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Modelling PAH partitioning during sludge disintegration: The key role of dissolved and colloidal matter

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HIGHLIGHTS

- PAH partitioning in activated sludge is related to particulate, colloidal and soluble matters.
- A three compartment model was calibrated for 16 PAHs with secondary sludge.
- Model calibration was performed with additional dissolved and colloidal matter.
- Both the partitioning coefficients K_{PART} and K_{DCM} were shown to be correlated to the $\log(K_{OW})$.
- Effect of sludge disintegration by sonication on PAH partitioning is well predicted.

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ABSTRACT

The partitioning between solids and the aqueous phase largely controls the fate of PAH compounds in biological treatment. The prediction of PAH sorption behaviour into activated sludge was investigated here. The suitability of a three-compartment model to describe partitioning in such a complex matrix was first evaluated by adding increasing quantities of dissolved and colloidal matter (DCM) (from 0 to 34.9% of the total matter). In a range of DCM concentrations varying from 0 to 1.4 g L^{-1}, the PAH aqueous fraction, including both freely dissolved and sorbed to DCM molecules, increased from 9.9% to 33% for naphthalene (the most soluble PAH) and from 0.29% to 13.3% for indeno(1,2,3,c,d)pyrene (the least soluble PAH tested). The sorption of PAHs on dissolved and colloidal matter (DCM) was assessed by determining two partitioning constants (K_{PART} and K_{DCM}) for the 16 PAHs listed by the US EPA. New experiments were carried out for model validation and show that the model properly predicts the PAH partitioning following sludge disintegration by sonication.

1. Introduction

The fate of a hydrophobic hazardous substance in wastewater treatment systems and soils is controlled by its partition between a mobile aqueous phase and a solid phase. The poly-aromatic hydrocarbons (PAH), known to be carcinogenic compounds, are typically partitioned between water and solid matter depending on their chemical hydrophobicity. The sorption of such compounds has been widely investigated in soils and sediments (Semple et al., 2007). PAH sorption to microbial sludge has also been studied on primary sludge (Artola-Garicano et al., 2003; Barret et al., 2010a, 2011), secondary sludge (Artola-Garicano et al., 2003; Barret et al., 2010a, 2010b; Dionisi et al., 2006; Holbrook et al., 2004) and sludge after anaerobic digestion (Barret et al., 2010a, 2010c). Nowadays, it is even more important to know the fate of such hazardous compounds as wastewater treatment plants are becoming considered as water resource recovery facilities (WRRF), encouraging the reuse of water and the recovery of nutrients and energy. Moreover, the current trend is to design wastewater treatment with minimum energy needs and maximum energy production by combining a high rate activated sludge system (HRAS), which is operated under high organic load, short hydraulic and sludge retention time in which organic matter is captured by the way of adsorption and storage, with anaerobic digestion and systems for boosting the sludge digestion through disintegration

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techniques. This could have considerable impact on the partitioning and accessibility of hydrophobic compounds, and finally, on their biodegradation or persistence.

The partitioning of organic micropollutants has been typically described by linear isotherms, considering the sludge as a two-compartment matrix (Byrns, 2001; Dionisi et al., 2006; Manoli and Samara, 2008; Urase and Kikuta, 2005). Hence the equilibrium sorption to particles can be described by a linear equation (Freundlich isotherms with a Freundlich coefficient close to 1). PAHs are slightly soluble in aqueous phase (PAH solubility at 25 °C varies between $1.94 \cdot 10^{-5}$ and 31 mg L^{-1} (EPA, 1996)) so they are present in water at low concentrations. The sorption of PAHs to dissolved organic matter has been widely studied and has highlighted the influence of the origin and the biochemical (i.e. aromaticity, hydrophobicity, composition) and physical (size and available specific area) properties of dissolved and colloidal matter (DCM) on the interaction between micropollutants and DCM (Akkanen et al., 2004, 2012; Haftka et al., 2010; Perminova et al., 1999). However, the sorption potential of the DCM has not often been considered in model intended to describe hydrophobic micropollutant sorption, especially in secondary sludge from an activated sludge process. A three-compartment model has been established, taking sorption to both compartments, particulate matter and DCM, into account (Amiri et al., 2005; Moon et al., 2003). It concerns sediments and soils and has been successfully applied to predict PAH sorption to sludge in the anaerobic treatment field (Barret et al., 2010d).

Regarding the three-compartment model, the presence of dissolved and colloidal matter can enhance the mobility of PAHs, traditionally immobilized in suspended solids. In addition, considering the possible relation between sorption on solids and inaccessibility for biodegradation, it is expected that the presence of dissolved and colloidal matter can even influence PAH biodegradation or persistence. For instance, more colloidal and soluble matter is maintained and released in the effluent in the HRAS process than in the traditional activated sludge process (Jimenez et al., 2015). As far as we know, no information is available on the impact of this fractionation on PAH retention and degradation. Regarding innovative systems for boosting sludge degradation and methanation, biological systems (either aerobic or anaerobic) have been coupled to a “disintegration” process for the hydrolysis of organic matter and/or for microbial biomass stress. Salsabil et al. (2010) reported that this reduced excess sludge production and possibly increased biogas production. They showed that the intrinsic sludge reduction (total suspended solid) was higher with ultrasound (47%) than with thermal (40–90 °C) (5–16%), ozone (0.1 $gO_3gTS_0^{-1}$) (15%) and autoclave (120 °C) (4.2%) processes. Ultrasounds led to the greatest improvement in total suspended solids removal after both aerobic (30%) and anaerobic digestion (20%). Finally, it would be of great interest to better quantify PAH partitioning when such modifications in organic matter fractionation occur, in order to be able to predict the fate of PAH in a complete treatment plant. When diverse processes are combined in WRRF, the PAH adsorbed on soluble and colloidal matters, and possibly released by sludge disintegration, can be transported from one process to another through liquid flows and recirculations. Other techniques for PAH solubilization have also been reported with direct consequences on removal efficiencies, such as addition of phenol (Kong et al., 2018) or ozonation (Carrère et al., 2006)

In this work, the partition of PAHs (16 different molecules) in secondary sludge and the suitability of a three-compartment model to describe the effect of DCM and sludge disintegration were investigated. DCM generated by sonication ex situ was mixed with sludge at different ratios [PART]/[DCM] in order to evaluate the sorption capacity of the DCM compartment and to determine equilibrium constants of micropollutant sorption to particles and DCM, respectively K_{PART} and K_{DCM}, for the 16 US-EPA PAHs. This model and the values of the constants were then validated by predicting the effect of sludge disintegration by sonication on PAH partitioning.

2. Materials and methods

2.1. Sludge disintegration

In this study, sonication was used for two different purposes: (i) to generate DCM for PAH mobility evaluations when increasing quantities of DCM were added to a sludge containing PAHs (cf. §2.2) and (ii) to evaluate the effect of disintegration on a sludge containing PAHs (cf §2.3). DCM (Dissolved and Colloidal Matter) was determined as in Mozo et al. (2016), described in paragraph 2.4.

In both cases, the same device, a SONOPULS HD 2200 homogenizer (Bandelin Electronic) equipped with a TT13 probe was used, and sonication was performed at maximum allowed power (200 W) and low frequency (20 kHz). All the sonication experiments were performed in glass beakers with the probe immerged to half the height of the liquid to avoid foaming or ineffective recirculation of the sample.

The specific energy supplied, E_s (kJ kg_{TS0}^{-1}), defined in Eq. (1), was modified by varying the sonication time.

$$Es = \frac{P \cdot t}{V \cdot (TS)_0} \tag{1}$$

where P is the ultrasonic power (W), t is the sonication time (s), V is the sample volume (L) and $(TS)_0$ is the initial total solid concentration (g L^{-1}). Treated samples had a volume of 1 L, corresponding to a power density of 0.2 W mL^{-1}. The beaker was placed in an ice bath during sonication in order to limit global temperature variation (±5 °C). 15 and 30 min of sonication were applied, which correspond to specific energy of 20 000 and 40 000 kJ kg^{-1} respectively.

2.2. Effect of DCM on PAH partitioning and model calibration

DCM was first generated ex situ by sonication of a secondary sludge (with an initial TS content of 7.1 g_{TS} L^{-1}). A specific energy of 200 000 kJ kg_{TS0}^{-1} was applied and the suspension obtained was centrifuged for 20 min at 8000 RCF. The supernatant obtained, enriched in DCM (5.93 g_{TS} L^{-1}), was added to raw sludge in different proportions to obtain four mixtures with a roughly constant total solid content (6.3 ± 0.6 g L^{-1}) and increasing TS_{-DCM}/TS ratios. Table 1 summarizes the characteristics of the four mixtures after 1 h of contact between sludge and DCM-enriched solution. . Indeed the variation of VS_{-DCM} observed between 1 and 2 h after DCM addition was lower than 2.7% while it was as high as 18.3% within the first hour.

2.2.1. Partitioning experiment

A commercial 16 EPA-PAH solution (TCL Polynuclear Aromatic Hydrocarbons Mix in acetonitrile:methanol (9:1)) was used in order to achieve the most reproducible concentrations in each beaker. The spiking was performed after stabilization of the DCM content (i.e. after possible partial re-aggregation) in the sludge sample. The resulting overall concentration of each of the 16 PAHs studied is summarized in Table 2.

A 1-h contact time between sludge and PAH was considered adequate to establish sorption equilibrium (Barret et al., 2010a, 2011; Dionisi et al., 2006). Preliminary tests showed that biodegradation was not significant during the sorption test (the variation