





## Modelling PAHs removal in activated sludge process: effect of disintegration

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### ABSTRACT

The removal of polycyclic aromatic hydrocarbons (PAHs) in activated sludge was evaluated using two laboratory-scale bioreactors, coupled or not with a disintegration system (sonication). Mass balances performed on each system underlined that PAHs removal was significantly improved after sludge disintegration, especially for the higher molecular weight PAHs studied, which tended to adsorb to suspended matter. A model was developed in order to study the effect of sludge disintegration on the content of dissolved and colloidal matter (DCM), and to predict the potential impacts on PAHs availability and degradation. Results showed that this new model was efficient for capturing apparent degradation improvement trends and for discriminating between the involved mechanisms. This study showed that DCM content increased after sludge disintegration, and proved to be the main driver for improving PAHs apparent degradation.

**Key words** | biodegradation, bioreactor, micropollutants, polycyclic aromatic hydrocarbon, sonication, wastewater treatment

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### INTRODUCTION

The presence of micropollutants in aquatic environments is an issue of growing concern. In the last decades, intensive work has been focusing on the occurrence and removal of these pollutants over a large range of municipal wastewater treatment plants (Choubert *et al.* 2011; Martin Ruel *et al.* 2011, 2012; Grandclément *et al.* 2017; Liu *et al.* 2017; Qiao *et al.* 2017). Removal of PAH (and micropollutants in general) within activated sludge can be related to three main biotic or abiotic phenomena: (1) volatilization by stripping (governed by the physical properties of the micropollutant through Henry's law constant), (2) sorption to the sludge due to hydrophobic interactions between pollutants and suspended solids that lead to removal through sludge wastage and (3) biotic transformation, including both complete biodegradation or transformation into byproducts, lead to the effective elimination of organic compounds, but can also induce an apparent elimination via the formation of bound residues, rendering them inaccessible to chemical extraction, as has been demonstrated on soils (Kästner *et al.* 1999). Abiotic degradation processes such as photolysis or cleavage of chemical bonds are not expected to be significant in WWTP (Margot *et al.* 2015). Modelling

the fate of these hazardous substances in wastewater effluents has now become an important topic to study (Plósz *et al.* 2013). Modelling represents a useful tool for assessing the design and control strategies that aim to improve the removal of micropollutants. However, extending the existing activated sludge models (ASM) by including micropollutants is still seldom done. The current status and challenges regarding the modelling of micropollutants in biological wastewater treatment processes have been reviewed (Plósz *et al.* 2013; Pomiès *et al.* 2013). Pomiès *et al.* (2013) provided a detailed insight into removal mechanisms (volatilization, sorption, biodegradation), mathematical equations and parameter values, thereby revealing the need for more confrontation between simulation and experimental data in order to better calibrate and validate the models (Pomiès *et al.* 2013).

The biodegradation kinetics of polycyclic aromatic hydrocarbons (PAHs) have been studied, but due to a large variety of bacterial biomasses (either pure or mixed culture), different treatment systems, and a wide range of different PAHs concentrations and wastewater mixtures, the comparison between studies was rather difficult. For

instance, [Zielińska \*et al.\* \(2012\)](#) determined the removal rate of phenanthrene by a nitrifying biomass and by membrane bioreactor (MBR) and [Mozo \*et al.\* \(2011\)](#) determined the removal rates of acenaphthylene, acenaphthene, phenanthrene, anthracene and fluoranthene by MBR and the biodegradation rate of PAHs decreases with increasing molecular weight ([Mozo \*et al.\* 2011](#)). Indeed, high molecular weight PAHs are more slowly biodegraded ([Kanaly & Harayama 2010](#)), and this is partly explained by the fact that such molecules are likely to adsorb to suspended matter, which reduces its bioavailability.

Degradation of these hydrophobic compounds is driven by their interaction with other organic compounds, either soluble, colloidal, or particulate. The effect of adsorption on particulate matter reduces the bioavailability and hence the biodegradation rate. [Stringfellow & Alvarez-Cohen \(1999\)](#) evaluated the relationship between adsorption of PAHs to bacterial biomass and its biodegradation. [Barret \*et al.\* \(2010a\)](#) assessed the overall removal of 13 PAHs during anaerobic digestion and highlighted the need to consider adsorption on particulate matter, but also on soluble and colloidal organic matter, which can on the other hand increase the bioavailability. A three compartment model was suggested, and successfully applied in an anaerobic digestion model by [Barret \*et al.\* \(2010b\)](#), by considering that the PAHs fraction present in the liquid phase, possibly adsorbed to dissolved and colloidal matter (DCM), was bioavailable. Indeed, [Johnsen & Karlson \(2004\)](#) also showed that bioavailability of PAHs (fluorene, phenanthrene, fluoranthene and pyrene) was increased with the presence of dissolved organic matter excreted in the liquid phase, such as bacterial biosurfactants or extracellular polymeric substances.

Modelling PAHs biodegradation kinetics in aerobic activated sludge (AS) systems is relatively seldom done. [Guha \*et al.\* \(1999\)](#) estimated the Monod kinetic parameters and yield coefficients for naphthalene, phenanthrene and pyrene in aerobic batch liquid systems inoculated with a mixed bacterial culture and [Moscoso \*et al.\* \(2012\)](#) estimated the specific growth rate and the specific degradation rate for phenanthrene, pyrene, and benzo(a)pyrene by a consortium of bacteria. However, kinetics are generally described by a simplified first-order model ([Tang \*et al.\* 2005](#); [Manoli & Samara 2008](#)). The acceleration of the PAHs biodegradation kinetics due to the presence of DCM has already been reported in the literature ([Holman \*et al.\* 2002](#); [Smith \*et al.\* 2009](#); [Ke \*et al.\* 2018](#)). As a consequence, sludge disintegration or solubilization, from particle to colloidal forms, is expected to improve the bioavailability and biodegradation of PAHs. Moreover, [Mozo \*et al.\* \(2011\)](#) already showed that

high shear stress could release PAHs initially adsorbed to suspended solids and hence increase the concentration of PAHs in the liquid phase (free or adsorbed to DCM). This study showed that residual PAHs measured in the wasted sludge was reduced and hence confirmed the positive effect of sludge disintegration on the bioavailability of hydrophobic micropollutants in the MBR. In this perspective, modifications of the actual ASM were suggested for modelling sludge reduction processes either by Cannibal™ process ([Johnson \*et al.\* 2008](#)) or by thermal treatment ([Laurent \*et al.\* 2011](#)).

The main goal of this present study is to extend the existing ASM1 in order to define the degradation of 16 PAHs stated as hazardous in the EU legislation. In addition, the effect of sludge disintegration and DCM content were both included and validated by confronting the model with experimental data obtained in two activated sludge (AS) systems run in parallel: one simple AS and one AS coupled with a sludge disintegration module (sonication). Experiments were here designed in order to test the ability of the new model to capture the effect of sludge disintegration on the removal of PAHs.

## MATERIALS AND METHODS

### Experimental set-up and operational conditions

Two laboratory-scale activated sludge processes were operated in parallel, fed with the same synthetic wastewater, during 96 days: a conventional activated sludge system (AS, reactor 1) and an activated sludge system coupled to an ultrasound loop (US-AS, reactor 2). Cylindrical bioreactors (20 cm inner diameter, 11 L volume) were equipped with fine bubble diffuser, Rushton impellers (100 rpm) and water jacket (temperature was controlled at 20 °C). The settlers had a volume of 2.5 L. Reactors, contactors and settlers were made out of glass and the piping, as other elements, were made in PTFE. Peristaltic pumps were used for feeding and recirculation (100% recirculation). Temperature and dissolved oxygen (DO) were monitored (optical probe, Hamilton) as well as pH (WTW probe). pH was naturally stabilized at  $7.5 \pm 0.5$ . Air flow rate was imposed to maintain DO at  $3.5 \pm 0.5 \text{ mg}\cdot\text{L}^{-1}$ . On the second reactor (US-AS), an ultrasonic device (SONOPULS HD 2070, Bandelin Electronic) was combined with the activated sludge process.

The bioreactors were seeded with secondary sludge which originated from an activated sludge process receiving

petrochemical effluent (Petrol refinery), in which bacteria acclimatised to PAHs were already present. After 20 days of similar operation, the ultrasonication system (US) was used in the second reactor. In this system, a volume of the mixed liquor was regularly (three cycles of 21 minutes per day) pumped to a 300 mL glass side stream vessel, where the tip of a TT13 ultrasonic probe (operating frequency of 20 kHz and supplied power of 70 W) was immersed. The provided power density was  $0.23 \text{ W}\cdot\text{mL}^{-1}$ . The sonicated sludge returned directly to the bioreactor after sonication. The treatment frequency by ultrasounds (defined as the ratio between the amount of sludge treated per day over the amount of sludge in the system) was  $0.08 \text{ d}^{-1}$  and a sludge recycle ratio (volume of sludge sonicated per day over the volume of wastewater treated per day) of  $0.08 \text{ L}\cdot\text{L}^{-1}$  was applied, leading to 30% of suspended solids solubilisation.

The synthetic wastewater was made with: (1) a solution containing sodium acetate and ethanol stored at  $4^\circ\text{C}$  and prepared with tap water, (2) a solution containing carbonate, ammonium, salts, buffer solution and oligo-elements prepared with tap water and (3) the PAHs solution prepared in methanol. The PAHs concentrations were chosen in order to mimic a real industrial wastewater comparable to different literature references (Sponza & Oztekin 2010; Sponza & Gok 2011). The inlet flow rates of each solution were  $2.1 \text{ L}\cdot\text{d}^{-1}$ ,  $8.9 \text{ L}\cdot\text{d}^{-1}$  and  $0.00415 \text{ L}\cdot\text{d}^{-1}$  respectively (total effluent flow rate was  $11 \text{ L}\cdot\text{d}^{-1}$  corresponding to 24 hours' hydraulic retention time). PAHs represented 0.17% of the total inlet chemical oxygen demand (COD) ( $1,325 \text{ mg}\cdot\text{L}^{-1}$ ) and the organic loading rate was  $1.06 \text{ kg}_{\text{COD}}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ . The PAHs solution was stored and injected with a specific device (Dosimat) for accurate control of very low flow rate. The resulting concentrations in the reactors feed are summarized in Table 1.

## Analytical methods

Sludge samples were separated by centrifugation (8,200 g, 20 min,  $20^\circ\text{C}$ ) followed by filtration through a glass fibre membrane ( $1.2 \mu\text{m}$  pore size). Two fractions were hence defined: a particulate fraction (solids after centrifugation and the residual particulate matter in the filter) and a liquid fraction containing DCM. Total solids, volatile solids and COD in total sludge, particulate phase and liquid phase were determined using the standard method (Afnor 1994) following the NFT 90101 and NFT 90105 for total suspended solids/volatile suspended solids (TSS/VSS) and COD measures respectively. The particle size distribution of aggregates was analysed using a laser diffraction technique (Mastersizer, Malvern 2000, UK) with a particle size ranging from  $0.02 \mu\text{m}$  to  $2,000 \mu\text{m}$ .

Total PAHs concentrations and PAHs concentrations in aqueous phase were measured by gas chromatography-mass spectrometry (GC-MS) following the NF EN ISO 17993 (quantification limit  $\text{Q.L.} = 0.05 \mu\text{gPAH}\cdot\text{L}^{-1}$ ). The PAHs concentration in the solid phase was measured on 1 g of solids after freeze-drying and applying an automatic solvent extraction method with dichloromethane (Soxtec HT2 Tecator, Foss). Analysis of each extracted sample was performed with a GC-MS analyser (Gas chromatograph VARIAN 3,900) equipped with a mass spectrometer detector (VARIAN 2,100 SaturnT) allowing the electronic impact and operating under 'Full Scan' acquisition mode. Liquid samples were analysed by the automatic headspace technique for volatile compounds (naphthalene, acenaphthylene, acenaphthene) and solid phase micro-extraction (SPME) with  $7\text{-}\mu\text{m}$  polydimethylsiloxane (PDMS) SPME fibres for other PAHs. Calibration was performed with deuterated PAHs semi-volatile internal standard mix reaching a detection limit of  $0.1 \mu\text{g}\cdot\text{L}^{-1}$ .

**Table 1** | PAHs concentrations in the influent

Compound		Conc. ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Compound		Conc. ( $\mu\text{g}\cdot\text{L}^{-1}$ )
NAP	Naphthalene	389	B(a)Ant	Benzo(a)anthracene	0.84
ACY	Acenaphthylene	65.6	CHRY	Chrysene	0.84
ACE	Acenaphthene	99.1	B(b)Fluo	Benzo(b)fluoranthene	0.67
FLUOREN	Fluorene	72.4	B(k)Fluo	Benzo(k)fluoranthene	0.74
PHEN	Phenanthrene	22.9	B(a)Pyr	Benzo(a)pyrene	0.74
ANT	Anthracene	22.9	DiB(ah)Ant	Dibenzo(ah)anthracene	0.58
FLUORAN	Fluoranthene	22.1	B(ghi)Per	Benzo(ghi)perylene	0.66
PYR	Pyrene	20.6	I(123cd)Pyr	Indeno(123cd)pyrene	0.04

## Model description

All simulations and parameter identifications were performed using AQUASIM software (Reichert 1994). The standard ASM1 model (Henze et al. 2000) was extended, as shown in Figure 1, in order to consider the fate of PAHs and sludge disintegration (see Table SI-1 for the stoichiometry and Table SI-2 for the kinetics, available with the online version of this paper). Each compound (16 PAHs) concentration was added as new variable ( $T_{PAH}$ ). For each compound, the total concentration ( $T_{PAH}$ ) was divided into three fractions: the free dissolved PAH ( $S_{PAH}$ ), the PAH adsorbed to particulate matter ( $X_{PAH}$ ) and the PAHs adsorbed to DCM ( $C_{PAH}$ ). Considering PAHs adsorption as rapid mechanisms, partition was predicted with a set of specific equilibrium constants for each molecule ( $K_{PART}$  and  $K_{DCM}$ ) as proposed by Barret et al. (2010b). The different concentrations can be determined by the set of following equations:

$$S_{PAH} = \frac{T_{PAH}}{1 + K_{PART} \cdot MLSS + K_{DCM} \cdot DCM} \quad (1)$$

$$C_{PAH} = \frac{K_{DCM} \cdot DCM \cdot T_{PAH}}{1 + K_{PART} \cdot MLSS + K_{DCM} \cdot DCM} \quad (2)$$

$$X_{PAH} = \frac{K_{PART} \cdot MLSS \cdot T_{PAH}}{1 + K_{PART} \cdot MLSS + K_{DCM} \cdot DCM} \quad (3)$$

Considering the literature studying the disintegration processes, it was also suggested to include a colloidal

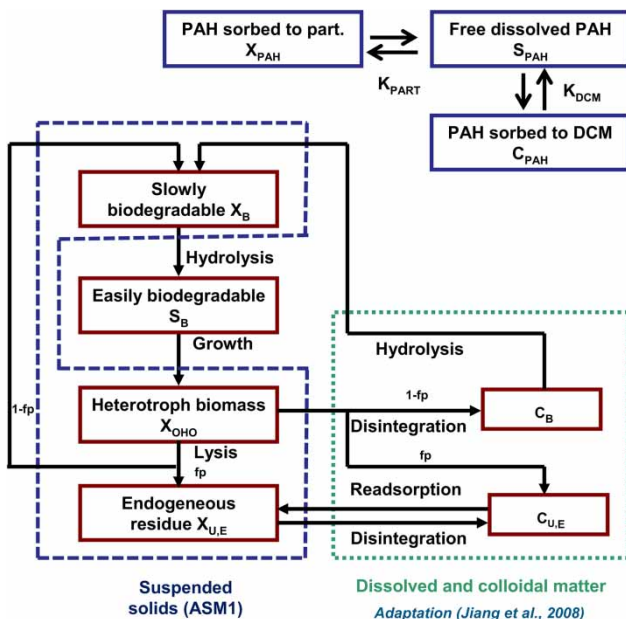


Figure 1 | Diagram of ASM1-based models for the modelling of PAHs biodegradation.

fraction for both biodegradable and unbiodegradable organic matter (Guellil et al. 2001; Laspidou & Rittmann 2002; Jiang et al. 2008). Hence biodegradable colloids ( $C_B$ ) and unbiodegradable colloids ( $C_{U,E}$ ) are considered. The model considers that ( $C_B$ ) are hydrolysed and transformed into particulate slowly biodegradable compounds ( $X_B$ ) and then into soluble readily biodegradable substrate ( $S_B$ ). The hydrolysis rate is modelled by a first order kinetic (Laspidou & Rittmann 2002; Jiang et al. 2008), with a first order constant  $q_{Hyd}$ . The ( $C_{U,E}$ ) are rapidly re-adsorbed into endogenous residue particles ( $X_{U,E}$ ) following a first order kinetic with a rate constant  $q_{ADS}$  as proposed by Guellil et al. (2001).

New kinetic processes described the fate of PAHs, including biodegradation (processes 9–24), volatilization (25–41) and sludge disintegration by sonication (42–47). Processes (1) to (41) are referred to in the following text as model ASM1-PAH (for conventional AS, i.e. reactor 1) while model ASM1-PAH-DCM also includes processes (42) to (47) (for US-AS, i.e. reactor 2).

## PAHs biodegradation

A first order kinetic expression was used for PAHs biodegradation. It was assumed that ordinary heterotrophic organisms can grow with both the easily biodegradable substrate and the specific substrate. PAHs concentration in the liquid phase, constituted by the free PAHs ( $S_{PAH}$ ) and the PAHs adsorbed to DCM ( $C_{PAH}$ ), was considered as the bioavailable fraction able to be metabolised by microorganisms (Delgadillo-Mirquez et al. 2011). Therefore, the fraction of PAHs adsorbed to particulate matter was not considered bioavailable unless this fraction was transferred into the liquid phase by applying sludge disintegration.

## PAHs gas/liquid transfer

Assuming that the equilibrium between the gas and liquid phases was rapidly reached for these hydrocarbons, the volatilisation rate was directly related to the Henry's constant of each compound ( $H_{PAH}$ ), known from literature, the air flow rate and the soluble concentration of PAHs ( $S_{PAH}$ ) as stated in Mozo et al. (2012):

$$q_{PAH,Vol} = \frac{Q_G}{VV_m} \frac{H_{PAH}}{P_{atm}} S_{PAH} \quad (4)$$

With  $Q_G$  the air flux ( $m^3 \cdot d^{-1}$ ),  $H_{PAH}$  the Henry's law constant ( $atm \cdot m^{-3} \cdot mol^{-1}$ ),  $V$  the reactor volume ( $m^3$ ) and



$V_m$  the molar volume,  $0.0224 \text{ m}^3 \cdot \text{mol}^{-1}$  for ideal gases at a temperature of  $20^\circ \text{C}$  and at the pressure,  $P_{\text{atm}}$ , of 1 atm.

## Disintegration

Disintegration of both the endogenous residue ( $X_{U,E}$ ) and active biomass ( $X_{OHO}$ ) with release of colloids and soluble matter ( $C_{U,E}$ ) and biodegradable colloids ( $C_B$ ) was considered. The disintegration was assumed to follow a first order kinetic (Jones *et al.* 2008; Ramdani *et al.* 2010) with the same disintegration specific rate ( $q_{US}$ ) for both  $X_{U,E}$  and  $X_{OHO}$ .

## Calibration and validation procedure

The overall approach was undertaken by performing two distinct steps: (1) calibrate the model with the data obtained from the AS reactor (reference) and (2) validate the model on data obtained from the US-AS reactor (sludge disintegration). Therefore, the exact same set of biological parameters values were used for both systems and only the physical description was different; that is, related to disintegration.

Most of the parameters (originated from ASM1) were provided from the literature (see Table 2). Regarding kinetic and stoichiometric parameters, only the heterotroph growth yield,  $Y_{OHO}$ , and the PAHs degradation rates ( $q_{\text{PAH,Bio}}$ ) were calibrated with the mass balance performed on AS process (reactor 1).  $Y_{OHO}$  was identified based on experimental VSS and excess sludge production in AS (reactor 1) was observed. Composite parameters and conversion factors for COD to VSS can be found in Table SI-3 (available online). Regarding the physical phenomena, the values of the partitioning coefficients  $K_{\text{PART}}$  and  $K_{\text{DCM}}$  for the 16 PAHs were determined in a previous study with dedicated experiments (Mozo *et al.* 2018); logarithmic values of these partitioning experiments are summarized in Table SI-4 (available online). The same values were used for both reactors 1 (AS) and 2 (US-AS). For the second reactor (US-AS), the specific disintegration rate ( $q_{US}$ ) was calculated based on the degree of solubilisation performed in the ultrasound cell (30%) and suspended solids solubilised per day in reactor 2. The values of  $q_{\text{hyd}}$  and  $q_{\text{ads}}$  were provided from the literature (Table 2). For the ASM1-PAH model, retention of suspended solids in the settler  $f_{\text{ret,X}}$  was estimated to predict  $\text{TSS}_{\text{out}}$ , VSS, sludge retention time (SRT) and  $Y_{\text{obs}}$ . For the

**Table 2** | Parameters used in the model

Symbol	Definition	Value	Units	Source
$b_{ANO}$	Decay rate for $X_{ANO}$	0.15	$\text{d}^{-1}$	Henze <i>et al.</i> (2000)
$b_{OHO}$	Decay rate for $X_{OHO}$	0.62	$\text{d}^{-1}$	Henze <i>et al.</i> (2000)
$f_{US,X_{OHO}}$	Fraction of $X_{OHO}$ transformed into $C_{UE}$ by sonication	0.08	$\text{g}_{CUE} \cdot \text{g}_{X_{OHO}}^{-1}$	Assumed equal to $f_{X_U,Bio,lys}$
$f_{X_U,Bio,lys}$	Fraction of $X_U$ generated in biomass decay	0.08	$\text{g}_{X_U} \cdot \text{g}_{X_{OHO}}^{-1}$	Henze <i>et al.</i> (2000)
$i_{N,X_{Bio}}$	N content of $X_{Bio}$	0.086	$\text{g}_N \cdot \text{g}_{X_{Bio}}^{-1}$	Henze <i>et al.</i> (2000)
$i_{N,X_{U,E}}$	N content of $X_{U,E}$	0.06	$\text{g}_N \cdot \text{g}_{X_{U,E}}^{-1}$	Sperandio <i>et al.</i> (2012)
$i_{TSS,X_U}$	Conversion factor $X_U$ in TSS	0.1	$\text{g}_{ISS} \cdot \text{g}_{VSS}^{-1}$	Sperandio <i>et al.</i> (2012)
$i_{TSS,X_B}$	Conversion factor $X_B$ in TSS	0.1	$\text{g}_{ISS} \cdot \text{g}_{VSS}^{-1}$	Henze <i>et al.</i> (2000)
$K_{La}$	Oxygen transfer coefficient	194	$\text{d}^{-1}$	Measured
$K_{O_2,OHO}$	Oxygen half-saturation coefficient for $X_{OHO}$	0.2	$\text{g}_{O_2} \cdot \text{m}^{-3}$	Henze <i>et al.</i> (2000)
$K_{SB,OHO}$	Half-saturation coefficient for $X_{OHO}$	20	$\text{g}_{O_2} \cdot \text{m}^{-3}$	Henze <i>et al.</i> (2000)
$K_{XB,hyd}$	Half-saturation coefficient for hydrolysis of $X_B$	0.03	$\text{g}_{O_2} \cdot \text{m}^{-3}$	Henze <i>et al.</i> (2000)
$\mu_{OHO \text{ max}}$	Maximum specific growth rate for $X_{OHO}$	6	$\text{d}^{-1}$	Henze <i>et al.</i> (2000)
$q_{ADS}$	Maximum specific adsorption rate of $C_{UE}$ on $X_{UE}$	331	$\text{d}^{-1}$	Guellil <i>et al.</i> (2007)
$q_{Hyd}$	Maximum specific hydrolysis rate of $C_B$ on $X_B$	$7.41 \cdot 10^{-7}$	$\text{d}^{-1}$	Jiang <i>et al.</i> (2008)
$q_{PAH,Bio}$	Rate constant for PAHs uptake rate	Table 4	$\text{m}^3 \cdot \text{g}_{O_2}^{-1} \cdot \text{d}^{-1}$	Estimated
$q_{PAH,Vol}$	Rate constant for PAHs stripping	Equation (4)	$\text{d}^{-1}$	Calculated
$q_{US}$	Disintegration specific rate	0.0243	$\text{d}^{-1}$	Calculated
$q_{X_B-S_B,hyd}$	Maximum specific hydrolysis rate	3	$\text{d}^{-1}$	Henze <i>et al.</i> (2000)
$Y_{OHO}$	Growth yield coefficient for $X_{OHO}$	0.525	$\text{g}_{COD-X_{OHO}} \cdot \text{g}_{COD}^{-1}$	Estimated

ASM1-PAH-DCM model, the retention of suspended solids and colloids in the settler,  $f_{\text{ret},X}$  and  $f_{\text{ret},C}$  respectively, were estimated simultaneously to predict the same parameters but also the effluent partitioning ( $\text{COD}_{\text{t,out}}$ ,  $\text{COD}_{\text{s,out}}$ ) and the filtered COD in the mixed liquor ( $\text{COD}_{\text{s,reactor}}$ ).

## RESULTS

### Modelling global parameters and performances

Evolution of total and filtered outlet COD and COD removal (shown in Figure SI-1, available with the online version of this paper) underlines that similar behavior was observed in both reactors before applying sonication in reactor US-AS (day 21), confirming a satisfying reproducibility under the same operating conditions. In the stabilized period, results showed that residual COD (total and soluble) in the effluent was higher in the conventional activated sludge system compared to the system coupled to sonication. Total outlet COD concentration was  $157 \pm 33$  and  $97 \pm 25 \text{ mgO}_2 \cdot \text{L}^{-1}$ ; meanwhile, filtered COD was  $51 \pm 10$  and  $34 \pm 12 \text{ mgO}_2 \cdot \text{L}^{-1}$  in AS and US-AS respectively. COD removal efficiency was good in both systems but significantly higher in US-AS (84.8%) compared to AS (75.5%). As shown in Table 3, experimental COD removal and mixed liquor volatile suspended solids (MLVSS) content values obtained in both bioreactors were correctly predicted by the model. Results revealed that by combining sonication with the AS system, suspended particulate matter disintegrated into colloidal and soluble matter. Simultaneous visual observations reported that the settleability of the sludge also improved (results not shown), resulting in lower TSS in the outlet of the US-AS process ( $89 \pm 20 \text{ g} \cdot \text{m}^{-3}$ ) compared to the AS system ( $107 \pm 20 \text{ g} \cdot \text{m}^{-3}$ ). This settleability improvement has already been reported in the literature: Gonze et al. (2003) underlined that by disrupting the flocs and releasing them into water, ultrasound

reduces the size of particles but also increases their cohesion and density. This increase in density causes the increase of settling velocity even if the volume of particles is reduced. Wunsch et al. (2002) also showed that ultrasound, by creating high local shear stresses capable of breaking the filamentous structure of the sludge, allows the tackling of bulking problems and thus improves solids retention. Another hypothesis is that ultrasound, by the release of polymeric substances, induced the aggregation of small particles. Indeed, the particle number size distribution was centered on  $2.2 \mu\text{m}$  in the AS reactor against  $3.6 \mu\text{m}$  in the US-AS reactor, while the two effluents had a similar size distribution (see Figure SI-2, available online) indicating that intermediate size particles were retained in the US-AS system. As a consequence, the suspended solids retention was better in the US-AS reactor ( $f_{\text{ret},X} = 0.985$  in US-AS) compared to the simple AS reactor ( $f_{\text{ret},X} = 0.969$  for AS) and this contributed to a significant increase of both the SRT and MLVSS content in the US-AS reactor. For both these reasons (SRT increase and suspended solids disintegration) the observed sludge production yield was slightly lower in the US-AS reactor compared to the AS reactor alone. This response in production yield was captured by the model, although the exact same intrinsic yield ( $Y_{\text{OHO}}$ ) was used for modelling both systems. Indeed,  $Y_{\text{OHO}}$  was calibrated to fit VSS, TSS, COD and sludge production. The obtained value ( $0.525 \text{ g}_{\text{COD}} \cdot \text{g}_{\text{COD}}^{-1}$ ) was slightly lower than the common value used for ASM1 modelling domestic wastewater ( $0.67 \text{ g}_{\text{XOHO}} \cdot \text{g}_{\text{SB-COD}}^{-1}$ ). This is rational regarding the fact that synthetic carbon sources were used in this study and the obtained sludge yield is comparable to the thermodynamic growth yield calculated for acetate, ethanol or methanol (Tchobanoglous et al. 2003).

### Estimation of PAHs biodegradation rates

Mass balances were calculated with average values over the last 40 days of the running experiment, including PAHs concentrations measured in both the mixed liquor and effluent

**Table 3** | Comparison of overall experimental and modelled performances for both activated sludge processes (retention factor  $f_{\text{ret},X} = 0.969$  for AS;  $f_{\text{ret},X} = 0.9853$  and  $f_{\text{ret},C} = 0.86$  for US-AS)

Parameter	Unit	AS process		US-AS process	
		Exp.	Model	Exp.	Model
COD removal (based on soluble)	%	92.1	95.2	94.7	99.7
COD removal (based on total)	%	75.5	82.4	84.8	88.0
MLVSS	$\text{g} \cdot \text{m}^{-3}$	$1,485 \pm 150$	1,533	$2,280 \pm 440$	2,352
Sludge production yield	$\text{g}_{\text{VSS}} \cdot \text{g}_{\text{COD}}^{-1}$	0.123	0.119	0.119	0.086
SRT	D	$12.6 \pm 1.1$	12.8	$24.1 \pm 4.5$	25.7

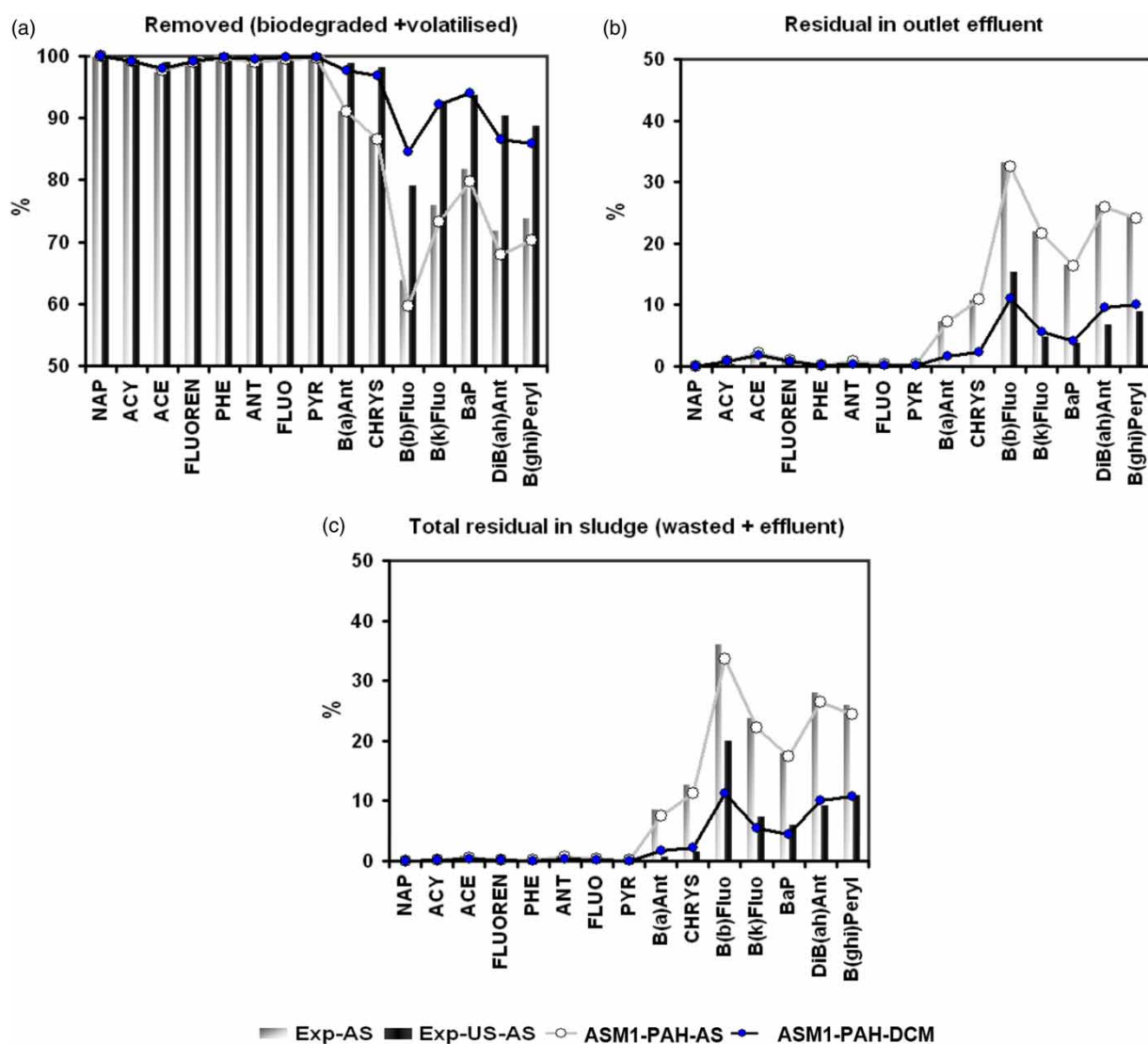
from AS and US-AS systems (Tables SI-5 and SI-6, available online). The mass balance was not performed for indeno(1,2,3-c,d)pyrene because the analytical error in concentration assessment was of comparable order to the inlet concentration. Regarding the mixed liquor, the total amount of low molecular weight PAHs (between 128.17 and 202.25 g·mol<sup>-1</sup>) was six-fold higher in the sludge obtained in the AS reactor compared to the US-AS reactor, whilst the total amount of higher molecular weight PAHs (between 228.29 and 278.35 g·mol<sup>-1</sup>) was two-fold higher in the US-AS reactor compared to the AS reactor. Total concentrations of low molecular weight as well as higher molecular weight PAHs in the effluent were more than three times lower in the US-AS reactor compared to the AS reactor and this was also true when considering the total amount of the 15 US-EPA PAHs with concentrations of 4.8 and 1.7 µg<sub>PAH</sub>·L<sup>-1</sup> in the AS and US-AS reactors respectively. Filtered effluent samples presented relatively low PAHs concentrations in both reactors; in most cases, values were below the quantification limit (0.05 µg<sub>PAH</sub>·L<sup>-1</sup>) especially for the higher molecular weight PAHs. At last, results show that, for all the PAHs compounds whose concentration levels were quantifiable, concentrations measured in the total and filtered effluent were systematically lower in the reactor combined with sonication compared to the AS reactor alone. The

decrease of concentration in US-AS compared to AS systems varied between 54% and 93%, see Tables SI-5 and SI-6.

Table 4 shows the specific PAHs removal rates ( $q_{\text{PAH,bio}}$ ) estimated for the 15 PAHs and the volumetric removal rates predicted and measured in both reactors. The range of specific PAHs removal rates were estimated based on results obtained in the AS reactor by using a non-linear least square method implemented in AQUASIM for fitting simulated values and experimental data and validate with the comparison to the US-AS process. The simulation was confronted to the content of PAHs adsorbed to wasted sludge, the flux of PAHs in the total effluent and the flux of PAHs associated to the particulate as well as the liquid fractions of the effluent. As expected, removal rates were higher for low molecular weight compounds compared to more complex and higher molecular weight PAHs. The volumetric removal rate was systematically higher in the US-AS reactor compared to the AS reactor alone, in particular for high molecular weight compounds, with up to 28% improvement for B(b)Fluo. This improvement was well reproduced by the model even though the same specific kinetic rates were used, while including the disintegration processes and adapting the solid retention factors. The volumetric removal rate, including the specific rates, the volumetric load but also the active biomass content and the availability of PAH,

**Table 4** | Estimated (on reactor AS) biodegradation specific rate  $q_{\text{PAH,bio}}$ , for PAHs, and volumetric removal rate predicted and experimental in AS and in US-AS

Molecule	Model specific rate $q_{\text{PAH, BIO}}$ ( $\text{m}^3 \cdot \text{g}_{\text{CO}}^{-1} \cdot \text{day}^{-1}$ )	AS (reactor 1) volumetric removal rate $\text{mg} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$		AS-US (reactor 2) volumetric removal rate $\text{mg} \cdot \text{m}^{-3} \cdot \text{d}^{-1}$	
		Experimental	Model	Experimental	Model
NAP	6.65	382.54 ± 0.05	382	382.53 ± 0.12	382
ACY	0.0926	63.86 ± 1.07	63.83	64.15 ± 0.77	63.92
ACE	0.0367	95.03 ± 3.23	95.21	96.46 ± 1.82	95.54
FLUOREN	0.0854	70.48 ± 1.97	70.36	71.04 ± 0.74	70.50
PHEN	0.551	22.43 ± 0.02	22.43	22.43 ± 0.01	22.45
ANT	0.235	22.30 ± 0.28	22.30	22.43 ± 0.06	22.40
FLUORAN	0.443	21.64 ± 0.12	21.61	21.65 ± 0.02	21.67
PYR	0.797	20.17 ± 0.04	20.17	20.17 ± 0.02	20.21
B(a)Ant	0.0450	0.764 ± 0.046	0.764	0.774 ± 0.002	0.815
CHRYC	0.0303	0.734 ± 0.026	0.735	0.774 ± 0.029	0.805
B(b)Fluo	0.0067	0.438 ± 0.246	0.442	0.556 ± 0.103	0.588
B(k)Fluo	0.0120	0.564 ± 0.141	0.568	0.688 ± 0.069	0.687
BaPyr	0.0208	0.605 ± 0.125	0.607	0.698 ± 0.055	0.697
DiB(ah)Ant	0.0093	0.418 ± 0.172	0.421	0.528 ± 0.077	0.510
B(ghi)Peryl	0.0099	0.488 ± 0.300	0.490	0.589 ± 0.123	0.578



**Figure 2** | PAHs mass balance. Experimental and simulated contribution of removal + volatilisation (a), final residue in effluent (b), and adsorbed to wasted sludge (c) for both AS and US-AS reactors.

the satisfying prediction given by the model underlines that solubilisation of PAHs and the increase of biomass retention time (SRT) are both liable to explain this improvement.

### Modelling mass balance for PAHs

Figure 2 shows the mass balance calculated for each PAHs compound and in each system, obtained experimentally and simulated. Volatilization was not significant for most of the PAHs except for acenaphthene with 10% and 5% in AS and US-AS respectively (results not shown). Results show that biodegradation was the most important contributing mechanism for the removal of all molecules, which indicates that the biomass was well acclimatized. PAHs

which adsorbed to particles in the wasted sludge and in the effluent contributed for up to 30% of the most hydrophobic molecules (from benzo(a)anthracene to benzo(ghi)perylene). The new model allowed prediction of the improvement of PAHs biodegradation observed previously in the US-AS reactor and this for all molecules except for benzo(b)fluoranthene which was only slightly overestimated. Moreover, besides for the latter compound, the standard deviation between experimental and modelled removal percentages was below 4.6%. The improvement of PAHs biodegradation in the US-AS reactor was especially visible for the most hydrophobic compounds, for which initial biodegradation (as found in the AS reactor) was limited by the adsorption on particulate matter. Moreover, the



residual PAHs measured in effluent and wasted sludge was lower in US-AS compared to the AS reactor, and this was also correctly captured by the model.

## DISCUSSION

Experimental results obtained in this study show that sludge disintegration clearly impacted the removal of PAHs in AS systems, and that the newly developed model was able to correctly predict these results. Previous experiments showed that sonication (operated under the same conditions in terms of specific supplied energy) did not have any direct impact on PAHs besides their transfer from the particulate to the liquid phase (Mozo *et al.* 2018). Therefore, the improvement of PAHs removal rates observed in the US-AS reactor highlights that solid disintegration had a positive effect on the apparent biodegradation of PAHs. At least two main mechanisms can be assumed: one being the increase of SRT due to a better retention of solids (increased settleability) and the other being an increase of PAHs bioavailability due to the adsorption and transport of PAHs with the soluble and colloidal matter.

Of course the question of the fraction actually accessible to biodegradation can be raised. If it is generally admitted that a sorbed micropollutant is not available for biotransformation by microorganism (Rittmann & McCarty 2001; Artola-Garicano *et al.* 2003; Barret *et al.* 2010c; Delgadillo-Mirquez *et al.* 2011; Plósz *et al.* 2013) no consensus emerges from literature and studies assuming that the fraction sorbed to particles is degraded can be found (Cowan *et al.*

1993; Lee *et al.* 1998). This is largely due to the difficulty of designing specific experiments that could dissociate the mechanisms. In any case degradation of the sorbed-to-particles compounds is indirectly taken into account when we consider, as is the case in this study, the hydrolysis of entrapped organics that simultaneously induces a transfer of PAHs to the aqueous phase via equilibrium equations. As a result, modeling was seen here as a tool for discriminating between the two mechanisms considered.

In order to evaluate the effect of solids retention on the improvement of PAHs biodegradation observed in the US-AS reactor, a simulation was performed using the ASM1-PAH model (meaning without processes 42–47) while maintaining SRT and  $f_{ret,X}$  at the US-AS values. Results from this simulation are referred as ‘model ASM1-PAH – US-AS (case 2)’ in Figure 3. ‘ASM1-PAH – US-AS (case 2)’ model predicted only a slight increase of the removed percentage of PAHs and a limited diminution of the PAHs concentration in the outlet compared to ASM1-PAH-AS. This increase is explained by the increase in the concentration of the mixed liquor and increase of the SRT, due to a better retention of particles (increase of  $f_{ret,X}$  and resulting decrease of  $TSS_{out}$ ) in the US-AS reactor. However, when considering these effects alone, the simulation clearly underestimated the difference of PAHs removal values observed between the two systems.

Indeed, the predicted fractions of removed PAHs and PAHs concentrations in the outlet are far from the experimental values. This result shows that the change in solid retention alone cannot explain the improvement of PAHs biodegradation in the US-AS bioreactor and it is therefore

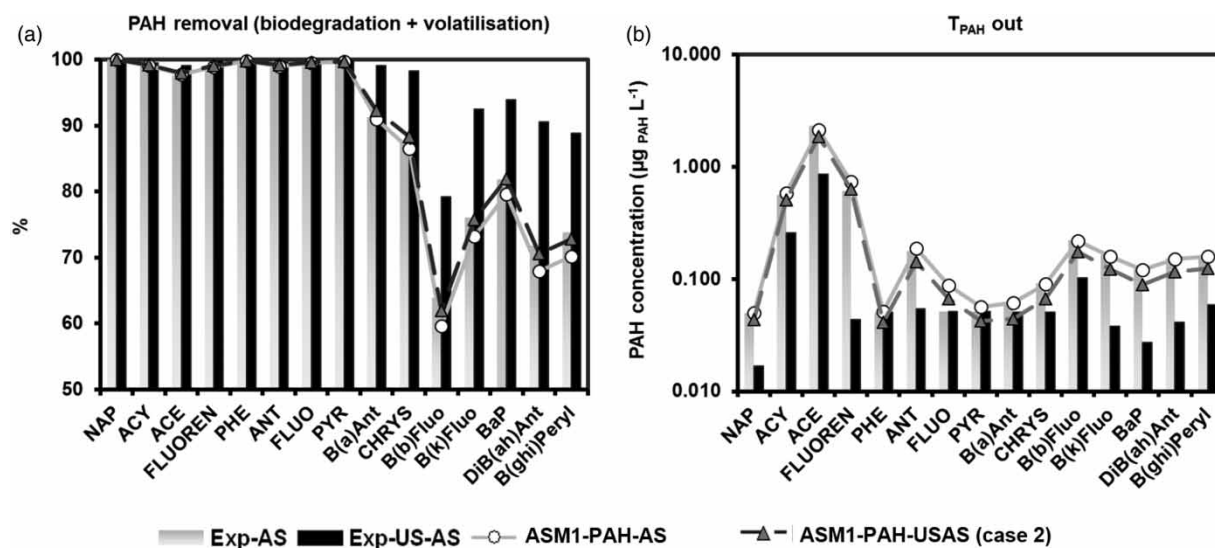


Figure 3 | Modelling only the effect of the retention on (a) PAHs removal (biodegradation + volatilisation) and (b) PAHs concentration in the effluent.

necessary to take into account sludge disintegration processes in order to efficiently predict observations.

The new model developed within this study captured the effect of sludge disintegration on the removal of PAHs by combining two concepts: the concept of PAHs adsorption on DCM and its bioavailability (a concept developed by Barret *et al.* (2010c) for anaerobic systems and validated by Mozo *et al.* (2018) for activated sludge), and the fact that sludge disintegration releases endogenous compounds and DCM (developed by Jiang *et al.* (2008)). The fact that these effects were successfully captured by the model supports the idea that DCM plays a major role in improving the bioavailability of PAHs. In the literature, two mechanisms have been reported for explaining the degradation of micropollutants adsorbed to DCM. The first mechanism is based on the assumption that low molecular weight DCM might cross microbial membranes and form a micropollutant-DCM complex. Indeed, molecules up to a few kDa have already been shown to cross bacterial membranes (Nikaido 2003). The second assumed mechanism considers that particles might transport adsorbed micropollutants in the vicinity of the cell surfaces (Smith *et al.* 2009), which is a preliminary step before diffusion through the cell membrane.

Concerning industrial perspectives, a techno-economic study could favour the implementation of this hybrid process. As an example, based on modelling, we estimate that an improvement in benzo(b)fluoranthene removal from 47% to 66% could be obtained with sonication applied in the sludge recycling loop, implying 3.2 kWh per m<sup>3</sup> of treated wastewater, whereas doubling the reactor volume of activated sludge would lead to an increase from 47% to only 51%. Thus a complete economic evaluation will have to compare the energy costs associated with the implementation of ultrasound and the infrastructure costs that would be required to achieve similar performances with a conventional process.

Finally, DCM content is generally relatively low in activated sludge systems. But new treatment systems with growing quantities of DCM are being developed (Wang & Chen 2018). Indeed, the short retention time applied in HRAS (High Rate Activated Sludge) is likely to significantly modify the partitioning of PAHs compared to conventional activated sludge, and hence impact the resulting biodegradation of PAHs. Furthermore, wastewater treatment plants are increasingly considered as facilities to recover water resources (van der Hoek *et al.* 2016; Solon *et al.* 2019) and in this perspective the combination of several processes would be needed. In such facilities, the disintegration of the solid phase is involved, whether experienced during

recirculation through a MBR or applied as an additional process to improve anaerobic digestion, for example. Recirculation between processes units may hence contribute to the transport of DCM-adsorbed-PAHs. The developed model will therefore be useful for such systems as it will be able to both determine the effect of disintegration on solubilization and predict the resulting fate of PAHs within the system.

## CONCLUSION

- Sludge disintegration (in our study, the use of sonication) can optimise conventional activated sludge systems by improving performances and reliability for the removal of PAHs in wastewater treatment plants.
- A new model was developed in order to include the effect of sludge disintegration on DCM content and subsequent PAHs bioavailability.
- The model predicted a better degradation of a large range of PAHs in an AS system coupled with sonication, a slight reduction of sludge production and a better effluent quality.
- Combining specifically designed experiments and modelling proved to be efficient to study the role of sludge disintegration on PAHs removal: increase of apparent biodegradation was shown to be better explained by the improvement of PAHs availability compared to the increase of solid retention.

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