Novel operational strategy of anaerobic processes to recover volatile fatty acids from food wastes

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ABSTRACT

In order to determine the critical pH for acid failure and establish the optimal operating condition for the VFA recovery reactor, the existing model was refined by incorporating a pH suppression equation. Through simulation of experimental data from other researchers, a range of pH parameters were identified that provide safety margins for efficient VFA recovery. For conservative calculations, low pH inhibition parameters (pH_{UL} = 6.41, pH_{LL} = 5.47 and n = 0.23) can be employed for biogas plant operations and process design, providing a safety buffer to prevent acid failure. Alternatively, optimistic curves (pH_{UL} = 5.55, pH_{LL} = 5.11 and n = 0.24) can be utilized to subtract 0.4 d^{-1} from the specific decay rate of acid-damaged methanogens, ensuring adequate acidification and maximizing VFA yield. Experimental results indicate that the optimal pH range for activity of acid-producing bacteria is between pH 5.5-6.2. This range is also beneficial for VFA recovery as the consumption of VFA by methanogenic bacteria is greatly reduced due to acid inhibition.

Keywords: *Anaerobic processes, Food wastes, Suppression of methanogens, VFA recovery.*

1. INTRODUCTION

Volatile fatty acids (VFAs) represent intermediate byproducts of anaerobic digestion and have recently garnered increased attention across a wide spectrum of industrial applications [1]. This group of VFAs comprises acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, iso-valeric acid, and caproic acid, all of which find utility in diverse industries including food and beverage, textiles, bioenergy, cosmetics, perfumes, and rubber and grease production [2]. Additionally, mixed VFAs can serve as a carbon source for cultivating fungi in animal feed production, and specific VFA combinations have been harnessed in the synthesis of biodiesel, biopolymers, or the cultivation of algae [3]. Consequently, VFA production through anaerobic digestion (AD) holds considerable promise for resource recovery. Nonetheless, the development of sustainable and economically viable production and recovery methods remains an ongoing challenge.

Currently, the recovery of VFAs from anaerobic processes is a prominent area of focus, necessitating precise control over the kinetics of acidogenesis and methanogenesis to achieve optimal recovery efficiency. One pivotal factor influencing VFA concentration and composition is pH. pH exerts its influence on both acidogenic processes, hydrolysis rates, and the methanogenic phase [4,5]. Regulating pH can enhance hydrolysis/acidogenesis activity and inhibit VFA consumption by methanogens, thereby promoting the conversion of organic waste into VFAs instead of methane [1]. Research has established that the most favorable VFA production conditions occur under alkaline pH levels [6], with pH exerting a positive influence on VFA production [7]. Alkaline fermentation enhances the disintegration and hydrolysis of organic matter in food waste, providing ample biodegradable substrates for acidogenic microorganisms while inhibiting the activities of methanogenic archaea [8,9]. Furthermore, adopting a stepwise pH fermentation strategy augments the activity of acid-producing bacteria

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and inhibits methanogen activity, leading to increased VFA production [10]. However, the operational pH in food waste systems is typically maintained at a neutral or slightly acidic level due to the inherent balance between VFA production and the NH_4/Na^+ buffer. Maintaining a consistently high pH for alkaline fermentation necessitates substantial chemical reagent consumption, rendering it economically unviable for small-scale WWTPs.

Conversely, acidic pH fermentation may offer advantages over alkaline fermentation in terms of VFA production [5]. Acidogens responsible for VFA production exhibit greater tolerance to low pH levels compared to methanogens [11-14]. Consequently, maintaining an appropriate acidogenic pH is crucial for maximizing VFA production [15]. Depending on the organic acids produced during the process, fermentation is categorized into ethanol-type fermentation, mixed acid-type fermentation, and butyric acid-type fermentation, typically occurring within pH ranges of 4.0–4.5, 4.5–5.5, and 5.5–6.5, respectively [16]. Thus, it is reasonable to conclude that pH plays a pivotal role in achieving the desired product [4]. While many studies have concentrated on operational pH's influence on acidification, the primary challenge remains in controlling metabolic activities and curtailing the persistence of methanogens during VFA production via bioprocess. Therefore, the foremost challenges lie in optimizing operational parameters for VFA production and selecting a feasible pH range for subsequent studies.

2. MATERIALS AND METHODS

2.1. Modified low-pH inhibition function on methanogens

The correlation between pH and the empirically determined values of methanogen-specific decay rate (b_{pH}) is described in Equation (1) [17]. This proposed equation enhances the specific decay rate under conditions of low pH. As per the proposed formulation, when the pH reaches the lower limit (pH_{LL}), the pH inhibition factor I_{pH} assumes a value of 0.05 (I_{pH} = exp (-3)), resulting in a twentyfold increase in methanogen decay rates. The upper pH level (pH_{UL}) acts as the pH threshold at which the acceleration of biomass decay commences. The power coefficient (n) is used to modulate the shape of the relationship between the plotted data. With the switching function (I_{pH}) ranging from zero to one, the specific decay rate fluctuates between b and infinity.

$$\begin{cases} b_{pH} = \dfrac{b}{I_{pH}} \\ I_{pH} = \exp\left(-3\left(\dfrac{pH_{UL} - pH}{pH_{UL} - pH_{LL}}\right)^n\right) \\ I_{pH} = 1 \text{ if } pH \geq pH_{UL} \end{cases} \quad (1)$$

Where, b_{pH} represents specific decay rate of methanogens with pH inhibition (d^{-1}), b is inherent decay rate of methanogens (d^{-1}), I_{pH} is an empirical lower-only inhibition switching function (-), n is the power coefficient (-), pH is the pH value in the system (-), pH_{UL} is the upper level pH where low-pH inhibition is initiated (-), pH_{LL} is the lower level pH.

2.2. Process modelling of a virtual biogas plant

To ensure the reliability of the experimental data and explore the connection between pH and decay rates, we employed the IWA Anaerobic Digestion Model No.1 (ADM1) to replicate the laboratory experiments [18]. Each chemostat reactor was subjected to steady-state simulation, utilizing the specific operational conditions of each reactor, to estimate the concentrations of various solid components in the reactor effluent. To simulate the responses of the batch plant in acidic conditions as detailed in Table 1, a computer-based virtual biogas plant was constructed. To perform these programming and process calculations, we utilized a commercial process simulator, GPS-X ver.8.0 (Hatch Co., Ltd., Mississauga, Canada). The kinetic and stoichiometric parameters used in the simulation were drawn from existing literature sources [19-21].

Table 1. Set-up and operational parameters for the virtual biogas facility

Configuration	Working volume	400 m^3
	Mode	CSTR
Operating condition	Temperature	35 °C
	Hydraulic residence time (HRT)	20 days
Input parameters	Composite carbohydrate	10 kgCOD/ m^3
	Composite protein	10 kgCOD/ m^3
	Composite lipid	12 kgCOD/ m^3
	Composite inert	5 kgCOD/ m^3
	Monosaccharide	Zero → 300 kgCOD/ m^3 → Zero
	Ammonium N	100 mg-N/L
	Phosphate	35 mg-P/L
	Initial pH in the system	7.0
	Inorganic carbon	500 mg-C/L

2.3. Benchmarks from literatures

The accuracy and applicability of the optimized model were validated by utilizing various experimental data from references for simulation analysis. Two categories of data selection process were employed: short-term batch experiments to analyze VFA concentration changes under different pH conditions [22-24], and long-term experimental scenarios where the anaerobic VFA recovery system was operated with pH fluctuations [25,26].

The necessary experimental data were extracted using the commercial software 'DataPicker', which enabled the selection of original data from images presented in literature. The benchmark data were acquired and organized before being utilized for adjusting the model parameters and refining the process model using the simulation software GPS-X. Subsequently, the simulation results and parameter ranges for each benchmark data were compared, facilitating further improvement and adjustment of the pH inhibition model.

3. RESULTS AND DISCUSSION

3.1. pH strategy of efficient VFA recovery

In Sun's (2023) study, a biocidal model was developed to offer technical insights into addressing malfunctioning anaerobic plants experiencing acidic failure or to intentionally maintain acidification for VFA recovery. This model serves as a valuable tool for systems lacking other mathematical models, such as ADM1 [17]. The study's experimental results demonstrated that low pH induced by acidogens in the system can irreversibly inactivate methanogens.

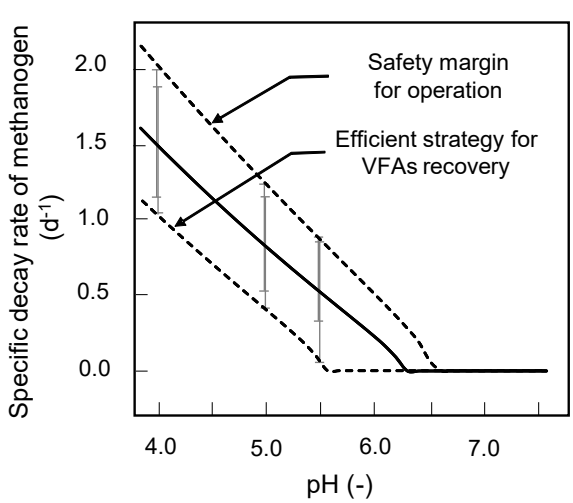

Figure 1 Methanogen-specific decay rate in relation to pH. (depict with error bars representing the range between the upper and lower CI_{95}, and regression curves denoted by dashed lines to encompass the error bars)

To assess the potential risks of acidic failure and determine optimal operating conditions for VFA recovery reactors, a safety margin parameter was introduced [17]. This led to the derivation of a methanogen-specific decay rate in response to pH, depicted by the thin line in Fig. 1. The associated parameter values were n (0.25), pH_{UL} (6.25), and pH_{LL} (5.74). To apply the biocidal model practically, two artificial curves (dashed lines) were superimposed on the graph: the upper curve (pH_{UL} = 6.41, pH_{LL} = 5.47, n = 0.23) provides a conservative estimate of low pH inhibition, whereas the lower curve (pH_{UL} = 5.55, pH_{LL} = 5.11, n = 0.24) offers an optimistic calculation for acidic failure.

The upper curve ensures a safety margin in plant operation and process design (the methanogen-specific decay rate plus 0.3-0.5 d^{-1}), minimizing risks associated with acidic failure. Meanwhile, the lower curve enables the reliable maintenance of the acidification process for VFA recovery (the methanogen-specific decay rate minus around 0.4 d^{-1}).

3.2. Implications of accelerated methanogen decay for biogas plant performance

Based on Sun's (2020) experimental findings, the pH inhibition equation for methanogen decay under acidic conditions was optimized and incorporated into the existing ADM1 model [21]. To illustrate the system's performance during acidic failure, we compared the time required for VFA accumulation and process recovery in a virtual biogas plant with and without enhanced methanogen decay, as demonstrated in Fig. 2.

The simulation of acidic failure involved introducing a high load of monosaccharide to the reactor, resulting in a sudden pH drop to pH = 5.0. Subsequently, influent feeding was discontinued for 5 days. After this 5-day pause, the pH in the reactor was adjusted to 7.0 through alkali dosing. To express the acceleration of methanogen decay, a low-pH inhibition switching function, I_{pH} ($0 < I_{pH} \leq 1$), was introduced to model the specific decay rates of methanogens, as detailed in Equation (1). This proposed switching function was an adaptation of the pH inhibition function used in ADM1 for growth inhibition [18]. It involved the utilization of the values n (0.25), pH_{UL} (6.6), and pH_{LL} (5.9).

Fig. 2 demonstrates that when the pH of the digester dropped to 5.0, VFA quickly accumulated. Although acidogens activity was not inhibited in this pH condition, it is widely known that acidic pH leads to growth inhibition of methanogens. However, by neutralizing the reactor pH without the enhanced pH inhibition on the decay stage of methanogens, the system performance recovered instantly from this acidic failure. The accumulated VFAs were then decomposed, allowing the plant to produce biogas. This simulation outcome implies that plant operators have the potential to restore normal

operation in a digester by pH adjustment, which contradicts the reported observations. Conversely, in simulations where the pH inhibition function was applied to model decay, the methanogen concentration experienced a significant 90% reduction over the course of the 5-day acidic failure. As a result, even after neutralizing the reactor pH, methane gas production remained almost non-existent. The accumulated VFAs were not decomposed quickly, and the process required an operation pause of approximately two weeks until the VFAs concentration reached acceptable levels. Furthermore, given the low methanogenic biomass concentration, it was necessary to regulate the influent loading to maintain VFA concentrations within acceptable limits. According to the above simulation results, it would take approximately 30 days to fully recover the methanogenic biomass.

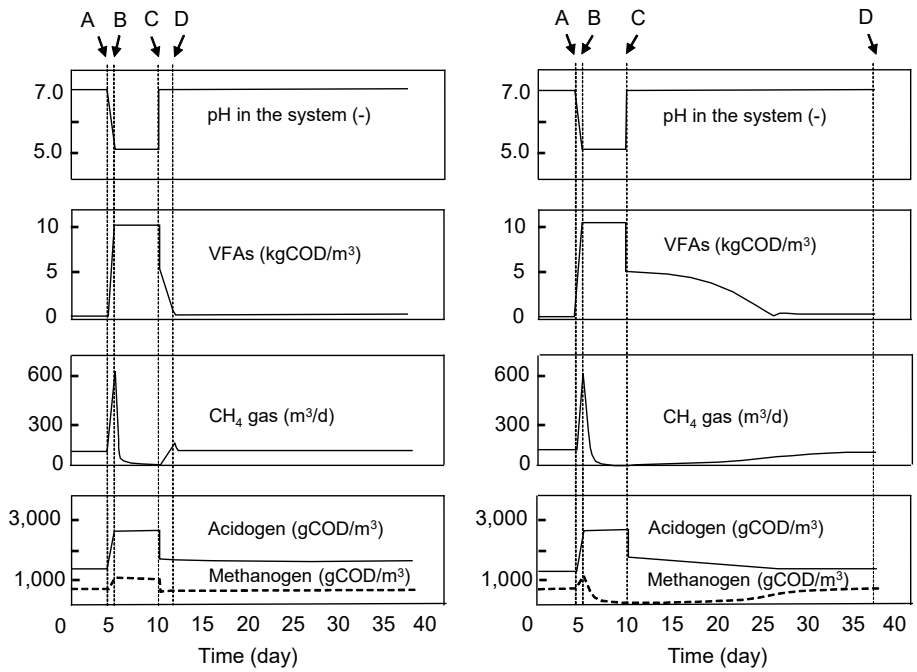

Figure 2 Comparative simulation of biogas plant dynamics with and without accelerated methanogen decay during acidic failure. (Left: ADM1 without the pH inhibition function on decay, right: ADM1 with the pH inhibition function). ~A: steady-state operation, A~B: high organic load, B~C: interruption of influent feeding, C: pH neutralization, D: full recovery of methanogen activity.

These findings suggest that maintaining optimal pH levels in digesters is paramount to safeguard methanogenic biomass and mitigate protracted recovery periods. Furthermore, pH control during anaerobic processes aimed at VFA recovery is essential and paramount.

3.3. Benchmark of biocidal rate expression

According to Ghofrani-Isfahani's (2020) findings in Fig. 3, on the 94th day, the infusion of glucose and NH_4Cl into the reactor was halted, leading to a reduction in the organic content of the feedstock [25].

On day 110, a transition was made from the original feedstock to bio-pulp, causing a rise in the volatile solids (VS) content from 2% to 6%. As anticipated, the introduction of bio-pulp resulted in an immediate surge in methane production, owing to its superior biodegradability compared to manure [27]. However, due to the faster metabolic rates of acidogens and acetogens in comparison to methanogens [28], the inclusion of bio-pulp triggered a swift increase in the total concentration of VFA and a subsequent decline in pH. In just 3 days, the methane production rate started dwindling as a consequence of methanogen inhibition, all the while VFA levels persisted in soaring beyond 2 g L^{-1}. Come day 8, the cumulative VFA concentration had surged to 9 g L^{-1}, and the pH had plummeted to 5.5, ultimately leading to a process breakdown.

On day 121, the feedstock in the digester was switched to manure with a 2% VS content. This resulted in an immediate conversion of accumulated VFAs to biogas, owing to the high buffer capacity of manure that

regulates pH levels. 8 days later, the digester reverted to a stable state, resembling the condition prior to the introduction of bio-pulp. The overall VFA concentration consistently declined and reached 0.3 g L^{-1} by day 143, causing a rise in pH levels to 7.5. On day 145, the digester was once again switched to bio-pulp with a higher VS content of 6%. Within three days, the total VFA concentration rebounded, surpassing 2 g L^{-1}, effectively restoring VFA levels to their pre-bio pulp addition values through a reduction in the feed flow rate.

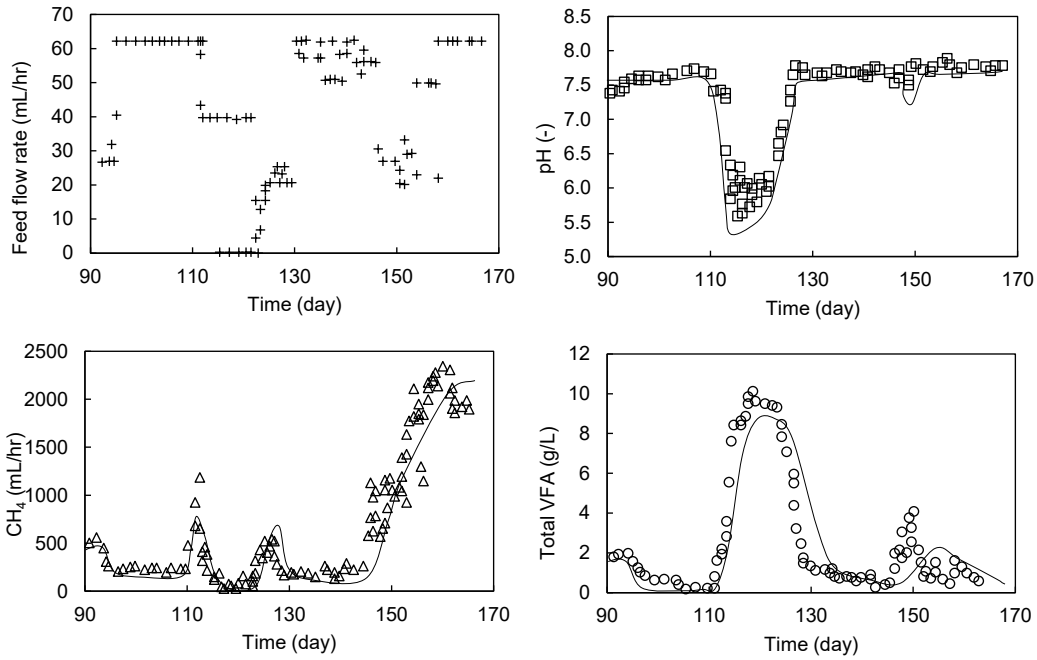

Figure 3 Reactor performance by manipulated Feed flow rate. [day 94-110]: Ceased glucose supplementation and reverted to a 2% VS feed; [day 110-121]: Transitioned to a 6% VS bio-pulp feed; [day 121-145]: Reverted to a 2% VS manure-based feed; [day 145-170]: Shifted back to a 6% VS bio-pulp feed.

The experimental data was fitted by adjusting the pH inhibition parameters, resulting in a set of inhibition parameters of pH_{UL} = 6.21, pH_{LL} = 5.57 and n = 0.25. These parameters allowed for a more accurate representation of the data by taking into account the pH-dependent inhibition effects on the system. By incorporating these parameters, the model was able to match the observed trends and provide insight into the mechanisms behind the inhibition of the system at different pH levels. Overall, the obtained parameters helped to improve the accuracy of VFA production rate and its ability to predict system behavior under varying conditions.

3.4. Effect of pH on VFA generation

According to previous research, low pH levels of 3, 4, and 5 can inhibit the activities of functional microorganisms responsible for hydrolysis and acidification, ultimately leading to a reduced total accumulation of VFAs [29]. Additionally, low pH conditions negatively impact methanogenic archaea, thus impeding the consumption of VFAs. However, as shown in **Figure 4**, fermentation conducted at a pH of 6.5 appears to be a promising approach for achieving high VFAs production efficiencies [24]. The experimental data above was fitted by adjusting the pH inhibition parameters, resulting in a set of inhibition parameters pH_{UL} = 6.25, pH_{LL} = 5.23 and n = 0.24, respectively.

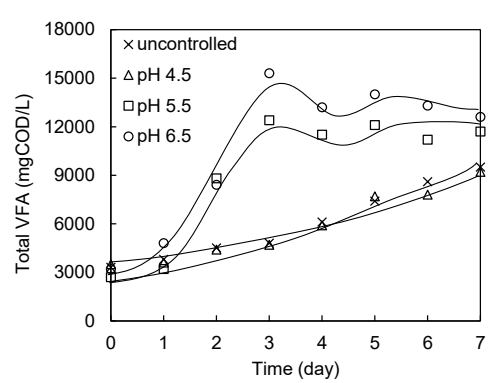

Figure 4 Variations in VFA concentration and simulation curves across reactors at different pH levels.

Hussain's (2017) study demonstrated that maintaining a pH within the neutral to slightly acidic range (around 6-7) enhanced the solubilization of particulate organic matter in food waste, leading to increased levels of COD leaching [22]. The impact of pH on food waste acidogenesis was also reflected in the varying concentrations of VFA. As shown in Fig. 5, VFA levels were highest at pH 7 (about 35 g COD/L) and lowest at pH 4 (6.0 g COD/L), with concentrations of 24 g COD/L at pH 6 and 7.5 g COD/L at pH 5. These results align with earlier research, which has consistently reported increased VFA production in neutral or mildly acidic anaerobic digestion conditions when processing food waste [13,26].

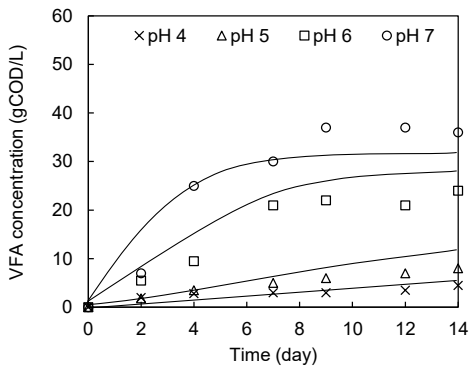

Figure 5 VFAs concentration in different pH reactors.

The pH range of 5.2 to 6.5 is known to be conducive to the growth of acidogenic microorganisms [30]. However, specific VFA production may require a different optimal pH range, as noted by Jankowska (2015) [31]. In Zhang's (2020) study, pH was not regulated, resulting in noticeable variations in pH across different fermentation reactors due to differences in feedstock acidification rates and extent (Fig. 6) [23]. The initial pH values for the three reactors containing potato peels, carrots, and celery were comparable, falling within the pH range of 5.5 to 5.8, which was conducive to the growth and reproduction of acidogenic microorganisms. However, the initial pH of the Chinese cabbage reactors was too low (around pH 4.8) for most acidogen to thrive, likely leading to its low VFA production [13].

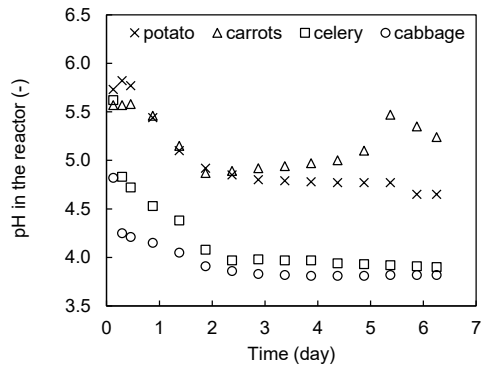

Figure 6 Variation of pH during anaerobic fermentation

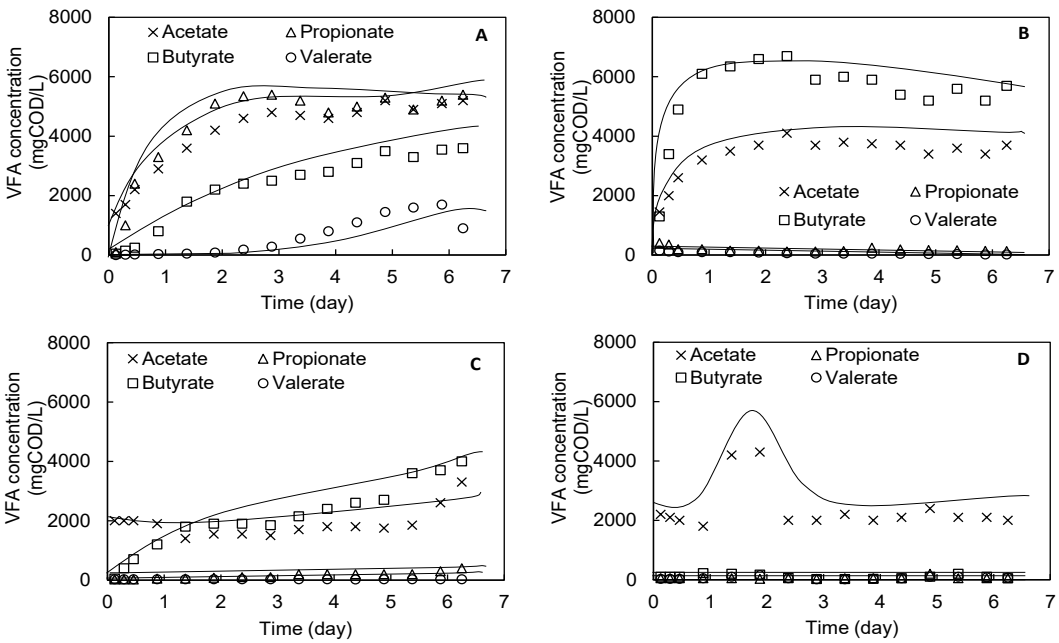

Figure 7 Changes in the concentration of individual VFAs throughout anaerobic fermentation. (A: potato peels B: carrots C: celery D: Chinese cabbage)

Fig. 7 demonstrates a significant variation in product composition across different feedstocks. Notably, acetic acid emerged as a major VFA component, accounting for a percentage ranging from 29% to 40% in all feedstocks. The distribution of microorganisms was closely linked to the fermentation product composition, where the high yield of a particular acid was attributed to the activity of specific acid-producing bacteria [32]. Lactate and ethanol, on the other hand, exhibited rapid degradation and were primarily observed during transient overload conditions in acidification reactors. It's worth noting that since ADM1 does not account for these components, there may be some inaccuracies in the simulation results concerning organic acids.

By adjusting the pH inhibition parameters, the experimental data mentioned above was successfully fitted, resulting in a set of inhibition parameters of pH_{UL} = 6.08, pH_{LL} = 5.45 and n = 0.23. Significantly, it was observed that potato peels exhibited a metabolic pathway akin to propionate, and this was notably more pronounced compared to the other feedstocks [33]. On the contrary, when fermenting carrots, the resulting product is simpler, primarily composed of butyric acid and acetic acid, where butyric acid constitutes about 54% of the product. In contrast, the fermentation of celery follows a mixed-acid metabolic pathway, yielding primary products of ethanol, butyric acid, and acetic acid [34]. In Chinese cabbage fermentation, a metabolic pattern characterized by ethanol and acetic acid predominates, with minimal presence of other byproducts. Wu (2017) had previously demonstrated the pivotal role of pH in ethanol production, with the optimal pH for ethanol production being at 4.0 [35].

Nevertheless, the research revealed that acidic conditions (pH 4 and 5) not only hindered hydrolysis but also impeded VFA production from solubilized substrates, leading to diminished VFA concentrations and yields. This suggests that while hydrolysis exhibited improved performance at pH 5 compared to pH 4, it did not result in increased VFA production. This lack of translation can be attributed to a metabolic shift towards lactate production at pH 5, as illustrated in Fig. 8. Notably, this finding aligns with the observations made in Zhang's (2005) study, where a shift towards lactate-type fermentation in kitchen waste was also observed at pH 5 [36]. The experimental data was fitted at pH_{UL} = 6.33, pH_{LL} = 5.56 and n = 0.25, respectively.

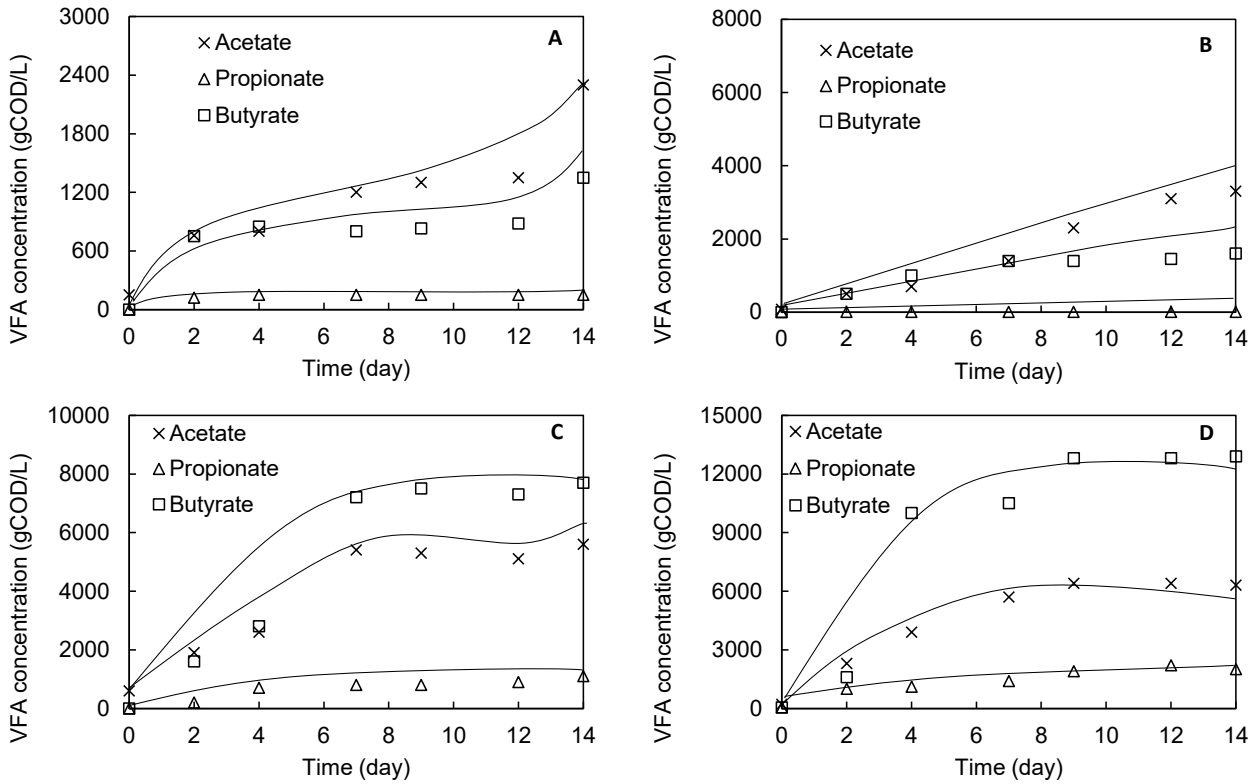

Figure 8 Concentration of main VFAs in different pH reactors. (A: pH= 4.0, B: pH= 5.0, C: pH= 6.0, D: pH= 7.0)

4. CONCLUSION

The experimental data yielded an empirical equation for the inhibition of methanogens at low pH, offering a collection of parameters that can guide the design and operation of anaerobic reactors. The highest possible VFA yield from food waste could be achieved by maintaining the pH level within the range of 5.5-6.2 in the anaerobic digester. This particular pH range stimulates the acidogens' activity while inhibiting methanogens, leading to an optimal VFA recovery rate. While the parameters in the pH inhibition model may vary slightly for different substrates, they can still provide accurate predictions of reactor performance at acidic pH conditions. To obtain specific target VFA products, the reaction process must carefully and accurately control the pH.

AUTHORS' CONTRIBUTIONS

Meng Sun: conceptualization, statistical analysis, writing-original draft and editing; Xi Zhang: writing-review and editing; Rajeev Goel: software; Bing Liu: writing-review and editing; Mitsuharu Terashima: project administration, funding acquisition, supervision, methodology, writing-review; Hidenari Yasui: funding acquisition, supervision, conceptualization, methodology, writing-review and editing.

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