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Approach of Describing Dynamic Production of Volatile Fatty Acids from Sludge

Alkaline Fermentation

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ABSTRACT. In this work, a mathematical model was developed to describe the dynamics of fermentation products in sludge alkaline fermentation systems for the first time. In this model, the impacts of alkaline fermentation on sludge disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis processes are specifically considered for describing the high-level formation of fermentation products. The model proposed successfully reproduced the experimental data obtained from five independent sludge alkaline fermentation studies. The modeling results showed that alkaline fermentation largely facilitated the disintegration, acidogenesis, and acetogenesis processes and severely inhibited methanogenesis process. With the pH increase from 7.0 to 10.0, the disintegration, acidogenesis, and acetogenesis processes respectively increased by 53%, 1030%, and 30% while methane production decreased by 3800%. However, no substantial effect on hydrolysis process was found. The model also indicated that the pathway of acetoclastic methanogenesis was more severely inhibited by alkaline condition than that of hydrogenotrophic methanogenesis.

Keywords: Production of volatile fatty acids, Sludge fermentation, Mathematical modeling

1. Introduction

Biological wastewater treatment is currently the most used process for treating municipal wastewater worldwide (Chen et al., 2016; Guerrero et al., 2012; Wang et al., 2012a; Wang et al., 2013a; Zhao et al., 2015a; Wang et al., 2017a). Large amounts of waste activated sludge (WAS), however, are produced as a byproduct (Hao et al., 2011; Ni and Yu, 2008; Wang et al., 2013b; Wang et al., 2014). WAS is generally employed to generate methane by anaerobic digestion process, because WAS consists of high contents of organic matters such as protein and carbohydrate (Appels et al., 2008; Wang et al., 2013c; Zhang et al., 2010a; Liu et al., 2016; Wang et al., 2017b). Compared with methane, volatile fatty acids (VFA), which a preferred carbon source for wastewater biological nutrient removal and also a raw material for biodegradable plastic production, is a more valuable and applicable substrate (Wang et al.,
Therefore, the production of VFA from sludge fermentation has recently attracted increasing attention (Ucisik and Henze, 2008; Wang et al., 2013d; Chen, et al., 2013; Luo et al., 2012), by which the amount of WAS is reduced, and the value added VFA is produced.

Several strategies such as thermal, Fenton, free nitrous acid, ozone, ultrasonic, acid, and alkaline treatments have been documented to promote VFA production from WAS (Carrère et al., 2010; Lee et al., 2014; Zhao et al., 2015b; Li et al., 2012). Among these, alkaline fermentation is considered as the most promising method since this approach can strongly inhibit the activities of methanogens (Zhang et al., 2010b; Zheng et al., 2013a). For example, Zhang et al. (2010b) found that the amount of total methanogenic *archaea* under pH 10.0 fermentation was much lower than that under neutral condition. It was further found that pH 10.0 fermentation significantly reduced the numbers of *Methanobacterium sp.* and *Methanobrevibacter sp.* (Zheng et al., 2013a). Previous work with both lab- and pilot-scale investigations showed that large amounts of VFA were accumulated under alkaline conditions (Yuan et al., 2006; Li et al., 2011). It is known that sludge fermentation contains several bio-transformation steps, and final products of sludge fermentation depend on the reaction kinetics of these transformations. Although extensive experimental investigations have been performed on this topic (Wang et al., 2013d; Lee et al., 2014; Zhao et al., 2015b; Zhang et al., 2010b; Zheng et al., 2013a), a mathematical model that can describe the dynamics of fermentation products in sludge alkaline fermentation are still lacking, which becomes one of major barriers for this technology applying in the full-scale situations.

Mathematical modelling is a powerful tool to fully understand the underlying mechanisms involved in the sludge fermentation systems. Also, it can effectively predict the dynamics of fermentation products in such systems. The most commonly used modelling toward a sludge digestion system is the International Water Association anaerobic digestion
model no. 1 (ADM1) (Batstone et al., 2002). This model includes the following bio-chemical reactions in anaerobic degradation, disintegration, hydrolysis, acidogenesis, acetogenesis, and two pathways of methanogenesis (namely acetoclastic methanogenesis and hydrogenotrophic methanogenesis). Based on this model, several extensions have been developed. For example, Ni et al. respectively incorporated the process of homoacetogenesis and the accumulation of storage polymers into the ADM1 (Ni et al., 2011; Ni et al., 2015). Zonta et al. (2013) introduced the inhibitory effects of long-chain fatty acids (LCFA) on anaerobic performance into the original model. However, all these models developed do not take into account the effects of alkaline condition on the fermentation products, which make all the existing models unable to remove this barrier. To date, mathematical model that can be used for describing sludge alkaline fermentation has seldom been proposed.

The aim of this work is to develop a mathematical model for describing the dynamics of fermentation products in the sludge alkaline fermentation systems. In such systems, free ammonia (FA) level would reach at high levels due to the high pH and high ammonium released (Zhao et al., 2015b; Li et al., 2016). It is reported that FA can lead to a strong biocidal impact on broad microorganisms, which may potentially impact the sludge fermentation under alkaline condition (Park, 2015). Thus, this new model was developed by incorporating the effects of FA into the widely used ADM1 model to describe the sludge alkaline fermentation. The validity and applicability of the new model developed were then examined by comparing simulation results with experimental data on fermentation products from four independent sludge alkaline fermentation studies using both full-scale and laboratory-scale WAS.

2. Materials and methods

2.1 Model development

The steps of disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis
are generally included in the sludge anaerobic digestion (Appels et al., 2008). Previous studies found that alkaline fermentation could effectively enhance sludge disintegration and inhibit methane production, which thereby achieved high levels of VFA accumulation (Wang et al., 2013d; Yuan et al., 2006). Moreover, all previous publications considered that alkaline condition was the main reason for VFA accumulation (Wang et al., 2013d; Zheng et al., 2013a; Yuan et al., 2006). However, ammonium was found to be substantially released in the sludge fermentation process (Zhao et al., 2015b; Li et al., 2016). It was indicated that the unionized form of ammonium, i.e., FA, caused a strong biocidal impact on many microorganisms (Park, 2015). The FA level in the fermentation systems is closely related to the pH value controlled and the ammonium released. The higher pH and ammonium are, the greater FA is. Therefore, the key factor for the increased VFA accumulation achieved in the sludge alkaline fermentation is likely due to the role of high FA levels under high pH and ammonium conditions. Hence, the promotion from FA on sludge disintegration and inhibitions of FA on VFA degradation and methane production were considered in the current biological model.

The new biological reaction kinetics were integrated with ADM1 to form the proposed new model with FA impacts for sludge alkaline fermentation (Batstone et al., 2002). The model describes the relationships mainly among twelve soluble variables, i.e., sugars, amino acids, LCFA, valerate, butyrate, propionate, acetate, hydrogen, methane, inorganic carbon, inorganic nitrogen, and soluble inerts, and thirteen particulate variables, i.e., particulate composites, carbohydrates, proteins, lipids, sugar degraders, amino acid degraders, LCFA degraders, valerate and butyrate degraders, propionate degraders, methanogenic Archaea (MA, grown on acetate or hydrogen), homoacetogens, and particulate inerts. Six types of biological processes were considered, namely disintegration of particulate composites, hydrolysis (carbohydrates, proteins and lipids), acidogenesis (from amino acids and sugars), acetogenesis (from LCFA, valerate, butyrate and propionate), methanogenesis, and homoacetogenesis.
Acidogenesis converts amino acids and sugars to fermentation products, namely hydrogen, acetate, propionate, butyrate, and valerate. Acetogenesis includes uptake of these products and LCFA. MA utilizes acetate and hydrogen as electron donors to produce methane.

Homoacetogens can use hydrogen and inorganic carbon to produce acetate.

Disintegration and hydrolysis are described by the first order kinetics, while kinetic control of the other enzymatic reaction rates is described by the Monod equation. Inorganic nitrogen can release or uptake during these processes. The promotion of FA on disintegration, and inhibitions from FA on acetogenesis and methanogenesis are also included. A promotion factor ($P_{FA}$) from FA was added into the kinetics of disintegration.

$$\frac{dX_c}{dt_{\text{degradation}}} = -k_{\text{dis}} X_c P_{FA}$$  \hspace{1cm} Eq.1

$$P_{FA} = \frac{S_{FA}}{K_p,FA} + 1$$  \hspace{1cm} Eq.2

Where, $P_{FA}$ indicates the promotion effect of FA on disintegration, $S_{FA}$ is the FA concentration, and $K_p,FA$ is the promotion constant of FA.

$$\frac{dS_{ac}}{dt_{\text{degradation}}} = -k_{\text{ac}} \frac{S_{ac}}{K_{ac} + S_{ac}} X_{ac} I_{\text{pH}} I_{\text{IN,lim}} I_{FA,ac}$$  \hspace{1cm} Eq.3

$$I_{FA,ac} = \frac{1}{1 + \frac{S_{FA}}{K_{FA,ac}}}$$  \hspace{1cm} Eq.4

Meanwhile, FA may inhibit acetogenesis and methanogenesis. Eqs. 3 and 5 are the kinetics of methanogenesis. $S_{H_2}$ is the hydrogen concentration while $I_{FA,ac}$ (Eq. 4) and $I_{FA,H_2}$ (Eq. 6) are the inhibition factors of FA on methanogenesis, respectively. $K_{FA,ac}$ and $K_{FA,H_2}$ are inhibition constant. For acetogenesis, a different inhibition factor ($I_{FA,other}$) is used (Eq. 8). Eq. 7 shows an example of propionate uptake, and $S_{pro}$ is the propionate concentration. Other inhibition factors in Eq. 7 are directly adopted from ADM1.

$$\frac{dS_{h_2}}{dt_{\text{degradation}}} = -k_{h_2} \frac{S_{h_2}}{K_{h_2} + S_{h_2}} X_{h_2} I_{\text{pH}} I_{\text{IN,lim}} I_{FA,h_2}$$  \hspace{1cm} Eq.5
\[ I_{FA,h2} = \frac{1}{1 + S_{FA} / K_I_{NH3,h2}} \]  
Eq.6

\[ \frac{dS_{pro}}{dt}_{\text{degradation}} = -k_{pro} \frac{S_{pro}}{K_{pro} + S_{pro}} X_{pro} h_2 I_{P HI,lim} I_{FA,other} \]  
Eq.7

\[ I_{FA,other} = \frac{1}{1 + S_{FA} / K_I_{NH3,other}} \]  
Eq.8

2.2 Experimental data for model evaluation

To evaluate the predictive capabilities of the developed model, experimental data collected from four independent case studies on sludge alkaline fermentation using both lab-scale and full-scale WAS were used. Among them, the data of Case I was collected from a batch sludge alkaline fermentation experiment in this work using WAS withdrawn from a bench-scale activated sludge process while the other data of Case II, Case III, and Case VI were derived from previous publications using WAS taken from real municipal wastewater treatment plants (WWTPs).

Case I, to obtain the bench-scale WAS for the subsequent alkaline fermentation, one sequencing batch reactor with a working volume of 50 L was operated. The seed sludge used here was taken from the secondary sedimentation tank of a municipal WWTP in Shanghai, China. The reactor was operated with three 8-h cycles daily. Each cycle contained approximately 90 min anaerobic, 80 min oxic, 50 min anoxic, 20 min oxic, 40 min anoxic, and 20 min, 55 min settling, 5 min decanting, and 120 min idle phases. During the first 5 min of the anaerobic phase 25 L synthetic wastewater was pumped into the reactor. The composition of the synthetic wastewater used was as follows (per liter), 448 mg CH\textsubscript{3}COONa, 120 mg NH\textsubscript{4}Cl, 44 mg KH\textsubscript{2}PO\textsubscript{4}, 0.01 MgSO\textsubscript{4}\cdot7H\textsubscript{2}O, 0.005 CaCl\textsubscript{2}, and 0.5 mL of a trace metal solution that was described previously (Wang et al., 2008; ). Air was supplied at a flowrate of 50 L/min during the oxic phases. In the decanting period, 25 L of the supernatant was discharged from the reactor, resulting in a hydraulic retention time of 16 h. Except for the
settling and decanting phases, the reactor was constantly mixed with a mechanic stirrer. The sludge retention time was approximately maintained at 20 d. During the domestication period, the effluent concentrations of phosphorus, ammonium, nitrite, and nitrate were determined twice weekly. It took about 64 d before these measured items reached relatively stable, and then the wasted sludge was used for the following sludge alkaline fermentation experiment. After concentrating at 4 °C for 12 h, it was determined that the wasted sludge included 14100 ± 380 mg/L total suspended solids (TSS), 11500 ± 290 mg/L volatile suspended solids (VSS), 15100 ± 260 mg/L total chemical oxygen demand (COD), 570 ± 16 mg/g VSS total protein, 245 ± 13 mg/g VSS total carbohydrate.

The batch fermentation test with three replicates was performed in one serum bottle with a working volume of 0.6 L at constant temperature (21 ± 1 °C). Firstly, 600 mL of the concentrated WAS, as mentioned above, was added into the bottle. The pH value of the sludge mixture was then adjusted to 10 by adding 4 M hydrochloric acid or 4 M sodium hydroxide. Afterwards, the bottle was flushed with nitrogen gas to remove oxygen, capped with a rubber stopper, sealed, and stirred at a speed of 80 rpm. During the entire fermentation process, the pH in the bottle was controlled at 10.0 ± 0.1. Fermentation mixture samples were taken periodically for the analysis of soluble chemical oxygen demand (SCOD), protein, carbohydrate, VFA, ammonium.

During the fermentation the gas production was periodically measured by releasing the pressure in the serum bottle using a 300 mL glass syringe to equilibrate with the room pressure according to the method documented in the literature (Owen et al., 1979). The methane fraction in the collected gas samples was measured by use of a gastight syringe to inject 0.2 mL of the samples into a gas chromatograph (GC112A, China), which equipped with a thermal conductivity detector and a 4mm × 32 m stainless column with nitrogen as the carrier gas. The flowrate of the nitrogen gas was at 30 mL/min. The temperatures of the
injection port, column, and detector were set at 40, 40, and 80 °C, respectively. The concentrations of VFA were determined by a HP5890 GC with flame ionization detector and equipped with a 30 m × 0.32 mm × 0.25 mm CPWAX52CB column. More detailed information was reported previously (Yuan et al., 2006). The measurements of ammonium, COD, TSS, and VSS were conducted in accordance with standard methods (APHA, 1998). Sludge levels of protein and carbohydrate were determined the same as described in the literature (Yuan et al., 2006).

Case II (Zhang et al., 2010b), the batch fermentation test of WAS collected from the secondary sedimentation tank of a municipal WWTP in Shanghai, China was performed in four identical reactors with a liquid volume of 5 L each. The main characteristics of WAS after concentration were 14.33 ± 0.56 g/L TSS, 10.02 ± 0.21 g/L VSS, 9.65 ± 0.16 kg COD/m³ total protein, and 2.32 ± 0.15 kg COD/m³ total carbohydrate. After the addition of WAS, all reactors were mechanically stirred at 100 rpm at ambient temperature (21 ± 1 °C). The pH in the four reactors was controlled at 7.0, 8.0, 9.0, or 10.0 during the entire fermentation period. For the analysis of SCOD, VFA, and methane variations, samples were taken from the reactors and measured periodically.

Case III (Chen et al., 2007), this batch test was carried out in two replicate reactors, each with a working volume of 1.5 L. The sludge used here was obtained from a municipal WWTP in Shanghai, China. It was measured that the sludge contained 13808 mg/L TSS, 10815 mg/L VSS, 13407 mg/L total COD, 8180 mg COD/L protein, and 1522 mg COD/L carbohydrate. The two reactors were maintained at room temperature (21 ± 1 °C) and mechanically stirred at 80 rpm. The pH in the two reactors was constantly maintained either at 9.0 or at 10.0 by adding 2M sodium hydroxide or 2M hydrochloric. The released protein and ammonium and the produced VFA were periodically determined in both reactors.

Case IV (Yan et al., 2010), the batch fermentation reactor was operated at 20 ± 1 °C in a
plexiglass reactor with a working volume of 1.0 L. The sludge was obtained from the secondary sedimentation tank of a municipal WWTP in Shanghai, China. The main characteristics of the sludge were 10119 mg/L TSS, 6982 mg/L VSS, 10004 total COD, 6159 mg COD/L protein, and 1026 mg COD/L carbohydrate. After the addition of the sludge, the reactor was stirred at a speed of 80 rpm. During the fermentation period, the pH in the reactor was constantly controlled at 10.0. Samples were periodically taken for the analysis of the released protein and carbohydrate and the produced VFA during fermentation period.

2.3 Evaluating the predictive capability of the model

The model developed contains 57 stoichiometric and kinetic parameters. Not all parameters were identifiable from the experimental data due to parameter correlation. Hence, the methodology has been to use typical parameter values reported in literature for sludge digestion processes including the kinetics of disintegration, hydrolysis, acidogenesis, acetogenesis, homoacetogenesis and methanogenesis, whenever possible. Of these, approximate 53 of these parameters are well established in previous models, thus these values reported in the literatures are adopted directly for these parameters. It is only estimated those parameters, which are unique to the developed model (i.e., $K_{p, V_A}$, $K_{I_{NH3, other}}$, $K_{I_{NH3, h2}}$ and $K_{I_{NH3, ac}}$), by fitting model predictions with the experimental data presented in the case studies. Parameter estimations were performed using AQUASIM. AQUASIM is a program, in which the spatial configuration of a model system is represented by compartments, which are connected by links. The program allows the user to define an arbitrary number of substances to be modelled and it is extremely flexible in the formulation of transformation processes. Execution of a simulation is equivalent to numerically integrating a system of ordinary and partial differential equations in time and simultaneously solving the algebraic equations. In AQUASIM, as a first step, the partial differential equations are discretized in space. Then, the spatially discretized partial differential equations together with the ordinary differential
equations and the algebraic equations are integrated numerically in time with the algorithm DASSL which is based on the implicit (backward differencing) variable-step, variable-order Gear integration technique. Model parameters represented by constant variables can be estimated by AQUASIM by minimizing the sum of the squares of the calculated model results (Reichert, 1998). Parameter values estimated in each case study are provided in Table 1.

3. Results and discussion

3.1 Model evaluation with the experimental data obtained from Case I

To assess the predictive power of the model developed in this work, the model was first tested with the experimental data of Case I. Figure 1 illustrates both the measured and predicted dynamics of sludge fermentation products at pH 10.0, and Table 1 shows the calibrated parameter values with the optimal model fittings with the experimental data.

With the increase of the fermentation time, the solubilized COD (i.e., SCOD) gradually increased. Meanwhile, the released ammonium also showed an increase trend in the fermentation period, which resulted in an increase of FA level. Although the level of soluble protein was much higher than the level of soluble carbohydrate, they exhibited a similar tendency of variation. In the first 2 d of fermentation, both the soluble protein and carbohydrate increased. However, further increase of fermentation time caused the decrease of both of them. This is because the released protein and carbohydrate undergo the hydrolysis and acidification processes. All the individual VFA increased with the fermentation time, which indicated that the process of methane production was effectively inhibited at pH 10.0. It was also found that acetic acid was the major VFA among these VFAs. The developed model in this study captured all these dynamics well. The good accordance between these simulated and determined data suggested that the mathematical model developed here effectively captured the sludge alkaline fermentation process.

3.2 Model evaluation with the experimental data obtained from Case II
In the second case, the experimental data obtained under pH 7.0 and pH 9.0 conditions were employed to calibrate the key kinetic values of the fermentation processes \( (K_{P, FA}, K_{I, NH3, \text{other}}, K_{I, NH3, h2}, \text{and } K_{I, NH3, ac}, \text{Table 1}) \), and the corresponding values obtained were used to simulate the dynamic profiles in comparison to the data obtained under pH 8.0 and pH 10.0 conditions as a validation.

From Figure 2, it can be seen that the particulate COD at all pH conditions decreased with the fermentation time accompanied with the increase of VFA. As the increase of pH value from 7.0 to 10.0, both the release of the particulate COD increased and the accumulation of VFA increased. For example, 4.5 kg/m\(^3\) of released particulate COD and 1.9 kg/m\(^3\) of accumulated VFA were measured at 13 d under pH 7.0 condition whereas the corresponding data were 6.9 and 2.9 kg/m\(^3\) at pH of 10.0, respectively. Although the amount of methane produced from all pH controlled systems was at low levels, the methane yield at pH 10.0 was lower than that at pH 7.0 (Dai et al., 2016). All these trends were captured reasonably well by the model developed in this study, which supported the predictive capability of this developed model.

3.3 Model evaluation with the experimental data obtained from Case III

To further assess the model developed in this work, the experimental data in terms of FA, VFA, and soluble protein collected from Case III were also used. The data obtained from pH 9.0 fermentation were used for calibration of the four kinetic parameters listed in Table 1 while the data of pH 10.0 fermentation were applied for validation of these kinetic values.

As shown in Figure 3, FA level increased with the fermentation time at both pH 9.0 and pH 10.0 conditions. Both the soluble protein and produced VFA increased at the initial days of fermentation, and further increase of fermentation time resulted in the decrease of both compounds. Compared with pH 9.0, all the FA, protein, and VFA levels were higher at pH 10.0 fermentation. In addition, the consumption of accumulated VFA at pH 10.0 was much
lower than that at pH 9.0. The predictions of our developed model matched well the experimental results, which supported again the predictive power of the model developed in this study.

3.4 Model evaluation with the experimental data obtained from Case IV

The developed model was finally evaluated using the experimental data obtained from Case IV (i.e., pH 10.0 fermentation using full-scale WAS with lower sludge concentration). The four kinetic parameter values calibrated at the maximum condition are also shown in Table 1, and the reproduced protein, carbohydrate, and VFA profiles with the established model as well as the experimental results are exhibited in Figure 4. It can be observed that the predicted data using the model established in this work matched the experimental data very well. The excellent agreement between the determined results and simulations further suggested that our developed model has capability to predict the dynamics of products in different sludge alkaline fermentation systems.

3.5 Discussion

Alkaline fermentation is the most promising approach for producing the valuable product, VFA, from sludge, because this method not only effectively promotes the sludge disintegration but also strongly inhibits the methane production. However, details of how it causes the VFA accumulation and how the fermentation products change during the fermentation process remain largely unknown. Mathematical modeling of the alkaline fermentation is a powerful tool to understand the underlying mechanism and predict the dynamics of the fermentation products, which can provide a strong support for full-scale applications. Although the ADM1 model contains the parameter of pH inhibition, this previously proposed model fails to describe the dynamics of fermentation process, especially the acceleration of sludge disintegration and the accumulation of VFA.

In this work, a new mathematical model is developed based on the ADM1 model to
describe the dynamics of fermentation products for the first time. The validity of this model developed was strongly demonstrated by four independent case investigations, where both lab-scale and full-scale produced sludge were applied. In all cases, the simulations matched the experimental data well, and the obtained parameter values were successfully predict all the dynamics of fermentation products under fermentation conditions of different sludge concentrations used, different sludge sources used, or at different alkaline pH levels. These facts indicated that the developed model in this study was applicable for different alkaline fermentation systems.

Nowadays, there is an ongoing paradigm shift in WWTP operations from “waste removal” to “resource recovery” (Li et al., 2014). This increasing recognition makes researchers and engineers seek for more promising technologies together with powerfully theoretical supports to recover more resources in WWTPs. The sludge fermentation model developed can explain the sludge alkaline process deeply and predict the dynamics of sludge fermentation products accurately, which thereby may guide engineers to design and optimize the sludge alkaline fermentation systems in real situations in future. Considering the huge amount of sludge daily treated worldwide, the model developed in this work should therefore have significant ecological and economic consequences.

The model developed reveals some underlying mechanisms involved in the sludge alkaline fermentation processes that have already existed but not been recognized before. According to Table 1, it can be indicated that alkaline condition promotes the disintegration, acidogenesis, and acetogenesis processes, but inhibited the methanogenesis process. As a result, more soluble substrates are provided for VFA generation while less VFA is consumed in the last step. It can be understood that high levels of VFA are accumulated in such fermentation processes. It can be also found that the hydrolysis process is unaffected by alkaline condition, which suggests that the optimization of this step can be neglected in the
full-scale operations in future. In addition, the pathway of acetoclastic methanogenesis was found to be more severely inhibited by alkaline condition than hydrogenotrophic methanogenesis one in majority of the cases studied (Table 1). For example, the values of $K_I_{NH_3 \text{, ac}}$ obtained in Case I, Case II, and Case IV are respectively 1.2e-005, 1.1e-005, and 9.5e-005 while the corresponding $K_I_{NH_3 \text{, h}_2}$ values are 4.7e-006, 9.5e-006, and 4.3e-006, respectively. This fact suggests that the activity of acetobacteria should be more carefully taken into account in sludge alkaline fermentation systems, especially those of hydrogen producing systems. However, the data obtained from Case III show an inconsistent result, where $K_I_{NH_3 \text{, ac}}$ is lower than $K_I_{NH_3 \text{, h}_2}$ (8.8e-006 vs 4.5e-005).

There are extensive studies performing on the topic of sludge alkaline fermentation (Wang et al., 2013d; Zheng et al., 2013a; Yuan et al., 2006). To date, almost all the previous investigations believed that alkaline condition was the reason for high levels of VFA accumulation (Wang et al., 2013d; Zheng et al., 2013a; Yuan et al., 2006; Li et al., 2011). The developed model, however, revealed that FA rather than alkaline condition seemed to be the major reason. Indeed, FA has been reported to cause a strong biocidal impact or inhibition on broad phylogenetic types, including nitrifiers, polyphosphate-accumulating organisms, anammox bacteria, and methanogens (Batstone et al., 2002; Park et al., 2015; Zheng et al., 2013b; Aktan et al., 2012;). Recently, the protonated form of another nitrogen compound, nitrite (i.e., free nitrous acid), has been verified to accelerate the disruption of extracellular polymeric substances and inhibit the activity of methanogens (Wang et al., 2013c; Zhao et al., 2015b).  It is suggested that the protonated form of compounds cause more severe impacts on the metabolic processes of organisms, such as the active transport of substrates across the cell membrane, energy generation, and oxidative phosphorylation, as compared with the compounds themselves (Park et al., 2015; Zhou et al., 2011; Wang et al., 2009).

It should be noted that FA level is closely relevant to pH value and ammonium
concentration. The higher pH and ammonium are maintained, the greater FA is. Since alkaline fermentation leads to a high pH, an increased ammonium concentration, and an increased FA level, it would be likely that all the pH, ammonium, and FA form a synergetic effect on the sludge fermentation process. However, it could not differentiate their contributions based on the current model developed here, and experimental studies are required to be performed in the future. This hypothesis may be merged into the current model in future, if more information in terms of pH, ammonium, and FA effects on the sludge fermentation process is available.

4. Conclusion

In this work, a mathematical model is successfully developed to describe the dynamics of fermentation products during the sludge alkaline fermentation process for the first time. To evaluate the predictive ability of the model developed, it has been used to reproduce experimental data obtained from four independent sludge alkaline fermentation case studies. The results of modeling matched well all the experimental data. According to the model, FA was suggested to be the major contributor for the VFA accumulation from WAS under alkaline fermentation conditions.

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Appendix A. Supporting Information

Useful supplementary data associated with this article can be found in the online version. The new biological reaction kinetics integrated with ADM1 to form the proposed new model with FA impacts for sludge alkaline fermentation are summarized in Table S1-S3 and Table
S4 lists the definitions, values, units, and sources of all parameters used in the developed model.

REFERENCES


Table Captions

Table 1. Best-Fit Parameters Describing Sludge Alkaline Fermentation in the Four Case Studies

Figure Captions

Figure 1. Model evaluation with the experimental data obtained from Case I (this study).

Figure 2. The evaluation of the developed model with the experimental data obtained from Case II (Zhang et al., 2010b). COD_X represents particulate COD.

Figure 3. The evaluation of the developed model with the experimental data obtained from Case III (Chen et al., 2007).

Figure 4. The evaluation of the developed model with the experimental data obtained from Case IV (Yan et al., 2010).
Table 1. Best-Fit Parameters Describing Sludge Alkaline Fermentation in the Four Case Studies

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Case I</th>
<th>Case II</th>
<th>Case III</th>
<th>Case IV</th>
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<td>1.1e-005</td>
<td>8.8e-006</td>
<td>9.5e-005</td>
</tr>
</tbody>
</table>
Figure 1. Model evaluation with the experimental data obtained from Case I (this study).
Figure 2. The evaluation of the developed model with the experimental data obtained from Case II (Zhang et al., 2010b). COD\_X represents particulate COD.
Figure 3. The evaluation of the developed model with the experimental data obtained from Case III (Chen et al., 2007).
Figure 4. The evaluation of the developed model with the experimental data obtained from Case IV (Yan et al., 2010).
Highlights:

- A model was developed to describe the sludge alkaline fermentation process
- The model proposed successfully reproduced the experimental data
- FA rather than alkaline condition was the major reason for SCFA accumulation
Graphical Abstract: