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IWA Anaerobic Digestion Model No. 1 extended with Phosphorus and Sulfur

Literature Review

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LITERATURE REVIEW

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CONTENTS

Abstract

Phosphorus is one of the limiting nutrients (for photosynthesis) known to cause eutrophication in aquatic ecosystems when discharged in excessive quantities, damaging the chemical and ecological quality of water bodies. In addition to this, phosphorus rock, which is the predominant source of phosphorus, is also a limited resource. These two aspects are the drivers of on-going efforts to recover phosphorus in wastewater treatment plants. Recovering phosphorus helps protect a limited resource and at the same time decreases its release onto surface waters thus helping prevent eutrophication.

On the other hand, sulfur has been known to cause a number of operational problems in wastewater treatment plants, the conversion of sulfate to hydrogen sulfide under anaerobic conditions being the main culprit. Corrosion, production of poisonous gas, and toxicity to methanogens are some of the problems brought about by sulfide in the waste stream.

In the past, the focus of wastewater treatment processes and technologies have been on the removal of carbon and nitrogen. Currently, there has been an emerging effort on development of processes for phosphorus and sulfur removal in wastewater. Alongside this development is the need to include these processes during wastewater treatment modelling in order to describe and understand the fate and mechanism of these pollutants and how they interact in a complex system such as a wastewater treatment plant.

This report aims to provide a background for modelling of phosphorus and sulfur. It is focused in including these two pollutants and their related processes in an established model such as the IWA Anaerobic Digestion Model No. 1.

Keywords: ADM1, Phosphorus, Sulfur

Background

It is a well-known fact that the presence of excessive nutrients, such as nitrogen and phosphorus, in surface waters may lead to eutrophication which is detrimental to the good chemical and ecological status of water bodies. In order to help regulate the quality of effluent released to surface waters, modelling of wastewater treatment processes could be performed. Modelling could help study different technologies, develop control strategies, optimization of the processes, etc. to guarantee that good effluent quality is achieved economically, and at the same time with minimal risks associated. Current wastewater treatment models take into account carbon and nitrogen removal processes; however, modelling of phosphorus is lagging behind.

In addition, there is a need to model phosphorus to better describe and study nutrient recovery technologies, an example is phosphorus recovery through struvite precipitation. This year's publication of the European Commission included phosphate rock as the 20th in the EU Critical Raw Materials list (European Commission, 2014). Europe has a very limited resource of this raw material and is largely dependent on imports. Phosphate rock was not included in the previous list published in 2011. This shows the growing importance of phosphorus as a resource in relation to how often it is released in excessive amounts onto surface waters.

This report aims to provide a background for the modelling of phosphorus within a wastewater treatment process, in particular, anaerobic digestion.

1. ADM1 extended with phosphorus

Modelling of phosphorus is one of the major limitations of the IWA Anaerobic Digestion Model No. 1 (ADM1) (Bastone et al., 2002). Phosphorus-related processes have been addresses in commercial software packages due to engineering demand but not in academically-distributed wastewater treatment models. Batstone et al. (2006) stated that phosphorus has been requested to be included in the IWA Anaerobic Digestion Model No. 1 in order to describe the phosphorus retention and release in the biomass and to close the phosphorus balances in plant-wide modelling.

An important aspect of phosphorus modelling is its effect on pH. In ADM1, major ions are tracked except the phosphorus-related ones. It should be noted that a prerequisite to adding phosphorus and its precipitation kinetics require taking into account physico-chemical effects (Solon et al., 2014), such as ion activity correction, ion-pairing behaviour, and relevant weak acid-base

reactions, since these effects are more pronounced when considering divalent and trivalent ions such as hydrogen phosphate and phosphate, respectively.

Johnson and Shang (2006) have also mentioned that tracking the fate of both sulfur and phosphorus in anaerobic systems are major areas that ADM1 does not currently address but are very important in municipal wastewater treatment systems. In nutrient cycle loads, it has been found that it can be as high as 30% of the total nutrient load. This high recycle load proves the importance of an accurate method of tracking phosphorus through the anaerobic digestion process. They have implemented phosphorus-related reactions within ADM1 including calculations for struvite formation within the digester.

Principally, two methods for incorporating phosphorus in the anaerobic digestion model have been developed. The first one is an oversimplified model wherein no biological reaction is taking place. The quantity of phosphorus within the system, i.e. in the particulate and soluble components, is tracked through introduction of a new state variable which will act as a source-sink for all phosphorus compounds. A similar method was done by Zaher and Chen (2006) where they assumed that there is instantaneous phosphorus-related processes and are taking place in the interface between the activated sludge and the anaerobic digestion process.

On the other hand, the second model takes into account some of the processes, those that occur under anaerobic conditions, which are considered in the IWA Activated Sludge Model No. 2d (ASM2d) (Henze et al., 1999) and are modelled kinetically within ADM1. Ikumi et al. (2011) proposed a 3-phase model when considering gas exchange (gas↔liquid), precipitation (liquid→solid), and redissolution (solid→liquid) processes.

One limitation in this report is that only a 2-phase model (gas-liquid) is considered, the precipitation and redissolution reactions are excluded but are going to be considered in future work.

1.1. Model ADM1_P1

Modelling phosphorus within ADM1 can be overly simplified. It can be assumed that there is specifically no phosphorus-related biological reactions taking place inside the anaerobic digester. Instead, all conversions and decay processes are assumed to be instantaneous and are occurring in the interface before the digester (Zaher et al., 2007).

Only one state variable, S_{IP}, which represents the concentration of inorganic phosphates, is added into the model. It is assumed that all phosphorus are inorganic phosphate-type. S_{IP} acts as a source-sink for all phosphorus-related compounds in the digester.

An important aspect of this model is defining the phosphorus content of all soluble and particulate components in the ADM1 through elemental balances as described by Takács and Vanrolleghem (2006). It is based on the hypothesis that the mass of each component is made up of constant mass fractions of the elements C, H, O, N and P (Reichert et al., 2001). This can be easily extended to include other elements such as sulfur, potassium, magnesium, etc., provided that the sum of all elemental mass fractions (α) of a given component *i* equals unity (Eq. 1). Listed in Table 1 are the phosphorus-containing ADM1 state variables (including S_{IP}). The requirement for this is to know the stoichiometric formulae of the components; however, when this is not known, a proper estimation must be carried out (Zaher et al., 2007).

$$\alpha_{C,i} + \alpha_{H,i} + \alpha_{O,i} + \alpha_{N,i} + \alpha_{P,i} = 1 \qquad \textbf{Eq. 1}$$

Table 1. Composition matrix of ADM1 state variables containing phosphorus.

Component →	**S_{IP}**	**S_I**	**X_{ch}**	**X_{li}**	**X_c**	**X_{su}**	**X_{aa}**	**X_{fa}**	**X_{c4}**	**X_{pro}**	**X_{ac}**	**X_{h2}**	**X_I**
$\alpha_{P,i}$ (kmole P / kg COD)	1	2.093E-4	1.12E-4	3.12E-4	6.947E-4	6.947E-4	6.947E-4	6.947E-4	6.947E-4	6.947E-4	6.947E-4	6.947E-4	2.093E-4

1.2. Model AM1_P2

The second concept in integrating phosphorus in ADM1 is to assume that the phosphorus-related microorganisms are still active when they reach the anaerobic digester. In order to handle this, some of the ASM2d processes (Henze et al., 1999), those which occur in anaerobic conditions, could be included as additional processes in ADM1.

NEW STATE VARIABLES

S_K Potassium

S_{Mg} Magnesium

S_{IP} Inorganic soluble phosphorus. It is assumed to be composed primarily of orthophosphates.

X_{PAO} Phosphorus accumulating organisms or PAO. They are assumed mainly to grow aerobically but some are also observed to grow anoxically. The concentration does not include the cell-internal storage materials, X_{PHA} and X_{PP}.

X_{PHA} Polyhydroxyalkanoates. This is a cell-internal storage material of phosphorus accumulating organisms (X_{PAO}). It occurs in association with X_{PAO}. It mainly includes polyhydroxyalkanoates (X_{PHA}) and glycogen. It is assumed to have the chemical composition $(C_4H_6O_2)_m$. It is a functional component which is required for modelling but cannot be identified chemically.

X_{PP} Polyphopshates. This is also a cell-internal storage material of phosphorus accumulating organisms (X_{PAO}). It occurs in association with X_{PAO}. It is assumed to have the chemical composition $(K_{0.34}Mg_{0.33}PO_3)_n$. It forms part of the particulate phosphorus and could be analytically observed.

Table 2. Additional stoichiometric matrix for the soluble and particulate components in ADM1 for phosphorus modelling.

Component →	i	4	5	6	7	20*	21*	22*	23*	24*	25*
j	Process ↓	S_{va}	S_{bu}	S_{pro}	S_{ac}	X_{PHA}	X_{PP}	X_{PAO}	S_K	S_{Mg}	S_{IP}
20*	Storage of S_{va} in X_{PHA}	-1				1	$-Y_{PO4}$		$Y_{PO4}*K_i$	$Y_{PO4}*Mg_i$	$-\sum_{i=1-9,12-24} p_i v_{i,20}$
21*	Storage of S_{bu} in X_{PHA}		-1			1	$-Y_{PO4}$		$Y_{PO4}*K_i$	$Y_{PO4}*Mg_i$	$-\sum_{i=1-9,12-24} p_i v_{i,21}$
22*	Storage of S_{pro} in X_{PHA}			-1		1	$-Y_{PO4}$		$Y_{PO4}*K_i$	$Y_{PO4}*Mg_i$	$-\sum_{i=1-9,12-24} p_i v_{i,22}$
23*	Storage of S_{ac} in X_{PHA}				-1	1	$-Y_{PO4}$		$Y_{PO4}*K_i$	$Y_{PO4}*Mg_i$	$-\sum_{i=1-9,12-24} p_i v_{i,23}$
24*	Decay of X_{PAO}							-1			$-\sum_{i=1-9,12-24} p_i v_{i,24}$
25*	Decay of X_{PP}						-1		K_i	Mg_i	$-\sum_{i=1-9,12-24} p_i v_{i,25}$
26*	Decay of X_{PHA}	$f\_S_{va}\_X_{PHA}$	$f\_S_{bu}\_X_{PHA}$	$f\_S_{pro}\_X_{PHA}$	$f\_S_{ac}\_X_{PHA}$	-1					$-\sum_{i=1-9,12-24} p_i v_{i,26}$

Marked with (*) are the new components and processes added in ADM1.

Components 20 to 25 are additional state variables included in the ADM1 to account for phosphorus inside the anaerobic digester. Moreover, processes 20 to 26, as adapted from ASM2d, are added into the model.

Process 20_{new}. Storage of S_{va} in X_{PHA}. This process describes the storage of valerate (S_{va}) in the form of cell-internal storage material (X_{PHA}). The storage is associated with phosphate release. The available energy during the lysis of polyphosphate (X_{PP}) is used to store the valerate. This process involves the release of potassium (S_K), magnesium (S_{Mg}), and inorganic phosphate (S_{IP}). This process occurs mainly under anaerobic conditions but is also observed in aerobic and anoxic conditions, thus, no inhibition terms are included in the kinetic expression.

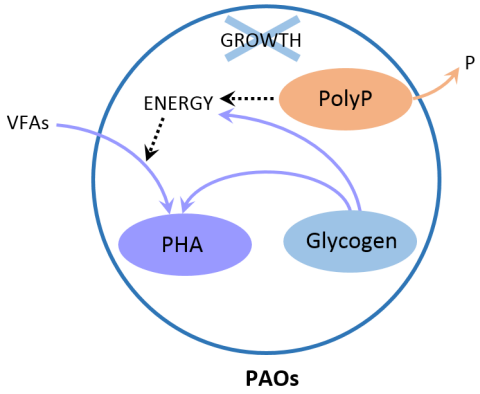

Figure 1. Simplified biochemical model for phosphorus accumulating organisms (PAOs) under anaerobic conditions.

Process 21_{new}. Storage of S_{bu} in X_{PHA}. This process describes the storage of butyrate (S_{bu}) in the form of cell-internal storage material (X_{PHA}). The storage is associated with phosphate release. The available energy during the lysis of polyphosphate (X_{PP}) is used to store the butyrate. This process involves the release of potassium (S_K), magnesium (S_{Mg}), and inorganic phosphate (S_{IP}). This process occurs mainly under anaerobic conditions but is also observed in aerobic and anoxic conditions, thus, no inhibition terms are included in the kinetic expression.

Process 22_{new}. Storage of S_{pro} in X_{PHA}. This process describes the storage of propionate (S_{pro}) in the form of cell-internal storage material (X_{PHA}). The storage is associated with phosphate release. The available energy during the lysis of polyphosphate (X_{PP}) is used to store the propionate. This process involves the release of potassium (S_K), magnesium (S_{Mg}), and inorganic phosphate (S_{IP}). This process occurs mainly under anaerobic conditions but is also observed in aerobic and anoxic conditions, thus, no inhibition terms are included in the kinetic expression.

Process 23_{new}. Storage of S_{ac} in X_{PHA}. This process describes the storage of acetate (S_{ac}) in the form of cell-internal storage material (X_{PHA}). The storage is associated with phosphate release. The available energy during the lysis of polyphosphate (X_{PP}) is used to store the acetate. This process involves the release of potassium (S_K), magnesium (S_{Mg}), and inorganic phosphate (S_{IP}). This process occurs mainly under anaerobic conditions but is also observed in aerobic and anoxic conditions, thus, no inhibition terms are included in the kinetic expression.

The storage products, X_{PP} and X_{PHA}, are accounted separately from the biomass, X_{PAO}. Thus, these three particulate components are also subjected to separate decay processes as detailed in the following:

Process 24_{new}. Decay of X_{PAO}. This process describes the decay of polyhydroxyalkanoates (X_{PHA}) and the associated conversion to X_c and release of phosphates.

Process 25_{new}. Decay of X_{PP}. This process describe the decay of the cell-internal storage material, X_{PP}, and the associated release of potassium (S_K), magnesium (S_{Mg}), and inorganic phosphate (S_{IP}).

Process 26_{new}. Decay of X_{PHA}. This process describes the decay of cell-internal storage material, X_{PHA}, which are converted back to organic products S_{va}, S_{bu}, S_{pro}, and S_{ac}.

It is important to mention that the growth of X_{PAO} and the cell-internal storage materials, X_{PP} and X_{PHA}, are not included as additional processes since these are known to occur only during aerobic and anoxic conditions.

Another important aspect in the simulation of this model is to make ensure that the influent to the anaerobic digester should already contain some concentrations for X_{PP}, X_{PHA}, and X_{PAO} as there is no growth for these biomass under anaerobic conditions.

1.3. Conclusions

Modelling of phosphorus is important in order to describe and study the fate of phosphorus-related compounds during anaerobic digestion. It should be a starting point in modelling of phosphorus removal and/or recovery processes.

Two methods are described in this report: (Model ADM1_P1) accounting for all phosphorus content of all particulate and soluble components of ADM1 but no biological reaction of any sort taking place and (Model ADM1_P2) ASM2d processes are adapted and included into ADM1. Model ADM1_P1 is also used as a starting point in the development of Model ADM1_P2.

BACKGROUND

Sulfate in the influent of a wastewater treatment plant has been a source of operational problems especially in the sewer system, pipelines, as well as in the anaerobic digester mainly due to its conversion to hydrogen sulfide (H_2S) when subjected to anaerobic conditions. Sulfide-containing waste streams are usually coming from industries such as petrochemical plants, leather tanning industries, ethanol production, and coal-fired plants.

One operational problem caused by H_2S is its odour. H_2S has a distinct "rotten egg" smell at low concentrations in air, can cause irritations at low to medium concentrations, and is very toxic at high concentrations. Another consequence of having H_2S is corrosion problems. It attacks several types of material which are normally used in wastewater treatment plants such as concrete, steel, copper, and iron. Finally, another operational issue is the toxicity effect of H_2S on the methanogenic population which can result to failure in operation of anaerobic digesters.

It could be useful to include sulfur in modelling in order to describe its fate within the wastewater treatment plant and assess control strategies to minimize H_2S production, at the same time this model could also be used for risk assessment of the operational problems associated with H_2S production.

2. ADM1 extended with sulfur

A proposed sulfur extension to ADM1 is important for operational and technical development. Sulfate in the influent can be very high that it significantly affects the methanogenesis phase during anaerobic digestion. This effect is not modelled in the current version of the IWA Anaerobic Digestion Model No. 1 (ADM1), but it is important in order to correctly predict the behaviour of the system under high-sulfate conditions. Modelling of sulfate reduction in the ADM1 is also one of the most widely requested extension so far. A shortcoming of ADM1 is the omission of processes related to sulfate reduction and the associated sulfide inhibition and the prediction of H_2S in the biogas.

Fedorovich et al. (2003) has developed extension to ADM1 on sulfate reduction, which is complex, since it is intended for systems dealing with high concentrations of sulfate. A simpler approach was developed by Batstone (2006) by assessing sulfate reduction by oxidation of available hydrogen.

In this report, the two models proposed are implemented in the Matlab/Simulink platform and were compared against each other for a range of S/COD influent loads.

2.1. Model ADM1_S1

One of the models which include sulfur in the ADM1 is the simplified model by Batstone (2006). This model only considers a single group of microorganism, hydrogen sulfate reducing bacteria (hSRB) that can oxidise hydrogen, with sulfate as electron acceptor to produce hydrogen sulfide according to the equation:

hSRB $$4H_2 + H_2SO_4 \rightarrow H_2S + 4H_2O$$ **Eq. 2**

This group of sulfate reducers are competing with hydrogen utilisers. According to Batstone et al. (2006), this simplified model is effective in predicting the behaviour with influent S:COD of up to 0.1 g S g COD^{-1}. It is said that above this level the sulfate reducers will start to oxidise the VFAs as well and the model will incorrectly predict the sulfate in the effluent, and there will be underprediction of the H_2S in the gas stream.

This is recommended by Batstone et al. (2002) and could also be potentially applied to any model as long as hydrogen and bicarbonate are included as separate states. Addition to the current ADM1 Gujer matrix when including sulfate reduction is provided in Table 3. This means an addition of two processes: growth of sulfate reducing bacteria (sulfate reduction) and decay of the sulfate reducing bacteria; three new state variables: total reduced sulphides (S_{IS}), sulphates (S_{SO4}), and sulfate reducing bacteria (X_{hSRB}).

Table 3. Additional processes and components represented in the Gujer matrix.

Component →	**i**	**8**	**(8a) 25**	**10**	**11**	**13**	**(12a) 26**	**(23a) 27**	**Rate (ρ_j, kg COD·m^{-3}·d^{-1})**
j	**Process ↓**	**S_{h2}**	**S_{IS}**	**S_{IC}**	**S_{IN}**	**X_c**	**S_{SO4}**	**X_{hSRB}**	
(12a) 20	Sulfate reduction	-1	$(1-Y_{so4})$	$-(Y_{so4})*C_{bac}$	$-(Y_{so4})*N_{bac}$		$-(1-Y_{so4})/64$	Y_{so4}	$k_{m,so4} \frac{S_{so4}}{K_{S,so4}+S_{so4}} \frac{S_{h2}}{K_{S,h2}+S_{h2}} X_{hSRB} I_1$
21	Decay of X_{so4}					1		-1	$k_{dec,X_{hSRB}} * X_{hSRB}$
		Hydrogen gas (kg COD·m^{-3})	Sulfides (kg COD·m^{-3})	Inorganic carbon (M)	Inorganic nitrogen (M)	Composites (kg COD·m^{-3})	Sulfates (M)	Sulfate reducers (kg COD·m^{-3})	

H_2S inhibition is included and was chosen to be implemented the same way for H_2 inhibition of LCFA uptake, c4 uptake, and propionate uptake as used in ADM1 in BSM2 (Rosen and Jeppsson, 2006).

$$I\_h2s\_h2 = \frac{1}{1 + \frac{S\_h2s}{K\_I\_h2s\_h2}}$$ **Eq. 3**

Where I_h2s_h2 represents the inhibition of sulfide on hydrogen-degrading organisms. The value of S_h2s is calculated from the speciation model, taking into account the activities of hydrogen ion and HS^- in calculation of the H_2S in the aquaeous phase from the acid-base equilibrium equation.

pH inhibition of hSRBS are also included and are also implemented the same way as the pH inhibition for acetate, hydrogen, and amino acid degraders.

$$\mathrm{I\_pH\_hSRB} = \frac{\mathrm{pHLim\_hSRB}^{\mathrm{n\_hSRB}}}{\mathrm{pHLim\_hSRB}^{\mathrm{n\_hSRB}} + \mathrm{S\_H\_ion}^{\mathrm{n\_hSRB}}} \quad \textbf{Eq. 4}$$

Where:

$$\mathrm{pHLim\_hSRB} = 10^{-\frac{\mathrm{pH\_UL\_hSRB} + \mathrm{pH\_LL\_hSRB}}{2}} \quad \textbf{Eq. 5}$$

$$\mathrm{n\_hSRB} = \frac{3.0}{\mathrm{pH\_UL\_hSRB} - \mathrm{pH\_LL\_hSRB}} \quad \textbf{Eq. 6}$$

The physico-chemical model takes into account the H_2S/HS^- acid-base equilibrium, as well as the inclusion of SO_4^{2-} in the charge balance. It takes into account activities via the Davies equation instead of concentrations for calculation of equilibrium equations and pH, and at the same time considers ion pairing and acid-base reactions more detailed than those provided in the original ADM1.

H_2S gas stripping is also included as well into the calculation of the total gas pressure.

2.2. Model ADM1_S2

According to the model by Fedorovich et al. (2003), the sulfate reduction process is carried out by four groups of microorganisms: X_{hSRB}, hydrogenotrophic sulfate-reducing bacteria (hSRB); X_{pSRB}, propionate-degrading sulfate-reducing bacteria (pSRB); X_{bSRB}, butyrate-degrading sulfate-reducing bacteria (bSRB); and X_{aSRB}, acetotrophic sulfate-reducing bacteria (aSRB). Eqs. 2, 7, 8, and 9 shows the stoichiometric reactions describing the conversion of sulfate to hydrogen sulfide by different types of sulfate-reducing bacteria using specific kinds of substrate as electron acceptor.

The sulfate reduction model extension to the ADM1 by Fedorovich et al. (2003) was calibrated against experimental data from literature and was able to predict sulfate removal; concentrations of butyrate, propionate, and acetate; methane and biogas production.

pSRB $$C_2H_5COOH + 0.75H_2SO_4 \rightarrow CH_3COOH + CO_2 + H_2O + 0.75H_2S$$ **Eq. 7**

bSRB $$C_3H_7COOH + 0.5H_2SO_4 \rightarrow 2CH_3COOH + 0.5H_2S$$ **Eq. 8**

aSRB $$CH_3COOH + H_2SO_4 \rightarrow 2CO_2 + 2H_2O + H_2S$$ **Eq. 9**

Due to the ability of SRBs to utilize other substrates during methanogenesis results in competition for these substrates. Three levels of substrate competition were described by Fedorovich et al. (2003): (1) between SRB and acidogenic bacteria for sugars and amino acids, (2) between SRB and acetogenic bacteria for VFAs, and (3) between SRB and methanogens for acetate and hydrogen.

The first level is won by acidogenic bacteria therefore there is no need to modify the disintegration and hydrolysis part of the ADM1. On the other hand, SRB are found to successfully compete with acetogenic and methanogenic bacteria indicating that to describe the VFA and hydrogen removal, sulfate reduction should be included in the model.

Table 3.1 Biochemical rate coefficients ($\nu_{i,j}$) for S model extension components

Component → i		4	5	6	7	8	13	14	15	16	24	30	31	32	33	34	35
j	Process ↓	S_{va}	S_{bu}	S_{pro}	S_{ac}	S_{h2}	S_I	X_{ch}	X_{pr}	X_{li}	X_I	S_{SO4}	S_{H2S}	X_{hSRB}	X_{aSRB}	X_{pSRB}	X_{c4SRB}
26	Growth of X_{hSRB} on S_{h2}					-1						$-\frac{(1-Y_{hSRB})}{64}$	$(1-Y_{hSRB})$	Y_{hSRB}			
27	Decay of X_{hSRB}						$f_{sI,xb}$	$f_{ch,xb}$	$f_{pr,xb}$	$f_{li,xb}$	$f_{xI,xb}$			-1			
28	Growth of X_{aSRB} on S_{ac}				-1							$-\frac{(1-Y_{aSRB})}{64}$	$(1-Y_{aSRB})$		Y_{aSRB}		
29	Decay of X_{aSRB}						$f_{sI,xb}$	$f_{ch,xb}$	$f_{pr,xb}$	$f_{li,xb}$	$f_{xI,xb}$				-1		
30	Growth of X_{pSRB} on S_{pro}			-1	$0.57\ (1-Y_{pSRB})$							$-\frac{0.43\ (1-Y_{pSRB})}{64}$	$0.43\ (1-Y_{pSRB})$			Y_{pSRB}	
31	Decay of X_{pSRB}						$f_{sI,xb}$	$f_{ch,xb}$	$f_{pr,xb}$	$f_{li,xb}$	$f_{xI,xb}$					-1	
32	Growth of X_{c4SRB} on S_{bu}		-1		$0.8\ (1-Y_{c4SRB})$							$-\frac{0.2\ (1-Y_{c4SRB})}{64}$	$0.2\ (1-Y_{c4SRB})$				Y_{c4SRB}
33	Growth of X_{c4SRB} on S_{va}	-1		$0.54\ (1-Y_{c4SRB})$	$0.31\ (1-Y_{c4SRB})$							$-\frac{0.15\ (1-Y_{c4SRB})}{64}$	$0.15\ (1-Y_{c4SRB})$				Y_{c4SRB}
34	Decay of X_{c4SRB}						$f_{sI,xb}$	$f_{ch,xb}$	$f_{pr,xb}$	$f_{li,xb}$	$f_{xI,xb}$						-1
		Total valerate (kg COD·m^{-3})	Total butyrate (kg COD·m^{-3})	Total propionate (kg COD·m^{-3})	Total acetate (kg COD·m^{-3})	Hydrogen (kg COD·m^{-3})	Soluble inerts (kg COD·m^{-3})	Carbohydrates (kg COD·m^{-3})	Proteins (kg COD·m^{-3})	Lipids (kg COD·m^{-3})	Particulate inerts (kg COD·m^{-3})	Sulfate (kmol S·m^{-3})	Hydrogen sulfide (kg COD·m^{-3})	H_2-degrading SRB (kg COD·m^{-3})	ac-degrading SRB (kg COD·m^{-3})	pro-degrading SRB (kg COD·m^{-3})	C4-degrading SRB (kg COD·m^{-3})

Two stages of inhibition are described by Chen et al. (2008) as a result of sulfate reduction in anaerobic digestion. The first one is due to competition for common substrates which results in suppression of methane production. The other inhibition is due to toxicity of several bacterial groups, including SRB themselves, to sulfide. The reduced product, sulfide, is inhibitory, wherein the fully associated form (H_2S) is the inhibitory agent (Speece, 1996).

H_2S inhibition is again included as:

$$\mathrm{I\_h2s\_i} = \frac{1}{1 + \frac{\mathrm{S\_h2s}}{\mathrm{K\_I\_h2s\_i}}} \qquad \textbf{Eq. 7}$$

Where i = hSRB, h2, c4, pro, and ac, each representing the inhibition of sulfide on sulfate reducers, hydrogen-, c4-, propionate-, and acetate-degrading organisms.

2.3. Conclusions

Modelling of sulfur is important to consider in ADM1 especially if the influent waste stream contains significant amounts of sulfate. This modelling could help in predicting H_2S in the gas phase and in the future aid in designing control strategies for sulfate and H_2S removal as well as in modelling the risk associated with H_2S production.

Two methods of modelling sulfate reduction during anaerobic digestion is presented here. Model ADM1_S1 is suggested by Batstone et al. (2003) for influent having low S/COD ratio. This simplified model assumes only hydrogen as electron acceptor to reduce sulfate to H_2S. Model ADM1_S2, on the other hand, is suggested by Fedorovich et al. (2003) is a more general model which takes into account several substrates, such as hydrogen, propionate, butyrate, and acetate, as electron acceptors to reduce sulfate into H_2S.

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