of the other possible removal mechanisms in our system, volatilisation and air stripping, is currently being studied.

Table 1. Summary of biodegradation and adsoprtion parameters for unacclimated (SBR1) and acclimated (SBR2) biomass

Substance	K <sub>biod</sub> (day <sup>-1</sup> )		$K_{P} (L/gVSS)$	
	SBR1	SBR2	SBR1	SBR2
Phenol	0.011	0.115	0	0
Naphthalene	0	0.0112	16.7	0.66
1,3,5-trichlorobenzene	0	0.0028	23.0	2.71
Pyrene	0	0	109	7.22
2,4-dichlorobiphenyl	0	0	111	12.6
Pentachlorophenol	0	0.0095	2.14	0.73
4-dodecylbenzenesulfonic acid	0	0	1.24	0.99



*Figure 2. Batch test with SBR2 (acclimated) biomass. Time profile of naphthalene (Filled circles: test with inactivated biomass; empty circles: test with active biomass).* 

## 4. Conclusions

The removal of 10 organic xenobiotics with unacclimated and acclimated biomass has been studied experimentally. During the operation of the SBR fed with micropollutants, these substances were removed from the liquid phase at an high extent (usually more than 80%). It was found that acclimation increases the biodegradation potential of several xenobiotics. In particular, only the acclimated biomass was able to biodegrade 1,3,5-trichlorobenzene, naphthalene and pentachlorophenol. On the other hand, both acclimated and unacclimated biomass were able to biodegrade phenol, even though with an higher rate by the acclimated biomass. Both biomasses showed the ability to adsorb most of the substances on the floc surface.

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