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Modelling phosphorus (P), sulphur (S) and iron (Fe) interactions during the simulation of anaerobic digestion processes

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Abstract: This paper examines the effects of different model formulations when describing sludge stabilization processes in wastewater treatment plants by the Anaerobic Digestion Model No. 1 (ADM1). The proposed model extensions describe the interactions amongst phosphorus (P), sulfur (S), iron (Fe) and their potential effect on total biogas production (CO_2 , CH_4 , H_2 and H_2S). The ADM1 version, implemented in the plant-wide context provided by the Benchmark Simulation Model No. 2 (BSM2), is used as the basic platform (A_0). Four ($A_1 - A_4$) different model extensions are implemented, simulated and evaluated. The first approach (A_1) considers P transformations by accounting for the kinetic decay of polyphosphates (X_{PP}) and potential uptake of Volatile Fatty Acids (VFA) to produce Polyhydroxyalkanoates (X_{PHA}) by Phosphorus Accumulating Organisms (X_{PAO}). The second model formulation (A_2) describes biological production of sulfide ($S_{\text{H}_2\text{S}}$) by means of Sulfate-Reducing Bacteria (X_{SRB}). This approach also considers potential $S_{\text{H}_2\text{S}}$ inhibition effect on biomass and mass transfer phenomena (aqueous-gas). The third evaluated model (A_3) considers chemical iron (III) ($S_{\text{Fe}+3}$) reduction to iron (II) ($S_{\text{Fe}+2}$) using hydrogen (S_{H_2}) as the electron donor. Finally, the last evaluated approach (A_4) is based on accounting for Multiple Mineral Precipitation. The ADM1 thereby switches from a 2-phase (aqueous-gas) to a 3-phase (aqueous-gas-solid) system. Simulation results show that the implementations of A_1 and A_2 lead to a reduction in biogas production. This reduction is attributed to two factors. Firstly, there is a fierce competition for substrate (S_{H_2} , VFA) between the existing and the new groups of microorganisms. Secondly, there is a decrease of acetoclastic and hydrogenotrophic methanogenesis due to $S_{\text{H}_2\text{S}}$ inhibition. Models A_3 and A_4 reduce the free $S_{\text{H}_2\text{S}}$ (and consequently inhibition) plus cationic load and soluble P availability due to ion pair formation and metallic carbonate/phosphate precipitation. The final version of the manuscript will provide a deeper analysis of the different model assumptions, the effect that operational/design conditions might have on the model predictions, a detailed description of the weak acid-base chemistry and practical implications in view of plant-wide modelling/development of resource recovery strategies.

1. INTRODUCTION

It has been more than 12 years since the publication of the Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002). The ADM1 describes organic carbon and nitrogen transformation processes in Anaerobic Digesters (AD) and has been effectively applied (in both industry and academia) to a large number of wastewater treatment plants (WWTPs) (Donoso-Bravo *et al.*, 2011). The implementation of the ADM1 within the Benchmark Simulation Model No. 2 (Gernaey *et al.*, 2014) and the need to evaluate plant-wide control strategies, in a relatively short period of time, promoted intensive research on computationally-efficient versions of the model (Rosen *et al.*, 2006). As a result, it is possible to simulate the ADM1 with several verified / ring-tested implementations and it is included in the standard model library in most software packages (MatLab, GPS-X, Mike-WEST, Simba, FORTRAN). In spite of the success of ADM1, the model still omits important processes taking place during anaerobic digestion of activated sludge (Batstone *et al.*, 2002). The objective of this paper is to show the effect on ADM1 predictions when including some of the most frequently requested extensions (Batstone *et al.*, 2006a). Therefore, ADM1 is upgraded with an improved physico-chemical description, phosphorus (P) and sulphur (S) biotransformation, iron (Fe) reduction and Multiple Mineral Precipitation (MMP). The extensions respond to new challenges/needs that wastewater engineers demand when it comes to optimizing WWTP operation, maximize energy production and resource recovery.

2. METHODS

2.1. INFLUENT CHARACTERISTICS

The influent characteristics follow the same principles as outlined in [Gernaey *et al.* \(2011\)](#). Average pH is set to 7 and therefore influent cations (S_{CAT}) (S_{K^+} , S_{Na^+} , $S_{\text{Ca}^{+2}}$, $S_{\text{Mg}^{+2}}$, $S_{\text{Fe}^{+3}}$) and anions (S_{AN}) (S_{Cl^-} , $S_{\text{SO}_4^{2-}}$) are adjusted accordingly. Chemical oxygen demand (COD), nitrogen (N) and P determine the concentration of acetate (S_{ac^-}), ammonium ($S_{\text{NH}_4^+}$) and phosphate ($S_{\text{PO}_4^{3-}}$). The water line of the WWTP under study is inspired by the BSM2 ([Gernaey *et al.*, 2014](#)), and comprised of a primary clarifier, an activated sludge unit (A₂O configuration) and a secondary clarifier. Additional information about the activated sludge design/operational conditions can be found in [Flores-Alsina *et al.* \(2012\)](#). Sludge wasted from the secondary clarifier passes through a thickener unit. The combined sludge from the primary clarifier and the thickener determines the influent characteristics of the anaerobic digester. Further details about the used models can be found in [Gernaey *et al.* \(2014\)](#).

2.2. MODEL FORMULATIONS

In this case study, four sets of model assumptions describing P/S/Fe related processes within the ADM1 framework are compared.

In the reference case (A_0), the BSM2 implementation of ADM1 ([Rosen *et al.*, 2006](#)) is selected to describe the anaerobic digestion process. pH calculation, ionic speciation/pairing are described in [Solon *et al.* \(2015\)](#). P is modelled using a source-sink approach assuming a predefined elemental composition ([de Gracia *et al.*, 2006](#)). The original composite material variable (X_c) is removed and decay products are directly mapped into biodegradable organics (X_{pro} , X_{li} and X_{ch}) and organic inerts (S_i , X_i). Interfaces between ASM2d and ADM1 follow the same principles as stated in [Nopens *et al.* \(2009\)](#). The main difference relies on assuming instantaneous decay of Phosphorus Accumulating Organism (X_{PAO}), Polyhydroxyalkanoates (X_{PHA}) and Polyphosphates (X_{PP}). Kinetic and stoichiometric parameters are set for 35°C ([Batstone *et al.*, 2002](#)).

The second model (A_1) describes P transformation according to the Activated Sludge Model No. 2d (ASM2d) ([Henze *et al.*, 2000](#)). Consequently, X_{PAO} , X_{PP} and X_{PHA} are included as state variables in the extended ADM1 model, which implies inclusion of six new processes: (1-3) uptake of butyrate (S_{bu}), propionate (S_{pro}), acetate (S_{ac}) to form X_{PHA} and (4-6) decay of X_{PAO} , X_{PHA} and X_{PP} . The latter causes differences in the COD, N, P and cationic (K, Mg) loads after the interface compared to A_0 (= do not decay). Growth of X_{PAO} and storage of X_{PP} are not included as there are no aerobic/anoxic conditions in the digester. Kinetic parameters reported in [Ikumi *et al.* \(2014\)](#) are used in this study.

In the third model formulation (A_2), sulfate (S_{SO_4}) is reduced to sulfide ($S_{\text{H}_2\text{S}}$) by means of specific Sulfate-Reducing Bacteria (SRB). Hydrogen (S_{H_2}) is used by these microorganisms ($X_{\text{SRB}_\text{H}_2}$) as electron donor. pH and N inhibition are based on the same mathematical structure as defined in [Batstone *et al.* \(2002\)](#). High $S_{\text{H}_2\text{S}}$ concentration inhibits the metabolism of hydrogen (X_{H_2}), acetate (X_{ac}), propionate (X_{pro}) and butyrate/valerate degraders (X_{C_4}). The same $S_{\text{H}_2\text{S}}$ inhibits growth of $X_{\text{SRB}_\text{H}_2}$ ([Federovich *et al.*, 2003](#); [Barrera *et al.*, 2014](#)). The model also includes mass transfer equations from $S_{\text{H}_2\text{S}}$ to $S_{\text{H}_2\text{S}}(\text{gas})$ and finally to biogas H_2S ($G_{\text{H}_2\text{S}}$). The latter has an effect on the total biogas production and the AD total gas pressure. In this case study, $S_{\text{H}_2\text{S}}$ is modelled in COD units. Kinetic values for $X_{\text{SRB}_\text{H}_2}$ are selected to out-compete X_{H_2} according to [Batstone \(2006b\)](#).

Iron reduction in the extended ADM1 (A_3) is modelled as follows: S_{H_2} is the electron provider, which will be received by $S_{\text{Fe}^{+3}}$ (and subsequently converted to $S_{\text{Fe}^{+2}}$). pH (and consequently S_{H^+}) will be adjusted automatically with the charge balance (there will be less $S_{\text{Fe}^{+3}}$ and more $S_{\text{Fe}^{+2}}$) ([Solon *et al.*, 2015](#)). $S_{\text{Fe}^{+2}}$ and $S_{\text{Fe}^{+3}}$ are also converted into COD units. A second order reaction rate is used to describe kinetics. Kinetic parameters are adjusted to ensure 75% conversion.

Finally, MMP (A_4) is modelled according to **Kazadi-Mbamba *et al.* (2015a,b)**. In this study, precipitation is described as a reversible process using the Saturation Index (SI) as the driving force. SI represents the logarithm of the ratio between the product of the different activities (reactants) and the solubility product constant (K_{SP}). The precipitation equation depends on the rate, the concentration of the product and the order of the reaction. The proposed framework accounts for the following compounds: calcite (X_{CaCO_3}), aragonite (X_{CaCO_3a}), ACP ($X_{Ca_3(PO_4)_2}$), HAP ($X_{Ca_5(PO_4OH)_3}$), (X_{CaHPO_4}), OCP ($X_{Ca_4(PO_4OH)_3}$), struvite ($X_{MgNH_4PO_4}$), newberyite (X_{MgHPO_4}), magnesite (X_{MgCO_3}), k-struvite (X_{KMgPO_4}), iron sulfide (X_{FeS}), iron phosphate (X_{FePO_4}) and aluminum phosphate (X_{AlPO_4}). Kinetic parameters can be found in **Kazadi-Mbamba *et al.* (2015a;b)**.

3. RESULTS

Figure 1 shows the model predictions after simulating the BSM2 digester 200 days in steady state conditions. Both P implementations (A_0 and A_1) show fairly similar results (**Figure 1a**). The main difference between A_1 and A_2 predictions is related to G_{CH_4} /biogas production. The variation is attributed to a reduction of VFA - due to the storage of X_{PHA} that consumes VFA which potentially cannot be converted into methane. The difference between methane and biogas production increases/decreases when the sludge retention time (SRT) of the AD is modified. At low SRT, the differences between the two implementations increase. This is attributed to the fact that some of the organics are still trapped in the form of X_{PHA} and consequently cannot be fermented (7.51 and 6.62% in G_{CH_4} and biogas, respectively). On the other hand, at high SRT the differences between the two models decrease. This is mainly due to the fact that X_{PHA} is totally hydrolyzed to VFA and consequently converted to biogas (1.47 and 1.76% in G_{CH_4} and biogas, respectively). No substantial differences can be observed in the weak acid-base chemistry (variation of pH ranges from 0.7 to 0.03%). The same pattern can be observed with the speciation of the involved cations, anions and organic acids (differences are lower than 1%).

The inclusion of the role of SRB (A_2) supposes a reduction in the G_{CH_4} production (**Figure 1b**). This reduction is attributed to several factors. First of all, there is a decrease of acetoclastic and hydrogenotrophic methanogenesis due to S_{H_2S} inhibition. Secondly, there is competition between two groups of microorganisms (X_{H_2} and $X_{SRB_H_2}$) for the same substrate (S_{H_2}) (= uptake of hydrogen by X_{H_2} is reduced) (up to 5.6%). Compared to the previous case (A_0 vs A_1), larger differences can be observed in pH (range of variation moves from 0.07 to 1.78%), which are mainly caused by a lower S_{SO_4} concentration (in A_2 S_{SO_4} is re-transformed to S_{H_2S}/S_{HS} and pH decreased). The latter affects the carbon system ($S_{HCO_3^*}/S_{HCO_3}$) and reduces the quantity of G_{CO_2} (up to 1.74%). It is important to highlight that at higher S_{SO_4} concentrations (> 300 g S.m⁻³) it would be necessary to reformulate the proposed model structure. Thus, additional SRB bacteria groups could be included capable to extract electrons from organic acids (**Federovich *et al.*, 2003; Barrera *et al.*, 2014**). A comparison of those two approaches will be included in the final version of the paper.

There is no S_{Fe+2} concentration in the AD influent, just S_{Fe+3} . An increasing concentration of S_{Fe+3} in the influent, which potentially will be converted in S_{Fe+2} , decreases the overall production of G_{H_2S} . This is mainly due to the changes in the system's physico-chemistry and the preferential binding of S compounds with Fe. Indeed, when S_{Fe+2} is not present, inorganic sulfur is basically speciated into S_{HS} (57%) and S_{H_2S} (43%). However, once reduced Fe conversions are included, these percentages are modified dramatically due to the increasing abundance of S_{FeHS} . The higher the S_{Fe+2} , the lower the concentrations of both S_{HS} and S_{H_2S} since S_{FeHS} is favored. The latter has a strong influence on G_{CH_4} production. **Figure 1c** shows the effect of increasing the same S/COD load with or without iron conversion. The reduction of free S_{H_2S} also reduces the inhibition of hydrogen (X_{H_2}), acetate (X_{ac}), propionate (X_{pro}) and butyrate/valerate degraders (X_{C_4}). The latter promote fermentation, decreases the quantity of free VFAs (S_{va} , S_{bu} , S_{pro} and S_{ac}) and consequently changes pH (slightly increased) It is important to highlight that in this base case, the sulfide production is quite low. A more pronounced effect is expected at higher influent S loads.

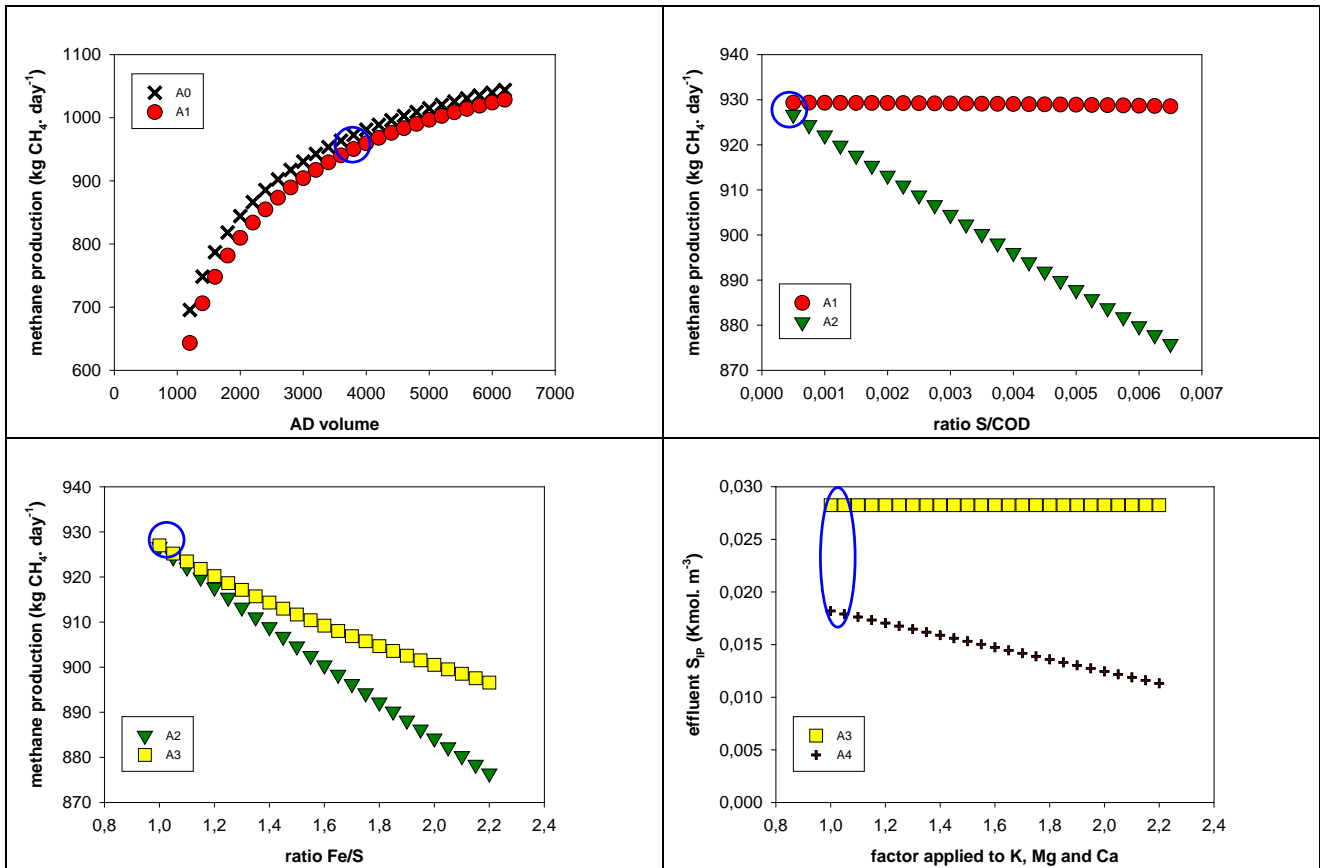


Figure 1. Effect of the different model extensions on ADM1 predictions: (a) Bio-transformation of P compounds (A_0 black; A_1 red), (b) Bio-transformation of S compounds (A_1 red; A_2 green), (c) Reduction of S_{Fe+3} (A_2 green; A_3 yellow) and (d) multiple mineral precipitation (A_3 yellow; A_4 black). Default values are shown by blue circles.

The last implemented model framework (A_4) shows only three precipitates from the list of potential compounds: ACP ($X_{Ca_3(PO_4)_2}$), struvite ($X_{MgNH_4PO_4}$) and iron sulfide (X_{FeS}). The two firsts supposes a reduction in the soluble effluent P. The Fe fraction that was paired with HS is now precipitated. Additional simulations were run modifying the cationic load (K, Ca, Mg). Results show that the number of compounds is the same, but the quantity of effluent P is lower (**Figure 1d**). This strategy can be used either to increase the quantity of recovered product or to decrease the P content in the AD supernatant when returning it to the water line. No substantial differences can be observed related to G_{CH_4} (<1%). Nevertheless, the reduced cationic load strongly impacts the distribution ($S_{HCO_3^{*}}/S_{HCO_3^-}$) and complexation (ion pairs) of the carbon system and therefore G_{CO_2} (up to 9.25%).

4. OUTLOOK / CONCLUSIONS

This paper has addressed some of the existing ADM1 structural limitations. A first step towards the Anaerobic Digestion Model No. 2 (ADM2) is made proposing a new model framework dealing with P/S/Fe and MMP simultaneously. All these elements are described with the aid of a new physico-chemical model. Simulation results are presented herein based on the first model prototype. The key findings of the presented research are summarized in the following points:

- 1) P transformations must be modelled kinetically at low SRT (not in the interface). Potential uptake of VFA by X_{PAO} to form X_{PHA} when X_{PAO} are still alive might have an important effect on the overall digester performance.
- 2) SRB have an important role treating sludge with high S loads. S_{SO_4} is susceptible to be transformed to S_{H_2S} , which is a potential inhibitor that affects the normal behaviour of the AD. In addition, the weak acid-base chemistry is modified and consequently pH. Finally, the competition between traditional (X_{H_2}) and SRB bacteria for the same substrate (S_{H_2}) reduces methane production and therefore energy recovery.

- 3) $S_{\text{Fe}+2}$ complexation substantially modifies the whole S chemistry (= species distribution). Anaerobic conditions promote a reductive environment. For this reason, when the traditional iron forms enter the digester, $S_{\text{Fe}+3}$ receives electrons and change oxidation state ($S_{\text{Fe}+2}$). The latter has an important effect on the S ionic/cationic complexation, $S_{\text{H}_2\text{S}}$ production and process inhibition.
- 4) MMP reduces the quantity of soluble P and associated cations (Ca, Fe). When coupled in a plant-wide context, this will have an enormous impact on the overall process performance (digester supernatants composition). The impact on methane production is poor, and changes in the system weak acid-base chemistry affect CO_2 production.

Extensive model calibration and validation will be necessary to consolidate the described modelling approach.

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