

A SCREENING BATCH TEST TO ASSESS THE FATE OF ORGANIC MICROPOLLUTANTS IN AN ACTIVATED SLUDGE SYSTEM

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ABSTRACT

Organic micropollutants are usually present in wastewaters at low concentrations (order of magnitude of mg L^{-1}), but their emission standards are often much lower (order of magnitude of $\mu\text{g L}^{-1}$). Therefore, the analysis of the removal processes of these substances within a Waste Water Treatment Plant (WWTP) via volatilization, biodegradation or sludge adsorption may be a significant feature to take into for the evaluation of the WWTP emissions. In this paper a simple screening lab scale batch test is presented, aimed at defining the environmental fate of organic micropollutants into water, sludge and air. In order to simulate full-scale plant operational conditions, the input concentrations are very low (usually between $0.02\div 1 \text{ mg L}^{-1}$) and the test was applied to four organic micropollutants with different chemical properties (i.e. toluene, benz(a)anthracene, phenol and benzene). In this test, not only one single removal mechanism is investigated (as happens during biodegradation or volatilization tests), but the whole removal process is analysed and the prevalent removal mechanism of the system may be found out in a relatively short time. The results obtained show that the screening test proposed is reliable and can constitute a useful tool to assess in about one month the fate of organic micropollutants in an activated sludge tank of a WWTP.

1 INTRODUCTION

Xenobiotic substances in the wastewater are often resistant to biodegradation and may reach and impact the environment by means of different pathways (Stangroom *et al.*, 1998). The concentrations of micro-pollutants are usually low in the wastewaters (i.e. order of magnitude of mg L^{-1}), but some xenobiotics may remain in the sludge after the biological treatment, may be volatilised into the atmosphere (so that the activated sludge plants constitute significant VOCs emission sources, as indicated in Hsieh, 2000) or may be transformed into by-products which may be more or less toxic than the parent (Katsoyiannis *et al.*, 2006).

Since the xenobiotics emission standards in the final effluent are often in the order of magnitude of $\mu\text{g L}^{-1}$, the removal ratio processes of organic pollutants become significant features to take into account during the usual design procedure. In fact, the observed overall removal process is the sum of different removal mechanisms (i.e. volatilization, biodegradation and adsorption) that compete in different ways and depends not only on the physical-chemical characteristics of the compound, but also on the operating conditions of the plant. In Hsieh (2000), the concept of “competing point” for VOCs is introduced, in order to identify the condition in which biodegradation equally competes to stripping rate. Therefore, for a given compound, the prevalence of one process with respect to the other is studied as a function of different operational parameters, such as the active biomass concentration, the air to water ratio, the hydraulic retention time and the VOC saturation in exit bubbles.

The quantification of the fate of xenobiotic compounds in the separate units of WWTPs can be performed by mathematical models (e.g. Rogers, 1996, Byrns, 2001, US EPA 1982, Clark et al., 1995), which are usually very sensitive to the biodegradation kinetic constants. These constants are often obtained by means of standardised biodegradability tests (e.g. OECD tests, 1993, or ISO 11733, 2004), which, however, were not designed to yield kinetic coefficients, but rather to assess the compounds biodegradability (Temmink and Klapwijk, 2003).

The experimental determination of the fate of chemicals into a WWTP is usually hard-working and expensive and many differences can be often found between experimental and real plant conditions. In this study a simple screening test for the evaluation in a short time (about one month) of the fate of organic micropollutants during an activated sludge process is presented. In order to simulate real operational conditions of a full-scale plant, the input concentrations are very low (order of magnitude of $0.02\div 1\text{ mg L}^{-1}$). The results of the proposed test obtained with four organic micro-pollutants with different chemical-physical properties (i.e. toluene, benz(a)anthracene, phenol and benzene) are reported.

2 MATERIALS AND METHODS

2.1 Screening batch test

The test presented is quite simple and is composed of ordinary laboratory instruments. The test is carried out for 24 hours and samples are taken at the beginning of the test (t_0) and at different times (closer in the first hours), according to the compound properties.

The reactor (Figure 1) consists in a glass three-necked bottle (total volume of 1L):

- one lateral entrance is used for aeration, adjusted to 0.41 L min^{-1} (by means of a pore diffuser stone), the air flow was set at $2\text{ m}^3\text{h}^{-1}\text{ m}^{-3}$, obtaining a DO concentration in the reactor of about 2 mg L^{-1} ;
- the second lateral entrance is dedicated to gaseous emission. The emission passes through a U-shaped glass pipe partially immersed in a cold water bath, working as a condenser. Downstream this, a tube filled with adsorbing material (active carbon for toluene and benzene or XAD-2 resin in case of phenol and benz(a)anthracene) is connected;
- the central neck was used for the intakes of the compound solutions and for the

samplings of the liquid phase (water + sludge).

The reactor is maintained at constant temperature of about 20 °C by means of a thermostat water bath. The entire system is sealed off, except for the gas emission flux.

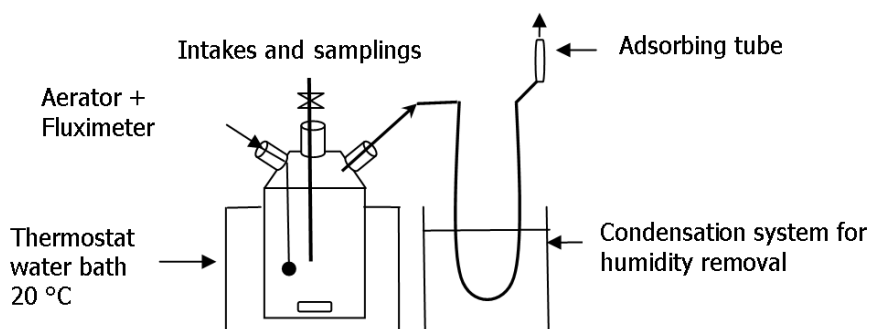


Figure 1. Experimental set-up of the lab scale batch test

The sludge (2 gVSS L⁻¹) was acclimated to the compound concentration for 15 days before the test and the micropollutant feeding was suspended two days before the test in order to have no residual compound concentration in the sludge.

Analysis (water, sludge and adsorbing tubes) were performed by means of gas chromatography (GC-FID and GC-MS) and, for water and sludge samples in case of benzo(a)anthracene, the samples were liquid-liquid extracted using hexane. Benzene, toluene and phenol were analysed by SPME extraction (Solid Phase Microextraction). Activated carbon adsorption tubes were desorbed by CS₂ and by dichloromethane for XAD-2.

The test was applied to four organic micropollutants (i.e. toluene, benz(a)anthracene, phenol and benzene), whose properties are summarised in Table I.

Table I. Characteristics of the studied molecules

	Solubility (25°C)	K _H (25°C) *	logKow *	Vapore pressure (25°C) *	K _{max} _ Biodegr. *
	mg L ⁻¹	m ³ atm mol ⁻¹		mm Hg	mg g ⁻¹ h ⁻¹
Benzene	1790**	0.00555	2.15	95.2	19.0
Phenol	93**	3.33x10 ⁻⁷	1.46	0.341	97.0
Toluene	535**	6.42 x10 ⁻³	2.69	30	73.5
Benz(a)anthracene	0.0094***	1.38x10 ⁻⁹	5.61	0.0000002	31.1

* US EPA (1994)

** Sawyer et al. (2003)

*** Hazardous Substances Data Bank (HSDB)

Samples from the reactor were acidified (pH<2) by means of H₂SO₄ (in case of toluene, benz(a)anthracene, benzene) or basified (pH>11) by means of NaOH (in case of phenol), so that the substance adsorbed on the sludge was released into water. Therefore, the compound fraction adsorbed on the sludge was calculated as difference between the total compound mass in water after acidification/basification and the

compound mass in water (after sludge separation by means of a centrifuge).

Since the initial and final compound mass in the reactor is known, the fraction lost via biodegradation is calculated by difference by means of the mass balance shown in eq. (1):

$$M_{to} = M_{biodegraded} + M_{adsorbed} + M_{volatilized} + M_{tf} \quad (1)$$

where:

M_{to} = initial compound mass;

$M_{biodegraded}$ = calculated by difference in the mass balance;

$M_{adsorbed}$ = difference between the total compound mass in water after acidification/basification and the compound mass in water (after sludge separation);

$M_{volatilized}$ = measured on the adsorbing tube;

M_{tf} = final compound mass.

A control test, consisting of the equipment described in Figure 1 filled with water and the compound (without activated sludge), was performed as well, in order to evaluate the possible losses (usually associated to the compound volatility) that may be related to the not perfect airtight of the system or that may occur during sampling operations.

2.2 Twenty-eight days biodegradation test

This test (APAT, 1999) allowed to obtain an indicative experimental confirmation of the batch activated sludge test results and to exclude the presence of by-products. It consists of a solution with the xenobiotic compound and a bacterial inoculum at very low concentrations. The supernatant of a 2 days acclimated sludge was further acclimated for 18 days and diluted 1:12 with deionized water (to consider adsorption on sludge negligible), with the addition of minerals and nutrients. 225 mL glass bottles were filled with this solution with no headspace, so that volatilization could be excluded. Therefore, the compound missing mass can be associated only to biodegradation.

In order to exclude the development of by-products, CO₂ and dissolved oxygen concentrations were measured (APHA *et al.*, 1998) and the stoichiometric mineralization was verified. The measured CO₂ and DO concentrations were compared to a theoretical concentration, which was calculated as the sum of two inputs:

- CO₂ production and DO consumption deriving from the stoichiometry of the oxidation reaction of the compound (at a given initial concentration)
- CO₂ production and DO consumption deriving from the endogenous respiration of the biomass (which was experimentally obtained by means of the same test performed without the compound, i.e. with bottles filled with sludge only).

3 RESULTS AND DISCUSSION

3.1 Activated sludge test

3.1.1 Toluene

Toluene was chosen as representative of volatile organic compounds (VOCs). In order to evaluate possible losses from the system, four control tests were performed (Table II). Considering an experimental error of the measurements of about 15%, the mass balance for toluene was considered closed for the four tests. The systematic lack of closure that occurred in the mass balance was likely due to losses during the experiment. These losses (on average 10%) were taken into account for the activated sludge test analysis. However, a good repeatability of the four stripping tests was observed and the method was found to be reliable.

Results obtained with the activated sludge test are presented in Table III. For each test, the repartition of toluene into water, air and sludge is indicated.

At the end of the test the residual toluene (both adsorbed on the sludge and dissolved in aqueous phase) was lower than the detection limit (i.e. 6 µg/l) and was therefore considered negligible. The volatilized fraction of toluene resulted to be quite constant, around 70%. Considering the losses assimilated to the volatilized fraction, it was concluded that volatilization accounts for about 80% and biodegradation (obtained by difference from the initial mass, the adsorbed mass, the dissolved in water mass and the losses) for about 20% (Figure 2).

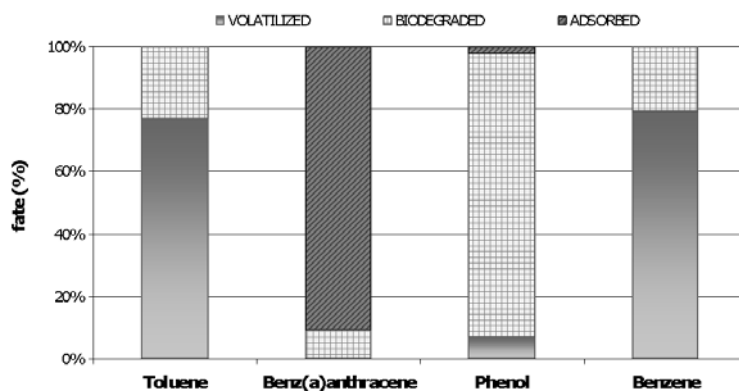
Toluene is usually considered a biodegradable molecule. The results obtained in the activated sludge test indicate therefore that, under these conditions, volatilization is the dominant process and this is supposed to be due to low oxygen transfer efficiency of the system and to the low active biomass fraction, according to *Hsieh (2000)*.

Table II. Results of the control test for the four considered compounds: volatilized, dissolved in water and loss percentages.

Substance	REMOVAL (%)	T1	T2	T3	T4	Mean	St.Dev.
Toluene ($C_0 = 0.17 \text{ mg L}^{-1}$)	VOLATILIZED	91	95	86	89	90.0	4
	WATER	<1	<1	<1	<1	<1	-
	LOSS	9	5	14	11	10.0	4
($C_0 = 0.018 \text{ mg L}^{-1}$)	VOLATILIZED	<1	<1	<1	<1	<1.0	
	WATER	99	99	99	99	99.0	
	LOSS	<1	<1	<1	<1	<1.0	
Phenol ($C_0 = 0.41 \text{ mg L}^{-1}$)	VOLATILIZED	5	5	6		5.3	1
	WATER	93	94	93		93.3	1
	LOSS	2	1	1		1.3	1
Benzene ($C_0 = 0.093 \text{ mg L}^{-1}$)	VOLATILIZED	82.9	81.6	78	78.8	80.2	2.5
	WATER	3.5	7.6	0.5	<1	2.9	-
	LOSS	13.6	10.8	22	21.2	16.9	5.6

Table III. Results of the screening batch tests for the four compounds: apportionment (%) between volatilized, adsorbed on the sludge and biodegraded mass.

Substance	Parameter	T1	T2	T3	T4	T5	Mean	St.Dev.
Toluene ($C_0 = 0.25 \text{ mg L}^{-1}$)	ADSORBED	<1	<1	<1	<1		<1	-
	BIODEGRADED	21	19	19	23		21	2
	WATER	<1	<1	<1	<1		<1	-
	VOLATILIZED	69	71	71	67		70	2
Benz(a)anthracene ($C_0 = 0.018 \text{ mg L}^{-1}$)	ADSORBED	89	90	89	89		89	0.5
	BIODEGRADED	10	8	9	8		9	1
	WATER	<1	<1	<1	<1		<1	-
	VOLATILIZED	<1	<1	<1	<1		<1	-
Phenol ($C_0 = 0.25 \text{ mg L}^{-1}$)	ADSORBED	2	3	1			2	0.6
	BIODEGRADED	91	90	93			91	1
	WATER	<1	<1	<1			<1	-
	VOLATILIZED	7	7	6			7	0.7
Benzene ($C_0 = 0.12 \text{ mg L}^{-1}$)	ADSORBED	<1	<1	<1	<1	<1	<1	-
	BIODEGRADED	18	12	18	22	18	17	4
	WATER	<1	<1	<1	<1	<1	<1	-
	VOLATILIZED	65	71	65	61	66	66	4

**Figure 2.** Partitioning (%) among volatilized, adsorbed on the activated sludges, dissolved in water and biodegraded mass of the four considered compounds.

3.1.2 Benz(a)anthracene

Benz(a)anthracene was chosen as characteristic molecule for its low solubility in water (about $17.8 \mu\text{g L}^{-1}$) and its high adsorption on sludges (typical of recalcitrant compounds like dioxin). The control test indicated negligible losses from the reactor (less than 1%, see Table II) and the measured values for the four tests are indicative of a good repeatability. The results of the activated sludge test reported in Table III show that the only significant removal process for this molecule is adsorption (considering an experimental error in case of benz(a)anthracene of about 25%).

3.1.3 Phenol

Phenol was chosen as characteristic molecule for its biodegradability. Also in this case, data on control test shown in Table II indicate a good repeatability of the results and not significant losses from the system. With regard to the activated sludge test, results reported in Table III indicate biodegradation as the only significant removal mechanism.

3.1.4 Benzene

As toluene, benzene was chosen as representative of VOCs. The control test results (Table II) showed higher losses with respect to the other molecules, of about 17%, probably due to the high volatility of the compound. Considering the losses associated to the volatilized fraction, the activated sludge test (Table III) indicated that most of benzene mass (83%) is volatilized, 17% is biodegraded, while the sludge adsorption is negligible.

3.2 Removal kinetics

The screening batch test can also be used for the evaluation of the kinetic processes for volatilization and biodegradation, when the analysis of the water/sludge and air samples taken at different times are performed. Considering that xenobiotic concentration in wastewater is very low, a first order kinetic can be assumed and the removal constants can be derived from the test.

With regard to the volatilization process, Figure 3 shows the difference between the mass transfer coefficient in water (i.e. control test) or in activated sludge (i.e. the complete test), obtained as difference between the initial mass and the mass adsorbed on the stripping tube. The effect of activated sludge on process removal is evident, since the volatilization kinetic is much lower in presence of biomass either because of the different liquid matrix (water or activated sludge) or because of the removal competition between volatilization and biodegradation.

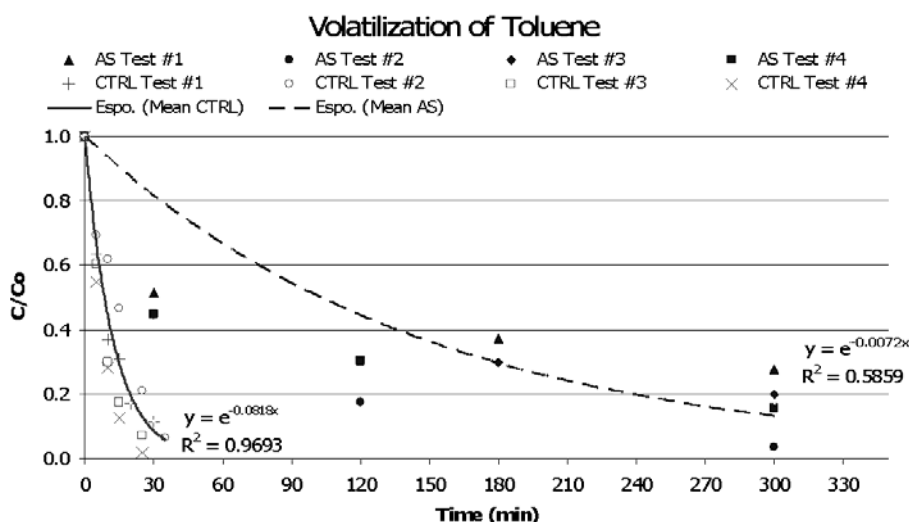


Figure 3. Volatilization process in the control test and in the activated sludge test.

Moreover, the kinetic apportionment of the overall removal process between volatilization and biodegradation can be assessed. This is an interesting application of the test, since it allows to analyse the prevalence of one process with respect to the other for specific organic compounds.

In Figure 4 the example of toluene molecule is proposed. As it can be seen, volatilization constitutes the major contribute to the total removal although toluene is usually considered a molecule with a good biodegradability. The volatilization and biodegradation kinetic constants obtained as the mean of the experimental values indicated a $k_{\text{volatilization}} = 0.43 \text{ h}^{-1}$, $k_{\text{biodegradation}} = 0.04 \text{ h}^{-1}$ and $k_{\text{overall}} = 1.11 \text{ h}^{-1}$.

These results indicate that volatilization is the dominant process within the system and this is supposed to be due to low oxygen transfer efficiency of the system and to the low active biomass fraction.

The determination of the kinetic constants is not possible for very volatile molecules like benzene, since different samples determine too high losses from the system.

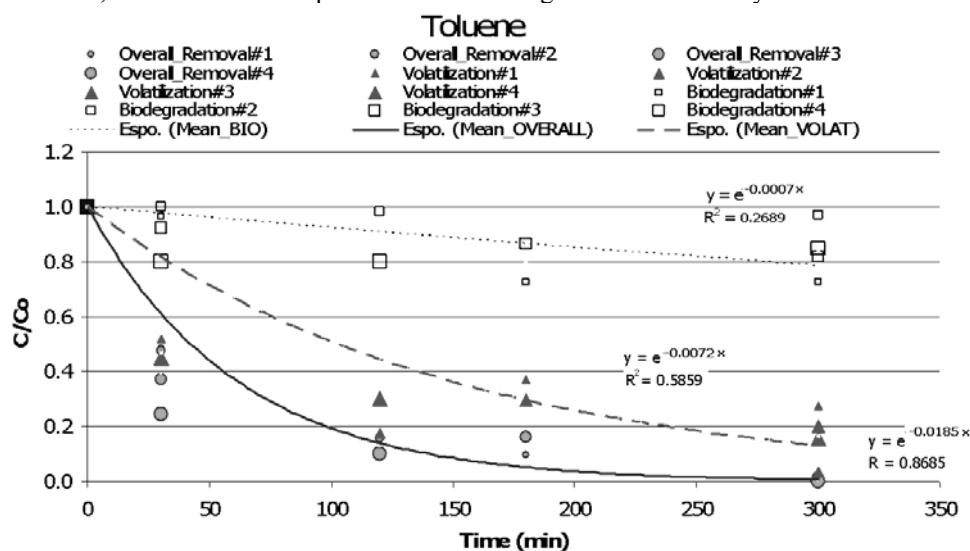


Figure 4. Toluene molecule: apportionment of the overall removal kinetic into volatilization and biodegradation.

3.3 Twenty-eight days biodegradation test

In Table 3 the results obtained in the test are reported (in case of benz(a)anthracene, the operational concentrations were lower than the detection limits of the analytical methods and therefore the test was not performed).

As shown in Table IV, a good correspondence between the calculated and the measured concentrations of CO_2 and DO was observed in the 28-days biodegradation test, allowing to confirm the biodegradation of the molecules and to rule out the formation of by-products.

Table IV. Dissolved Oxygen consumption and CO₂ production in the 28-days biodegradation test: theoretical stoichiometric values vs observed values

	D.O. concentration (mg L ⁻¹)		CO ₂ concentration (mg L ⁻¹)	
	Calculated	Measured	Calculated	Measured
Toluene (C ₀ = 0.96 mg L ⁻¹)	2.99	3.10	3.21	3.10
Benz(a)anthracene	-	-	-	-
Phenol (C ₀ = 1.33 mg L ⁻¹)	2.90	2.72	2.81	2.70
Benzene (C ₀ = 0.3 mg L ⁻¹)	1.40	1.00	1.00	1.1

4 CONCLUSIONS

In this paper a screening batch test to assess the fate of organic micropollutants in an activated sludge system was presented. The results obtained from the test applied to four compounds (toluene, benz(a)anthracene, phenol and benzene) showed that:

- the screening batch test is suitable for molecules with different chemical-physical properties. In particular, the good results obtained for toluene allow the application of this test for the VOCs;
- the test is reliable, since both the tests with only water and the tests with the activated sludge lead to repetitive results;
- moreover, the test allows to analyse the kinetics of the different removal mechanisms that occur in an activated sludge unit, also in terms of competition between the two processes.

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This study was already presented in a paper accepted for publication on the journal “Environmental Technology” (Taylor and Francis Group): Roberta Salvetti, Renato Vismara, Ilaria Dal Ben, Elena Gorla and Laura Romele “Proposal for a screening test to evaluate the fate of organic micropollutants in activated sludge” (in press)

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