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Simulating the Degradation of Odor Precursors in Primary and Waste-Activated Sludge During Anaerobic Digestion

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Abstract Degradation of known odor precursors in sludge during anaerobic digestion was systematically studied and simulated using the Anaerobic Digestion Model Number 1 (ADM1). The degradation of various protein fractions (particulate, soluble, and bound), volatile fatty acids (VFAs), lipids, and amino acids of primary sludge (PS) and waste-activated sludge (WAS) were monitored during anaerobic digestion. The degradation kinetic constants of the odor precursors namely, protein, lipid, and VFAs were determined. Relationships between degradations of protein fractions and volatile suspended solid were established; a strong relationship between bound protein, a major odor precursor, and volatile suspended solid degradation was found. No statistically significant difference in bound protein reduction was observed between PS and WAS. ADM1 was successfully used to simulate the lab scale continuous anaerobic digestion; model results with optimized parameters showed good agreement with the experimental data for methane production and several other sludge parameters including odor precursors such as lipids, VFAs, and proteins.

Keywords Anaerobic digestion · Odors precursors · Cell protein · Bound protein · ADM1 model

Introduction

Anaerobic fermentation is the most commonly applied process for stabilization of biosolids. A disadvantage of the fermentation technique is the slow degradation rate of biosolids; usual residence times in anaerobic digesters are about 20–40 days, requiring large digesters. Noxious odor production during anaerobic digestion and from the stored biosolids is considered to be a significant disadvantage of this useful process [1].

Although H_2S is considered to be the most prevalent odor compound, there are typically other organic odorous compounds, such as mercaptans and amines, present in anaerobic

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digestion. Prior research has implicated volatile sulfur compounds (VSCs) including hydrogen sulfide (H_2S), methanethiol or methyl mercaptan (MT), dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide in odors from biosolids [2]. In addition to VSCs, ammonia and volatile fatty acids (VFAs), phenols are also implicated as possible odor causing compounds in the excretion of pigs, cattle, and human wastes [3].

Laboratory tests have indicated that protein degradation and, especially the degradation of methionine, an amino acid, is the main source for the production of VSCs. Proteins are hydrolyzed by extracellular enzymes (proteases) into their constituent polypeptides and amino acids. The pathway for the production of MT from methionine is described as [2]:

$$\text{Proteins} \xrightarrow[\text{enzyme}]{\text{Protease}} \text{Polypeptides} \xrightarrow[\text{enzyme}]{\text{Peptidase}} \underset{\text{Methionine}}{C_4H_8O_2NSCH_3} \xrightarrow[\text{Lyase}]{\text{Methionine}} \underset{\text{Methanethiol}}{HSCH_3}$$

Hydrogen sulfide (H_2S) can be formed from the degradation of cysteine, sulfur-containing amino acid, as shown below:

$$\text{Proteins} \xrightarrow[\text{enzyme}]{\text{Protease}} \text{Polypeptides} \xrightarrow[\text{enzyme}]{\text{Peptidase}} \underset{\text{Cysteine}}{C_3H_6O_2NSCH_3} \xrightarrow[\text{Lyase}]{\text{Cysteine}} \underset{\text{Hydrogen Sulphide}}{H_2S}$$

While the carbohydrate, lipid, and protein content of municipal biosolids often accounts for the majority (90%) of the organic load [4], in some industries, protein is the predominant part of the organic load. For example, the protein component of a dairy wastewater stream can account for more than 40–60% of the total chemical oxygen demand [5]. Although the presence of proteins has been confirmed in the organic matter of treated municipal waste water and sludge [6], literature on protein degradation during anaerobic digestion is both sparse and contradictory.

In a pioneering work, Breure et al. [7] studied degradation of a model protein, gelatin, in controlled anaerobic digestion, and observed that it was converted at high rates and to a substantial extent to volatile fatty acids. Since proteins, carbohydrates, and lipid are almost always present simultaneously in biosolids, complete degradation of protein in the presence of carbohydrates may not be achieved as glucose and other easily fermentable substrates can repress the synthesis of exoproteases (a necessary enzyme) in pure cultures of bacteria [7], and the degradation of gelatin was retarded by increasing concentrations of carbohydrates present in the feed as a second substrate. In contrast, in a controlled study, it was found that as much as 70% of the protein was broken down in the acidogenic reactor and inclusion of protein had no effect on the reaction pathway for lactose degradation [8].

Proteins in wastewater and sludge are generally divided into three fractions: soluble, bound/labile (loosely attached with the cells), and tightly bound fractions (within the bacterial cells) [2]. Labile proteins are thought to become readily bioavailable during dewatering giving rise to higher odor potential [9].

Mathematical anaerobic digestion models (ADM) have been extensively investigated and developed during the last three decades [10]. As one of the most sophisticated and complex ADM, the Anaerobic Digestion Model No. 1 (ADM1) is the integrated anaerobic model developed by the International Water Association Task Group for modeling of Anaerobic Digestion Processes [4]. It consists of a number of processes to simulate all possible reactions occurring in anaerobic sludge digestion including not only biological reactions, such as disintegration and hydrolysis of suspended solids, uptake (growth), and decay of microorganisms, but also physico-chemical reactions, including ion association/dissociation and liquid–gas transfer. In total, 19 processes, 24 components, and 56 relative stoichiometric and kinetic parameters are assumed for biological

processes. Some of the limitations of this model include the absence of phosphorus modeling and the fate of sulfur compounds. This includes the generation of H_2S in the digester gas and the fate of sulfur species in the digested sludge, as a predictor of odor-generating potential [11].

Although Higgins et al. [2] studied the fate of odor precursors (such as protein) in anaerobic digestion, systematic research on odor precursors in anaerobic digestion of municipal biosolids is very limited [1]. The objectives of this work are to monitor the degradation of various protein fractions (particulate, soluble, and bound) in primary and secondary municipal sludge during anaerobic digestion, determine the relationship between degradations of various protein fractions and volatile suspended solids in the sludge, simulate the degradation of odor precursors such as protein, lipids, and VFAs, and estimate their kinetic constants using ADM1.

Materials and Methods Primary sludge (PS), waste-activated sludge (WAS), and anaerobic sludge (seed sludge) were obtained from a full-scale anaerobic digester at St. Marys, Water Pollution Control Plant (Ontario, Canada) twice a week. The sludges were then stored in a cool room at 4 °C. Four 4-L reactors were used as anaerobic bioreactors, with a working volume of 3.5 L and hydraulic retention time of 14 days. The working volume in all reactors was filled with anaerobic sludge at the beginning. Subsequently, two reactors (duplicates) were fed with 250 mL/day of primary sludge and the other two (duplicates) were fed with 250 mL/day of waste-activated sludge. The reactor contents were continuously mixed using the WU-50007-30 Cole-Parmer® Stir-Pak® mixer. A temperature of 38 °C was maintained by using hot water recycled from a water bath, and pH was controlled in a narrow range of 6.5–7.5 during the experiments using either NaOH or HCl. Both influent and effluent of the reactors were analyzed once a week over the entire duration of experiments. Biogas volume was measured using a Wet-Tip gas meter (Gas Meters for Laboratories, Nashville, TN). All four reactors were operated continuously over a period of 70 days and served to maintain constant inoculums for the experiments described. All the experiments and analysis were conducted in duplicates.

Analytical Standard methods [12] were used to determine total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), biological oxygen demand (BOD), total suspended solids (TSS), volatile suspended solid (VSS), alkalinity, lipid, total nitrogen (TN), total phosphorus (TP), and H_2S content of the biogas (iodometric method) and will not be described for brevity; only analysis procedures of VFAs and proteins are presented below. About 50 mL samples were centrifuged at 3,000×*g* for 15 min at 5 °C to separate the liquid and solids in the sample. The centrate was filtered with a 0.45-μm membrane, and the filtrate was used to measure the VFA concentrations using a gas chromatograph (Varian 8500, Varian Inc., Toronto, Canada) with a flame ionization detector equipped with a 30-m length×0.32-mm internal diameter fused silica column (CP-Sil 5 CB column) containing a 100% dimethyl polysiloxane phase. Helium was used as carrier gas at a flow rate of 5 mL/min. The temperatures of the column and detector were 110 °C and 250 °C, respectively. Protein was determined by micro-bicinchoninic acid protein assay (Pierce, Rockford, USA), which was modified by Lowry et al. [13]. Methane was determined by injecting 0.5 mL of the biogas composition into a gas chromatograph (Model 310, SRI Instruments, Torrance, CA) equipped with a 182.88-cm length×0.3175-cm internal diameter thermal conductivity detector (TCD) and a molecular sieve column (Mol sieve 5A, mesh 80/100) with Silcosteel® Coated Tubing. The temperatures of the column and the TCD detector were 90 °C and 105 °C, respectively. Argon was used as carrier gas at a flow rate of 30 mL/min.

Anaerobic Digestion Simulation ADM1 is a complex model involving many input parameters in addition to the interrelation between the decay and the regeneration cycles of microorganisms [14]. The decay processes of all microorganisms result in the production of carbohydrates, proteins, and lipids, which can be used as substrates after disintegration and hydrolysis. The regeneration of organic matter from biomass decay makes the model more complex [14]. Inhibition and gas transfer are also complex steps in the model. The default stoichiometric matrix and rate of reactions equations described by the ADM1 technical report [4] were used. MATLAB 2008 (The MathWorks, Inc. Natick, US) ODE23S ordinary dynamic equation solver was used to solve the dynamic differential and algebraic system of equations.

Statistical Analysis The Student *t* test was used to test the hypothesis of equality at the 95% confidence level. The null hypothesis was defined as no difference between the two groups tested vs. the alternative hypothesis that there is a statistical difference between the two groups.

Results and Discussion

Performance of Anaerobic Digesters

The biodegradability of waste components in anaerobic digestion varies widely [15] depending on many factors, such as the concentration and components of sludge, types and amount of anaerobic bacteria, organic loading rate, hydraulic residence time, temperature, and pH. The reductions of TSS, VSS, TCOD, SCOD, and BOD are usually used to evaluate the removal efficiency of waste substances in anaerobic digestion.

Steady-state data collection was after 30 days of operation corresponding to two turnovers of the mean SRT, and steady-state reductions of TSS, VSS, TCOD, and SCOD in both PS and WAS are shown in Fig. 1(a–d), respectively. A summary of the steady-state performance data for the digesters is also shown in Table 1. Average TSS reduction of 42±5% and 27±3%, VSS reduction of 54±1.7% and 36±2%, TCOD reduction of 55±1.2% and 39±2.3%, and SCOD reduction of 71±3.9% and 59±3% for PS and WAS, respectively, are in consistent with the literature [15–17]. Average $TBOD_5$ reduction was 78±5% and 61±3.7% for PS and WAS, respectively, on the other hand, TN and TP removal in both systems were insignificant (practically zero) as expected and not identifiable within the analytical accuracy. In both PS and WAS, the order of reductions was: $TBOD_5$ > SCOD > TCOD > VSS > TSS. The above results indicate that WAS is more difficult to be degraded than PS as widely reported in the literature [18, 19].

The accumulation of methane from PS was greater than that in WAS as the total experimental methane was 84±1.6 and 49±0.1 L vs. theoretical methane of 89±1.3 and 41±0.5 mL, respectively. Experimental methane production rates were 1.2 and 0.7 L/days vs. theoretical production rate of 1.3 and 0.6 L/days for PS and WA, respectively. Theoretical methane was determined based on CH_4 equivalent COD of 0.395 L CH_4/gCOD at 37 °C [20].

It is necessary to note that in the case of PS the theoretical values of CH_4 were 6% higher than the experimental values, while the opposite (19% lower) was observed in the case of WAS. Nonetheless, based on the results obtained from the *t* test analysis, we can conclude that there is no statistically significant difference between experimental and theoretical methane for both PS and WAS at the 95% confidence level.

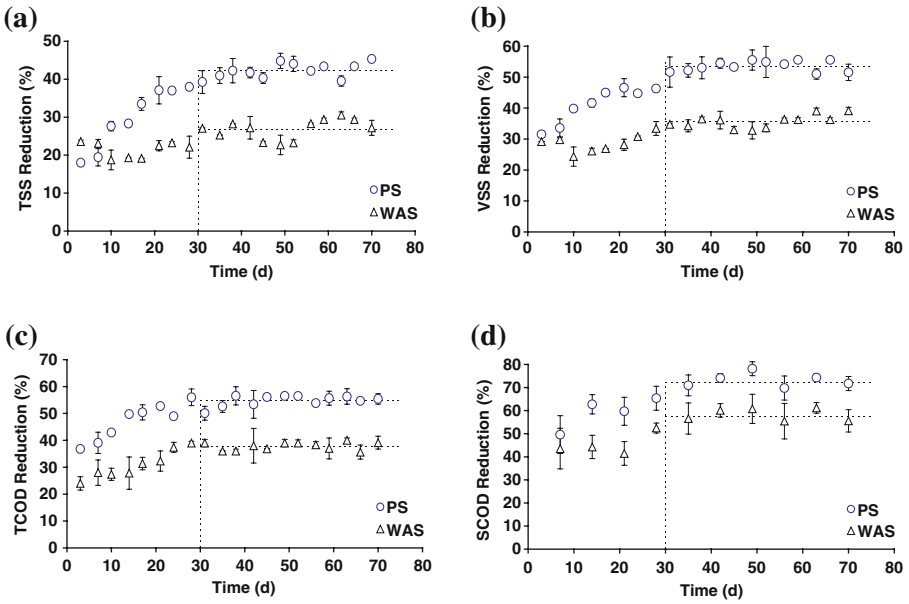

Fig. 1 Reduction in PS and WAS in anaerobic digestion. **a** TSS. **b** VSS. **c** TCOD. **d** SCOD

The composition of biogas in both systems is shown in Table 1. Although the WAS digester exhibited lower VSS and COD destruction efficiencies, higher methane content was observed at 62% vs. 54% in the PS digester. The above results indicated that both PS and WAS digestion reactors were working well and produced expected results.

Odor Precursors

Volatile Fatty Acids Figure 2a shows the influent concentrations of the volatile fatty acid components in PS and WAS. The concentration of VFA in PS (1,855±58 mg/L) was much higher than that of WAS (506±17 mg/L). For PS, acetic acid (482±59 mg/L), propionic

Table 1 Performance of AD during PS and WAS runs

	Steady-state performance [AVG±SD (*n*)]					
	Primary sludge (mg/L)		Waste-activated sludge (mg/L)		Ave. red. (%)	
Parameter	Influent	Effluent	Influent	Effluent	PS	WAS
TSS	20,521±768(12)	11,843±627(24)	17,914±721(12)	13,138±412(24)	42.3	26.5
VSS	15,729±1,364(12)	7,990±679(24)	12,728±397(12)	8,485±611(24)	53.7	35.7
TCOD	30,827±1,223(12)	13,931±1,010(24)	23,402±1,069(12)	14,288±477(24)	54.8	38.6
SCOD	3,078±61(12)	878±77(24)	2,092±212(12)	852±69(24)	71.4	58.5
$TBOD_5$	7,532±542(6)	1,690±434(12)	7,345±798(6)	2,886±463(12)	77.6	60.7
	54.0±3.0	CH_4 %	62.0±3.0	CH_4 %		
	44.5±5.0	CO_2 %	36.2±4.0	CO_2 %		
	1.06±0.4	H_2S %	1.62±0.5	H_2S %		

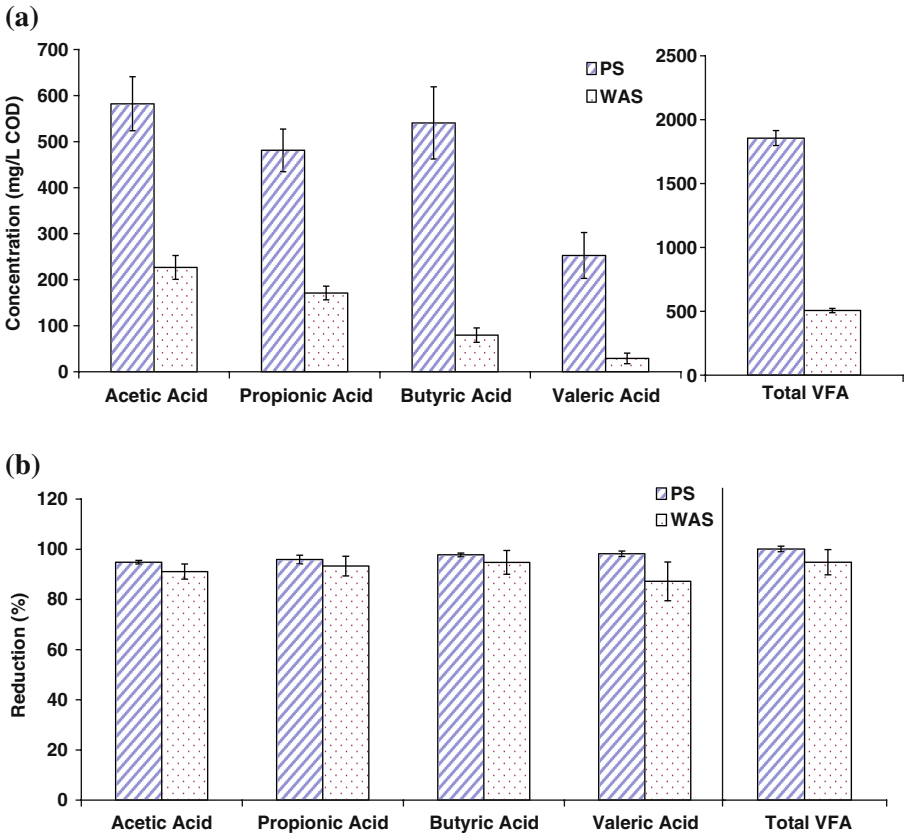

Fig. 2 Average VFA in PS and WAS. **a** Influent concentrations. **b** Reduction

acid (481±46 mg/L), and butyric acid (540±79 mg/L) were the predominant VFA, while in WAS only acetic and propionic acid concentrations were high at 226±26 and 171±15 mg/L, respectively. The ratio of VFA in PS to WAS was around 3.7. The average VFA/SCOD ratios were 2.2% and 0.6% for PS and WAS, respectively.

Higher concentrations of the organic acid in PS may indicate septicity of the sludge [21]. In addition, higher concentrations of VFAs after anaerobic digestion in PS indicate greater odor potential for this sludge. Figure 2b presents the average reduction of each VFA for both systems. The removal efficiencies are very high for all volatile acids. The average VFA reduction reached 97±1% for PS and 92±5% for WAS.

Protein Fractions Table 2 displays the average influent concentrations of various protein fractions in PS and WAS. Soluble protein was 12% and 10% of the SCOD for PS and WAS, respectively, while the particulate protein was 9% and 12% of the particulate COD. The labile and particulate protein fractions of the PS were lower than those of WAS, whereas higher soluble protein was observed in the PS compared to WAS. The relatively higher labile and particulate protein concentrations in WAS relative to PS are reasonable since labile and particulate proteins are associated with bacterial cell mass and the WAS is

Table 2 Average concentrations and reductions of various protein fractions in PS and WAS

Proteins	Primary sludge (mg/L)			Waste-activated sludge (mg/L)		
	Influent	Effluent	Red. (%)	Influent	Effluent	Red. (%)
Soluble protein (mg/L)	387±98			230±77		
Particulate protein (mg/L)	2,158±119			2,531±87		
Bound protein (mg/L)	380±37	158±16	61.4±4.8	702±33	294±28	58.5±3.2
Cell protein (mg/L)	1,777±92	1,204±82	31.2±5.0	1,828±64	1,481±71	18.0±5.5
Particulate Protein (g/gVSS)	0.133	0.171		0.199	0.211	
Bound Protein (g/gVSS)	0.024	0.020		0.055	0.036	
Cell Protein (g/gVSS)	0.110	0.151		0.143	0.174	

primarily biomass. As seen above, average reduction of soluble protein and particulate protein in PS was 67±3.4% and 40±2.5%, respectively, which is slightly higher than that of WAS, 61±3.2% and 31±3%, respectively.

Figure 3a shows that particulate protein reduction correlated well with the VSS reduction in both PS and WAS with R^2 of 85% and 82%, respectively. Since particulate protein is composed of the cellular protein and bound protein (loosely attached with the cell), it is also considered as a component of VSS, and the correlation of its degradation with that of VSS is reasonable. As indicated earlier, odor potential is directly related to the labile/bound protein content in sludge/biosolids [2, 22] and its removal can substantively reduce the malodor of sludge.

The average reduction of bound or labile protein for both PS and WAS were 61±4.8% and 59±3%, respectively. It is also noticeable that there is no statistically significant difference between the bound protein reductions in both PS and WAS at the 95% confidence level. Figure 3b shows the relationship between bound protein reduction and VSS reduction; bound protein reduction increases from 45% to 68% with VSS reduction from 28% to 37% in the case of PS. For WAS, bound protein reduction increased from 51% to 67% with VSS reduction changed from 31% to 50%; bound protein or the labile fraction of protein reduction are also positively correlated with VSS reduction. Further analysis was conducted using the particulate protein data. The difference between particulate and bound protein is the cellular protein of the bacterial mass; degradations of bound and cell protein in both PS and WAS are compared in Table 2. Although, bound protein removals in both sludges were comparable, the cellular protein removal was slightly higher in PS than WAS consistent with the relatively higher VSS destruction in PS. Cell protein removal was reasonably correlated with VSS removal (Fig. 3c). Bound protein removal was better than cell protein in both sludges reflecting the biodegradability of bound protein [14].

The particulate protein content was normalized with respect to VSS content and is presented in Table 2 for the raw and digested sludges. As expected, WAS has more particulate protein than PS due to the fact that WAS is predominantly biomass and both bound and cell protein are parts of the biomass in WAS. Data in Table 2 confirm that bound protein per unit mass of VSS in primary sludge and WAS decreased by about 17% and 33%, respectively, implying that odor generation potential downstream of anaerobic digestion is mitigated not only as a result of anaerobic VSS reduction, but also by a

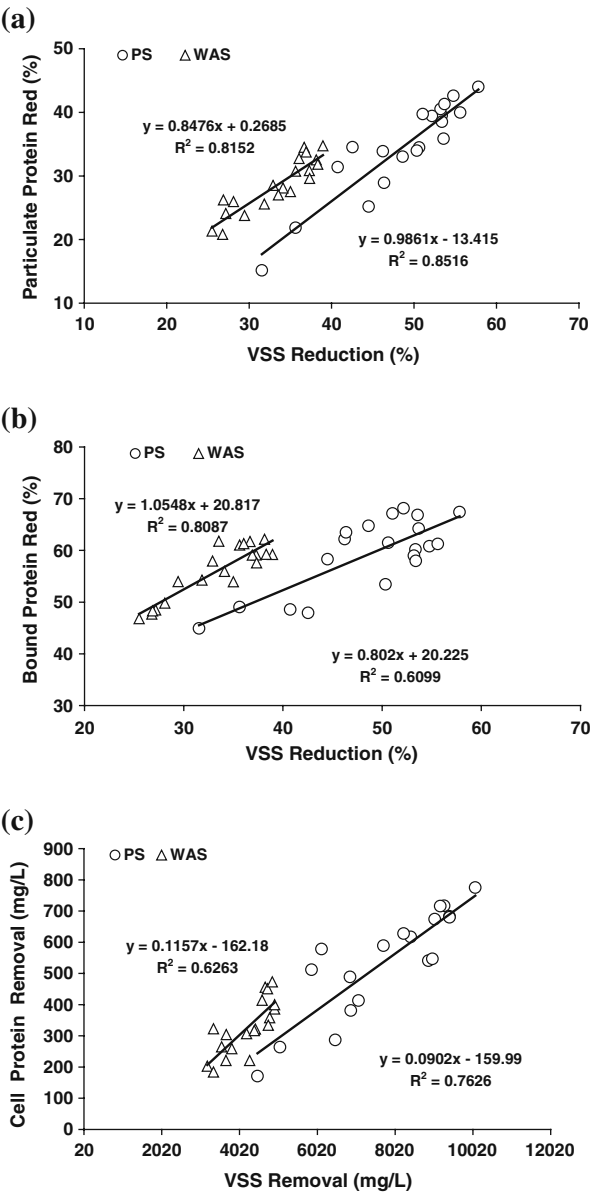

Fig. 3 Relationship between VSS degradations and protein fractions during anaerobic digestion for PS and WAS. **a** Particulate. **b** Bound. **c** Cell

reduction in bound/labile protein per unit mass, as bound protein is also a constituent of VSS. In this study, cell protein removal was only about 7–8% of the VSS removal.

Lipid Degradation Lipids are also a source of odor [23]. The average concentrations of lipids in raw PS and WAS were 1,486±423 and 367±144 mg/L, respectively. Compared to other constituents, lipid reduction for both types of sludges exhibited greater variability, as reflected by the steady-state averages of 64±6.8% and 38±4.7% for PS and WAS, respectively. The higher lipid reduction in PS is intriguing as fats and greases, which predominate in PS, are generally less biodegradable than oils [24].

Kinetics and Simulation of Odor Precursors

The steady-state ADM1 had been used with good success for approximately 2 years on a wide range of full-scale wastewater treatment facilities [10, 25, 26]. All biochemical extracellular solubilization steps are divided into disintegration and hydrolysis, of which the first is a largely non-biological step and converts composite particulate substrate to inerts, particulate carbohydrates, protein, and lipids. The second is enzymatic hydrolysis of particulate carbohydrates, proteins, and lipids to monosaccharides, amino acids, and long-chain fatty acids (LCFA), respectively. Disintegration is mainly included to describe degradation of composite particulate material with lumped characteristics (such as primary or waste-activated sludge), while the hydrolysis steps are to describe well defined, relatively pure substrates (such as cellulose, starch, and protein feeds). All disintegration and hydrolysis processes are represented by first order kinetics. Two separate groups of acidogens degrade monosaccharide and amino acids to mixed organic acids, hydrogen, and carbon dioxide. The organic acids are subsequently converted to acetate, hydrogen, and carbon dioxide by acetogenic groups that utilize LCFA, butyrate and valerate (one group for the two substrates), and propionate. The hydrogen produced by these organisms is consumed by hydrogen-utilizing methanogenic bacteria and the acetate by aceticlastic methanogenic bacteria. Death of biomass is represented by first order kinetics, and dead biomass is maintained in the system as composite particulate material. Inhibition functions include pH (all groups), hydrogen (acetogenic groups), and free ammonia (aceticlastic methanogens). pH inhibition is implemented as one of two empirical equations, while hydrogen and free ammonia inhibition are represented by non-competitive functions. The other uptake-regulating functions are secondary Monod kinetics for inorganic nitrogen (ammonia and ammonium), to prevent growth when nitrogen is limited, and competitive uptake of butyrate and valerate by the single group that utilizes these two organic acids [4].

Total protein, lipids, carbohydrate, inert particulates, as well as soluble components that include amino acids, long-chain fatty acids, sugars, and VFAs were the model inputs with protein (measured) based on $C_5H_7NO_2$, lipid (measured) based on $C_{57}H_{104}O_6$ [26], inert particulates (measured as TS minus VS), carbohydrate (estimated from the particulate COD mass balance), long-chain fatty acids (measured), amino acids (measured as soluble protein), sugars (estimated from the soluble COD balance), acetate (measured), propionate (measured), and butyrate (measured). The various components of biomass, i.e., sugar, amino acid, long-chain fatty acids, valerate and butyrate, propionate, acetate, and hydrogen degraders, all were set to zero following the recommendation of Batstone et al. [4]. The input values of ADM1 parameters as percentages of particulate chemical oxygen demand were 10% protein, 15% lipids, and 57% carbohydrate with sugars, amino acids, long-chain fatty acids, and VFAs contributing 2%, 8%, 5%, and 60% of the SCOD, respectively, in the case of PS, while in the case of WAS, the corresponding contribution of protein, lipid, and carbohydrate to PCOD were 6%, 5%, and 55% with sugars, amino acids, long-chain fatty acids, and VFAs contributing 13%, 7%, 27%, and 24% of the SCOD, respectively. It is evident that PS contained higher percentage of lipids and VFAs than WAS, while the sugars and long-chain fatty acids were higher in WAS than PS. The kinetics, stoichiometric, and physico-chemical parameters used in this simulation are the recommended/default values reported in the ADM1 technical report [4], whereas the modified (optimized) kinetics parameters were determined after calibration of the ADM1 simulations with the experimental data of the anaerobic reactors used in this work. It is important to mention that the reaction rates (kinetics) vary widely based on the type of sludge or substrate used; Christ et al. reported that the hydrolysis rate coefficient (k) were in the range of 0.025–0.2,

0.015–0.075, and 0.005–0.01 day^{-1} for carbohydrates, proteins, and lipids in sewage sludge, respectively [14]; Gujer and Zehnder reported that the k were in the range of 0.041–0.13, 0.02–0.03, and 0.08–0.4 day^{-1} [4]; O'Rourke et al. found them to be 0.21–1.94, 0.0096–0.1, and 0.0096–0.17 day^{-1} in PS [4]; while Batstone et al. reported that k was 0.25 day^{-1}±100%, 0.2 day^{-1}±100%, and 0.1 day^{-1}±300% [4].

The first step was to set the initial (default) values for all model parameters. Subsequently, the simulation was undertaken to fit the model output to the experimental data. Based on the simulation outcome, the kinetic values were optimized. Initial parameter values, percent variation, and estimated parameter values for PS and WAS that better fit the experimental data are given in Table 3. To better describe the process, the initial values of the carbohydrate, lipid, and protein hydrolysis rate coefficients, for example, were set based on the technical report [4], k_{hyd_ch}=0.25, k_{hyd_pr}=0.2, and k_{hyd_li}=0.1 day^{-1}, respectively, then ADM1 model was applied and its outcomes were compared to experimental data, based on the comparison the kinetics were optimized to k_{hyd_ch}=0.3, k_{hyd_pr}=0.05, and k_{hyd_li}=0.09 day^{-1} in the case of PS and k_{hyd_ch}=0.1, k_{hyd_pr}=0.03, and k_{hyd_li}=0.05 day^{-1} in the case of WAS. As expected, the hydrolysis kinetic parameters were higher in PS than WAS, since primary sludge contains more particulate substrates such as lipids, carbohydrates, and proteins than the WAS, which is predominantly biomass with large biopolymers that are more difficult to degrade. The relative ease of biodegradability of PS as compared to WAS is well documented in the literature [16]. Table 4 displays the influent and effluent sludge characteristics as well as the methane production along with the ADM1 predictions for both PS and WAS, respectively. It is evident that the model results with optimized parameters showed good agreement with the experimental data for methane production

Table 3 Default and optimized ADM kinetic parameters for both PS and WAS sludge

				ADM[a]	Varies within[a] (%)	Estimated PS	Estimated WAS
Hydrolysis	Carbohydrate	K_hyd_ch	day^{-1}	0.25	100	0.3	0.1
	Protein	K_hyd_pr	day^{-1}	0.2	100	0.05	0.03
	Lipids	K_hyd_li	day^{-1}	0.1	300	0.09	0.05
Maximum uptake rate	Sugars	km_su	day^{-1}	30	100	30	30
	Amino acids	km_aa	day^{-1}	50	100	4	5
	Long-chain fatty acids	km_fa	day^{-1}	6	300	6	6
	Propionic acid	km_pro	day^{-1}	13	100	15	20
	Acetic acid	km_ac	day^{-1}	8	100	8	11
	Valeric acid + Butyric acid	km_c4	day^{-1}	20	100	20	30
Half saturation constant	Sugars	Ks_su	$kgCOD/m^3$	0.5	100	0.5	0.5
	Amino acids	Ks_aa	$kgCOD/m^3$	0.3	30	0.3	0.3
	Long-chain fatty acids	Ks_fa	$kgCOD/m^3$	0.4	300	0.4	0.4
	Propionic acid	Ks_pro	$kgCOD/m^3$	0.1	100	0.1	0.1
	Acetic acid	Ks_ac	$kgCOD/m^3$	0.15	100	0.1	0.1
	Valeric acid + Butyric acid	Ks_c4	$kgCOD/m^3$	0.3	300	0.1	0.1

[a] Batstone et al. [4]

Table 4 Experimental influent and effluent characterization with the ADM prediction for primary and WAS sludge

	Exp. Influent	ADM Effluent	ADM	Reduction Exp. (%)	Reduction ADM (%)
Primary sludge					
Gas (L/d)	1.2	1.24			
SCOD (mg/L)	3,078	878	961	71	69
TCOD (mg/L)	30,827	13,931	14,627	55	53
Lipid (mg/L)	1,485.0	665	657.4	55	56
P Protein (mg/L)	2,158.0	1,367	1,281.5	37	41
Amino acid (mg/L)	193.5	81.5	85.2	58	56
Propionate (mg/L)	481	19	20.8	96	96
Butyrate (mg/L)	540	12	10.7	98	98
Valerate (mg/L)	252	4	4.9	98	98
Acetate (mg/L)	582	30	31.1	95	95
VFA (mg/L)	1,855.0	65.0	67.6	96	96
SCOD (mg/L)	3,078	878	961	71	69
TCOD (mg/L)	30,827	13,931	14,627	55	53
Lipid (mg/L)	1,485.0	665	657.4	55	56
P Protein (mg/L)	2,158.0	1,367	1,281.5	37	41
Amino acid (mg/L)	193.5	81.5	85.2	58	56
Propionate (mg/L)	481	19	20.8	96	96
Butyrate (mg/L)	540	12	10.7	98	98
Valerate (mg/L)	252	4	4.9	98	98
Acetate (mg/L)	582	30	31.1	95	95
VFA (mg/L)	1,855.0	65.0	67.6	96	96
Waste-activated sludge					
Gas (L/d)	0.68	0.65			
SCOD (mg/L)	2,092	852	788	59	62
TCOD (mg/L)	23,402	14,288	14,993	39	36
Lipid (mg/L)	367	215	228.3	41	38
P Protein (mg/L)	2,529	1,828	1,774.3	28	30
Amino acid (mg/L)	115	56	56.4	51	51
Propionate (mg/L)	171	11	13.6	94	92
Butyrate (mg/L)	80	5	6.3	94	92
Valerate (mg/L)	29	3	2.9	90	90
Acetate (mg/L)	226	19	19.5	92	91
VFA (mg/L)	506.0	38.0	42.2	92	92

with average percentage error of 3% and 5% for primary and WAS, respectively. Similar agreement was observed in case of odor precursors, namely, protein, VFAs, lipids, and amino acid as the percentage error were 6%, 4%, 1%, and 5% for PS and 3%, 11%, 6%, and 0.1% in the case of WAS, respectively. Maximum deviation in the fitted parameter values from the default values occurred for hydrolysis rate constant for protein and maximum uptake rate for amino acids.

Conclusions

Degradation of odor precursors such as VFA and bound protein in sludge during anaerobic digestion was systematically monitored and modeled using the ADM1. Below are the highlights of the major findings of this study:

1. In general, anaerobic digestion efficiency for all sludge primary parameters such as TSS, VSS, TCOD, SCOD, and $TBOD_5$ for primary sludge was higher than waste-activated sludge.
2. The concentration of VFA in the raw PS of 1,855±58 mg/L was considerably higher than the raw WAS of 506±17 mg/L, with average removal efficiencies during anaerobic digestion of 97±1% and 92±5%, respectively. The average concentrations of lipids in the raw PS and WAS were 1,486±423 and 367±144 mg/L, respectively, and the removal of lipid varied during anaerobic digestion.
3. Average reductions of various protein fractions were 40±2.5% and 31±3% for particulate protein, 67±3.4% and 61±3.2% for soluble protein, and 61±4.8% and 59±3% for bound or labile protein for PS and WAS, respectively. Reduction of bound protein or the labile protein, which is implicated in odor production in sludge, was positively correlated with VSS reduction for both sludges. No statistically significant difference was observed between the bound protein reductions in both PS and WAS. A 17% and 37% reduction in bound protein per unit VSS indicates a possible reduction in odor generation potential not only associated with stabilization of VSS, but also due to bound protein degradation.
4. The ADM1 was used to simulate the steady-state lab scale anaerobic digester. The model predicted well both the methane production and degradation of odor precursors. The model results with optimized parameters showed good agreement with the experimental data for methane production with average percentage errors of 3% and 5% for primary and WAS, respectively. Good agreement was also observed for protein, VFAs, lipids, and amino acids as reflected by percentage errors of 6%, 4%, 1%, and 5% in the case of PS and 3%, 11%, 6%, and 0.1% in the case of WAS, respectively.

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