Anaerobic digestion modelling: innovative characterization tool and extension to micropollutant fate

Julie Jimenez, Quentin Aemig, Jean-Philippe Steyer, Dominique Patureau

(41) Anaerobic Digestion Modelling: Innovative Characterization Tool And Extension To Micropollutant Fate

Julie Jimenez, Quentin Aemig, Jean-Philippe Steyer,, Dominique Patureau
INRA, UR0050, Laboratoire de Biotechnologie de l'Environnement, Av. des Etangs,
Narbonne, F-11100, France (E-mail: *julie.jimenez@supagro.inra.fr)*

Abstract
Advanced dynamic anaerobic digestion models, such as ADM1, requires both detailed organic matter characterisation and intimate knowledge of the involved metabolic pathways. In the current study, a methodology for municipal sludge characterization previously developed is used to describe two key parameters: biodegradability and bioaccessibility of organic matter. The methodology is based on coupling sequential chemical extractions with 3D fluorescence spectroscopy. Experimental data, obtained from two different laboratory scale reactors, were used to validate the model. The proposed approach showed a strong application potential for reactor design and advanced control of anaerobic digestion processes. In order to complete the modified model, the organic micropollutants fate modeling is considered, since their degradation is strongly linked with the organic matter biodegradation, and addition of micropollutants kinetics terms in the overall model is proposed.
Keywords
Modelling; ADM1, organic matter characterization, bioaccessibility, organic micropollutants

INTRODUCTION

In the current context, where anaerobic digestion has become a key process for organic matter treatment and energetic valorization, precise control and prediction of process performance is a must-be. Concomitantly to the organic matter degradation and valorization, some Organic MicroPollutants (OMPs) like Polycyclic Aromatic Hydrocarbons (PAHs) have been shown to be removed during anaerobic digestion (Trably et al., 2003; Barret et al. 2012). The fate of OMPs from wastewater has become an important environmental issue due to their toxicity in the aquatic environment and their effect to the human health (i.e. endocrine disrupting effects). During the biological wastewater treatment (water line), mass balances have shown that the main pathway of degradation is the sorption of OMPs on sludge (Barret *et al*., 2012). As a consequence, anaerobic digestion of sludge has to deal with the OMPs degradation, above all from a sanitation and regulations point of view (sludge spreading for agriculture). In order to predict both organic matter and OMPs degradation, advanced mathematical models have to be implemented. Ten years ago, the International Water Association (IWA) specialist group on anaerobic digestion developed the Anaerobic Digestion Model N°1 (ADM1) (Batstone *et al.,* 2002). For a particulate and complex substrate such as municipal sludge, hydrolysis of macromolecules has been identified as the limiting step (Yasui *et al*., 2006; Mottet *et al*., 2013). In terms of organic matter characterisation, two concepts are of the most relevance: bioaccessibility and biodegradability. Both were traditionally obtained from time consuming and tedious laboratory batch tests used to determine the biochemical methane potential (BMP). An innovative methodology based on the three dimensional excitation emission matrix (3D-EEM) fluorescence spectroscopy (complexity aspect) combined with chemical sequential extractions (bioaccessibility aspect) has been developed (Jimenez *et al.*, submitted). Both parameters was assessed in 5 days instead of the 30 days or more required for BMP. The results obtained from testing 52 municipal sludge samples (primary, secondary, digested and thermally treated) showed a successful correlation with sludge biodegradability and bioaccessibility. One part of this study focuses on evaluating this methodology by using the parameters obtained as input variables of a modified ADM1 model (Mottet *et al.*, 2013) taking into account the bioaccessibility aspect. A second part of the paper will focus on the modeling of the OMPs fate during anaerobic digestion of sewage sludge, using the ADM1 modified model and taking into account of the partition of the OMPs into the various organic matter compartments issued from the sequential extractions.

MATERIAL AND METHODS

Organic matter characterization

Based on the floc definition, the applied sequential extraction (SE) correlates bioavailability of sludge organic matter to its chemical accessibility. The obtained fractions were Dissolved Organic Matter (DOM) obtained by centrifugation and filtration at 0.45µm, soluble Exo-Polymeric Substances (S-EPS), readily bound EPS (RE-EPS) and Humic Substances Like (HSL) obtained by chemical extractions using salt and/or soda of increasing molarity. The non extracted (NE) fraction is the non extractible fraction.Extracts were then measured by fluorescence spectroscopyas explained by (Jimenez *et al.*, submitted). Combining SE with the 3D liquid phase fluorescence (LPF) methodologies was named the 3D-SE-LPF method.

Modelling

Concerning the organic matter degradation, the modified ADM1 model from Mottet *et al.* (2013) has been chosen because (i) the limiting step is the hydrolysis (Contois equation) and (ii) two complex substrates with different hydrolysis rates are considered as Yasui *et al*. (2008) on the two-shaped curve obtained for methane production rate for sludge. The 3D-SE-LPF methodology is used in order to calculate the non biodegradable X_I, readily biodegradable X_{RC} and slowly biodegradable X_{SC} fractions through the Partial Least Square model developed by (Jimenez *et al.*, submitted) using a linear combination of COD fractionation and fluorescence intensity data. OMPs degradation modeling is based on the work made by Delgadillo *et al.* (2011) and applied to the Mottet *et al.* (2013) model.

RESULTS: VALIDATION OF THE METHODOLOGY FOR MODIFIED ADM1 IMPLEMENTATION

Using the modified model of Mottet *et al*. (2013), calibration and validation of two lab scale mesophilic continuous reactors (4 liters, hydraulic retention time of 18 days, organic load of 0.13 $gCOD.gVS_{reactor}^{-1}.d^{-1}$) were performed with few parameters change (growth rate kinetic of hydrolytic biomass). One reactor (P1) was fed with a secondary sludge and the second reactor (P2) with the same sludge but deprived of some extracted fractions (DOM, S-EPS and RE-EPS).

Concerning the methane production, PLS predicted variables used for ADM1 implementation led to a satisfying fit of experimental methane production as shown by figure 1. Changes of organic loading and organic matter characteristics were well managed by the model. Indeed, depriving the most accessible fractions of the sludge led to depriving the most readily biodegradable fractions as shown by the zoom of figure 1, as explained by Yasui *et al.* (2006). This means that the chemical accessibility fractionation defined in this study is well correlated to bioaccessibility. From the results obtained in this study, fluorescence spectroscopy will lead to main achievements for better knowledge of organic matter.

PERSPECTIVES: ORGANIC MICROPOLLUTANT MODELLING IN ADM1

Some studies related the strong correlations between OMPs degradation and organic matter degradation in anaerobic digestion (Trably *et al*., 2003, Barret *et al*., 2012). Moreover, Delgadillo-Mirquez (2011) has demonstrated that the OMPs biodegradation are mainly related with the upper biological pathway of anaerobic digestion (hydrolysis, acidogenesis and acetogenesis). As a consequence, the bioavailability and bioaccessibility concept of organic matter (hydrolysis considered as the limiting step) could be used for OMPs fate characterization. Consequently, the SE protocol has been applied for OMPs partition assessment into the organic matter compartments in order to estimate their bioavailability. Delgadillo *et al.* (2011) showed that combining bioavailability and cometabolism concepts on a dynamic simplified model allowed the prediction of the OMPs fate in anaerobic digestion. Besides, Barret *et al.* (2012) and Delgadillo (2011) confirmed that the bioavailable fraction is contained in the aqueous phase (free OMPs and sorbed to colloidal matter) and that the bioaccessibility depends on the pollutants sorbed to particles. However, as shown by simulation results from Delgadillo (2011), using a first order model for hydrolysis does not fit well with experimental data. As a result, OMPs degradation modeling is impacted. From these observations, modifications and additions in the Mottet *et al.* (2013) model could be made. A schematic overview of the model is presented in the figure A.1 of Annex. Results from generated lab data will be presented at the conference in order to calibrate and validate the new model.

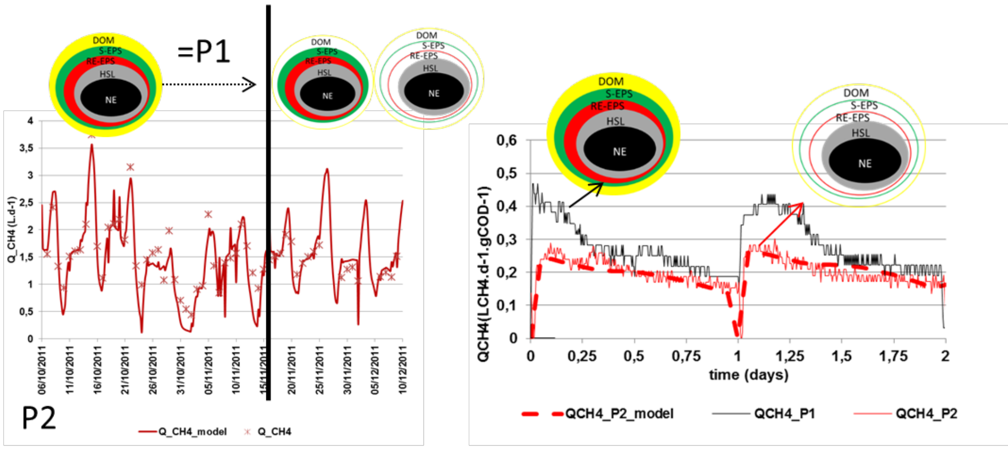

Figure 1. Results obtained on methane production: experimental data versus model

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ANNEX

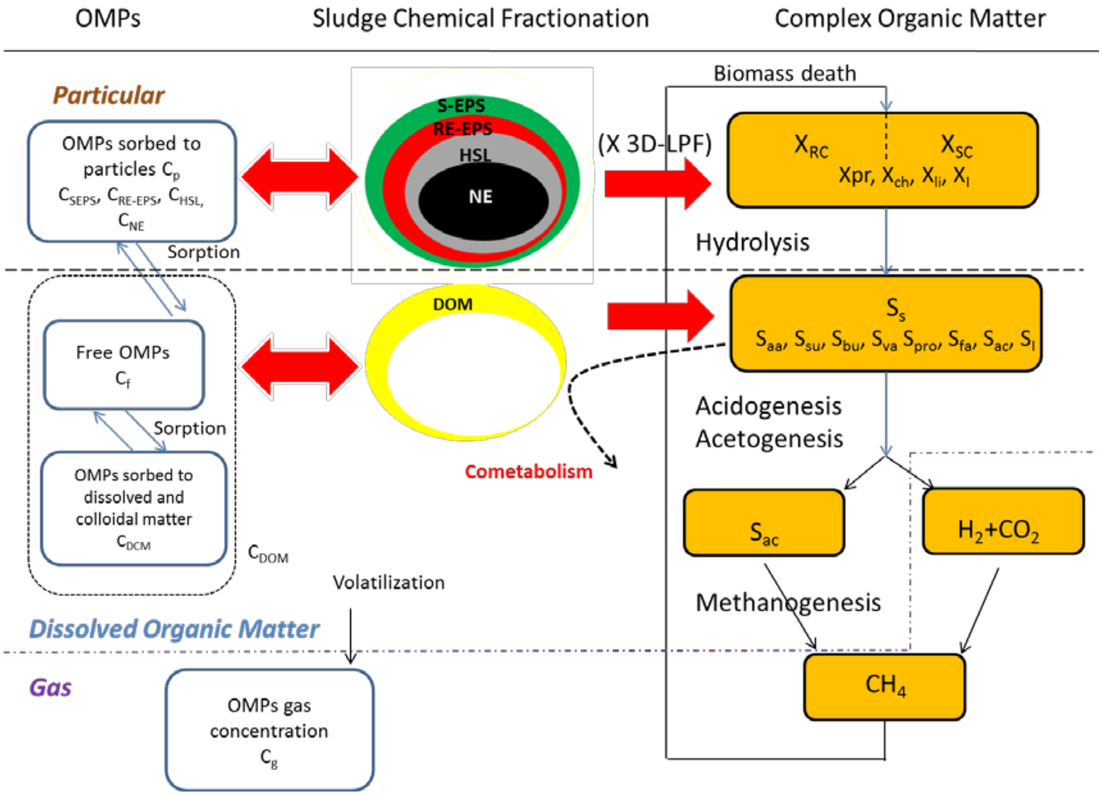

Figure A.1. Schematic overview of the modified ADM1 model for OMPs fate modeling in regards with the sludge chemical fractionation

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