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Zero-Valent Iron and Activated Carbon Coupled to Enhance Anaerobic Digestion of Food Waste: Alleviating Acid Inhibition at High Loads

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Abstract: Anaerobic digestion (AD) has the advantages of utilizing complex substrates and producing renewable energy and is currently one of the mainstream technologies for food waste (FW) resourcing. However, at high organic loads and low inoculum-to-substrate ratios (ISRs), AD with FW as substrate is prone to acid accumulation, resulting in a drastic decrease in gas production and system collapse. This study investigated the effect of the coupled addition of zero-valent iron (ZVI) and activated carbon (AC) on the AD of FW at three low ISRs of 0.715, 0.625, and 0.5. The results showed that the control group acidified and stopped producing biogas when the ISR decreased to 0.625 and 0.5, but ZVI coupled with AC alleviated the acidification and increased the cumulative biogas yield. Especially at ISR = 0.5, the cumulative biogas yield for the ZVI + AC group was 31.5%, 99.5%, and 11.43 times higher than that of the ZVI, AC, and control groups, respectively. ZVI coupled with AC also increased the degradation of volatile fatty acids (70.5–84.4%) and soluble chemical oxygen demand (50.0–72.9%) while decreasing propionate concentration and improving the stability of the AD system. COD mass balance analyses indicated that the coupled addition of ZVI and AC promoted the conversion of particulate organic matter to soluble organic matter and increased the conversion of carbon sources to methane.

Keywords: fermentation; methane production; acidification; acid accumulation

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1. Introduction

In recent years, with rapid economic development, accelerated urbanization, and the rapid development of catering enterprises, the generation of food waste (FW) has increased rapidly [1,2]. Due to weaknesses in traditional management practices and the lack of corresponding treatment facilities, a large amount of untreated FW and gutter oil has flowed into communities through various ways, which has not only affected environmental hygiene but also brought about serious hidden dangers to people's dietary safety [3]. The large amount of generated FW is a threat to environmental protection, public health, and social management, and is gradually becoming a global problem [4]. Globally, up to 1.3 billion tons of FW is produced annually, which is about 44% of the total amount of solid waste [5]. FW is one of the main causes of greenhouse gas emissions, and traditional treatment methods, such as incineration and landfill, contribute to greenhouse gas emissions and leachate pollution [6]. According to statistics, global FW contributed 8–10% of all anthropogenic greenhouse gas emissions from 2010 to 2016 [7]. Therefore, material or energy recovery of FW is important for reducing carbon emissions and achieving environmental sustainability.

FW has a high content of organic matter, which can be utilized in resourceful ways to produce fertilizers [8], lactic acid [9], methane [10], etc. Anaerobic digestion (AD) is a widely accepted resourcing technology that reduces FW while producing biogas, which can be purified and used as fuel [11,12]. Biogas production in AD usually follows four phases carried out by the metabolism of numerous bacteria and methanogens [13]. Macromolecule organic matter in the substrate is first broken into easily dissolved monomers, including the conversion from carbohydrates, proteins, and fats to sugars, amino acids, and long-chain fatty acids, which is a process called hydrolysis. The second stage is known as acidogenesis, where the monomers are further broken into short-chain fatty acids, including volatile fatty acids (VFAs), lactic acid, pyruvic acid, acetic acid, and formic acid. Then, in the acetogenesis stage, acids such as lactate and pyruvate are digested into acetic acid and hydrogen. The final stage is called methanogenesis, where hydrogen and acetic acid are converted to methane by the action of methanogenic archaea [11,14]. The digestate produced by the AD process can also be used for composting, biopesticides, insect feed, etc., thus realizing reduction, resourcefulness, and harmlessness. Therefore, methane production by AD using FW as the substrate has become an important resource technology, which is of great significance for achieving the goals of circular economy development, environmental protection, reduction in greenhouse gas emissions, and production of renewable energy [15]. Organic load is one of the important factors that affect the AD of FW. High organic loads can increase the amount of substrate processed and greatly increase methane production. However, the AD of FW at high loads usually shows fast acidification and slow methane production, resulting in a significant accumulation of VFAs. Accumulation of VFAs, especially propionate and butyrate, can severely inhibit the methanogenic process, which is known as the phenomenon of "acid inhibition" [16].

Zero-valent iron (ZVI) can be added to AD systems to increase methane production by alleviating acidification and stimulating microbial metabolic performance [17,18]. The addition of ZVI to AD with high organic loading rates can promote the degradation of VFAs and increase system pH, thereby alleviating system acidification [19]. The inoculum-to-substrate ratios (ISRs) can determine the ability of the AD system to resist organic acid loading, which is a direct factor affecting the performance of AD. An inadequately low ISR will lead to system acidification and gas production stopping. Wu et al. found that acidification occurred at ISRs below 1.0 [20]. A previous study showed that methane production stopped at ISR = 0.65, but the mean concentration of total volatile fatty acid (TVFA) decreased by about 19.0% and pH increased to approximately 7.5 with ZVI, which successfully resumed methane production [21]. However, adding ZVI required considerable time to alleviate acid accumulation with a certain lag time, which resulted in an inefficient AD system.

On the other hand, it has been shown that activated carbon (AC) can effectively shorten the lag time and improve the system hydrolysis efficiency and methanogenic efficiency [22]. Interspecies electron transfer using hydrogen or formate as carriers is known as interspecies hydrogen transfer (IHT) and interspecies formate transfer (IFT). However, these processes are relatively inefficient due to the diffusion limitations of electron carriers, and thus become limiting steps in overall methanogenesis [23]. Recent studies have demonstrated that direct interspecies electron transfer (DIET) is an alternative to IHT in the metabolism of AD [24]. The addition of a conductive material, such as AC, can facilitate DIET by dispensing with the involvement of conductive hairs and exo-c-type cytochromes, which allow the attachment of mutualistic microorganisms to the surface of the conductive material for electron exchange [25]. DIET, when established in AD using conductive material delivery, has an electron transfer rate that is 10^6 times faster than that of IHT [24]. Studies showed that the addition of AC enhances the mutualistic metabolism between bacteria and methanogens capable of performing DIET, thereby facilitating DIET and methanogenic efficiency [26–28]. Studies have also shown that carbon-based materials also play an important role in improving the efficiency of AD. Liu et al. showed that the coupled addition of ZVI and activated carbon, graphite, or Fe-C materials further shortened the methanogenic lag and enhanced the degradation of soluble organic matter [29]. Eraky et al. found that the addition of tween 20 and magnesium@ functionalized graphene oxide increased the biohydrogen productivity by >200% compared to the control, and enhanced the acetate fermentation pathway, the enzymatic activities, and the biodegradation of phenolic compounds [30]. Wang et al. investigated the effect of biochar-supported nano-ZVI on a two-phase AD of FW. Results suggested that a 3:1 carbon/iron ratio increased the concentration of VFAs in the acid-producing phase and the cumulative methane production in the methanogenic phase by 31.4% and 24.8%, respectively [31]. Calabrò et al. found that ZVI coupled with AC helped to enhance the stability of a semicontinuous AD experiment and to increase methane production, but this study was conducted with pretreated orange peel waste as a substrate [32]. Therefore, it is expected that ZVI coupled with AC may be able to increase the rate of anaerobic digestion while alleviating the acidification of low ISR systems. However, the above studies were conducted at high ISR and only investigated the promotional effects of the ZVI or AC on AD, and did not investigate the alleviating effects of the ZVI and AC on the acid inhibition system.

In this study, from the point of view of the application of AD engineering for FW, the effect of low ISRs (ISR = 0.715, 0.625, 0.5) on the AD of FW was first investigated. Subsequently, four groups (only ZVI, only AC, ZVI + AC, and control) under each ISR condition were conducted to investigate the effects of the coupled addition of ZVI and AC on AD from a comprehensive analysis of gas production performance, system stability, and COD balance. The objective of this study was to investigate the alleviating effects of coupled ZVI and AC additions on acid inhibition in the AD system under high loading (three different low ISRs) conditions. This aims to provide a simple and effective new method to mitigate acid accumulation during AD and to provide theoretical support for the resource utilization of FW and the industrial application of AD.

2. Materials and Methods

2.1. Substrate and Inoculum

The FW was obtained from the student canteen of the University of Science and Technology Beijing (Beijing, China). The FW was picked out from bones and peels, then mechanically milled and frozen in the refrigerator at −20 °C. It was removed and thawed in a −4 °C refrigerator for 12 h before use. The inoculated sludge was obtained from the Dongcun Waste Treatment Plant in Tongzhou District, Beijing, China. The sludge was acclimated at 37 °C for one week with 0.5 g vs. of FW as substrate every two days before use. Zero-valent iron (98% purity, 0.2 mm diameter, 0.05 m^2/g specific surface area) and activated carbon (32–60 mesh) used for the experiments were produced by Aladdin Co., Ltd., Shanghai, China. The physicochemical characteristics of FW and sludge are shown in Table 1.

Table 1. Physicochemical characteristics of FW and sludge.

	FW	Sludge
TS (%)	26.30 ± 0.03	3.73 ± 0.01
VS (%)	25.10 ± 0.03	2.07 ± 0.03
pH	4.70 ± 0.07	8.84 ± 0.05
C * (%)	46.80 ± 0.30	30.80 ± 0.17
N * (%)	3.00 ± 0.25	5.75 ± 0.15
C/N	15.60 ± 1.48	5.35 ± 1.20
H * (%)	7.05 ± 0.07	4.39 ± 0.04
O * (%)	31.40 ± 0.31	22.40 ± 0.34

Note: * refers to dry basis.

2.2. Experimental Operation

Based on three ISRs (VS_{sludge}: VS_{FW}) of 0.715, 0.625, and 0.5, sludge and FW were mixed in different proportions. The experiments were conducted in 100 mL fermentation bottles with an effective volume of 50 mL. It has been proved that 5–10 g/L of ZVI or AC can effectively increase methane production and promote AD [29,33]. Therefore, four experimental groups were designed under each of the three ISRs: 5 g/L ZVI + 5 g/L AC, 10 g/L ZVI, 10 g/L AC, and a control group in which neither of them was added, which were referred to as the ZVI + AC, ZVI, AC, and control groups, respectively. After the addition of ZVI or AC, each bottle was aired with nitrogen for 3 min to remove oxygen from the system, and then sealed with butyl rubber stoppers and aluminum caps. All bottles were incubated in an incubator at 37 °C, 120 rpm. The experiment was destructive, and no samples were collected throughout to ensure its anaerobic environment. The experiment lasted for 53 days, and samples were collected at the initiation and end of the experiment to determine the pH, alkalinity, total ammonia nitrogen (TAN), soluble chemical oxygen demand (SCOD), and VFAs. Gas volume and components were determined at two-day intervals. Parallel experiments were conducted, the results of the repeated experiments were averaged, and standard deviations were calculated.

2.3. Analytical Methods

The total solids (TS) and volatile solids (VS) were determined according to the method determined by the State Environmental Protection Administration (2002). The pH values were determined using a PHS-3C digital pH meter (INESA Scientific Instrument Co., Ltd., Shanghai, China). The contents of C, H, O, and N were determined by an elemental analyzer (FlashSmart; ThermoFisher Scientific, Dreieich, Germany). Samples were centrifuged at 12,000 rpm and 4 °C for 10 min and the supernatant was filtered through a 0.45 μm microporous membrane. The alkalinity was determined using the bromocresol green–methyl red indicator titration method (State Environmental Protection Administration, 2002). The soluble chemical oxygen demand (SCOD) and total ammonia nitrogen (TAN) concentration were determined using a UV–visible spectrophotometer (UV-8000; Metash Instruments Co., Ltd., Shanghai, China). Volatile fatty acids (VFAs) were measured with a Shimadzu CP3800 gas chromatograph, which was equipped with a DB-FFAP capillary column (30 m × 0.53 mm × 0.5 μm; Agilent Technologies Co., Ltd., Santa Clara, CA, USA) and a flame-ionization detector. The gas volume was determined by the differential gas pressure method, and the gas components were determined with GC (GC2010Plus; Shimadzu, Kyoto, Japan) packed with ShinCarbon ST Micropacked Column (19,043; 1.00 m × 0.53 mm, 80–100 mesh; Restek, Bellefonte, PA, USA) and thermal conductivity detector (TCD). Argon was used as the carrier gas. The column, detector, and injection port temperatures were set to 190 °C, 200 °C, and 190 °C, respectively.

3. Results and Discussion

3.1. Biogas Production and Methane Concentration

Figure 1 compares the changes in cumulative biogas yields between the groups adding ZVI or AC and the control group under different ISRs. The results showed that the control group acidified and stopped gas production as the ISR decreased from 0.715 to 0.625 and 0.5 while adding ZVI or AC significantly alleviated acidification and increased biogas yield. The coupled addition of ZVI and AC further increased the cumulative biogas yield; for example, the cumulative biogas yield of the ZVI + AC group increased by 59.5%, 23.7%, and 92.7% compared to the single ZVI, single AC, and control groups, respectively, at the ISR = 0.715. At ISR = 0.625, the cumulative biogas yield of the ZVI + AC group was 15.6%, 59.6%, and 10.29 times higher than that of the ZVI, AC, and control groups, respectively. At ISR = 0.5, the cumulative biogas yield of the ZVI + AC group was 31.5%, 99.5%, and 11.43 times higher than that of the ZVI, AC, and control groups, respectively. A previous study also showed that the coupled addition of ZVI and AC increased cumulative methane production by 2.77–35.0% compared to the addition alone and the control [34]. Similarly, the addition of biochar-supported nano-ZVI increased cumulative methane production by 24.8% [31]. This indicated that the addition of ZVI or AC to a low ISR system could promote substrate degradation to methane, while the coupled addition of ZVI and AC further increased the cumulative biogas production.

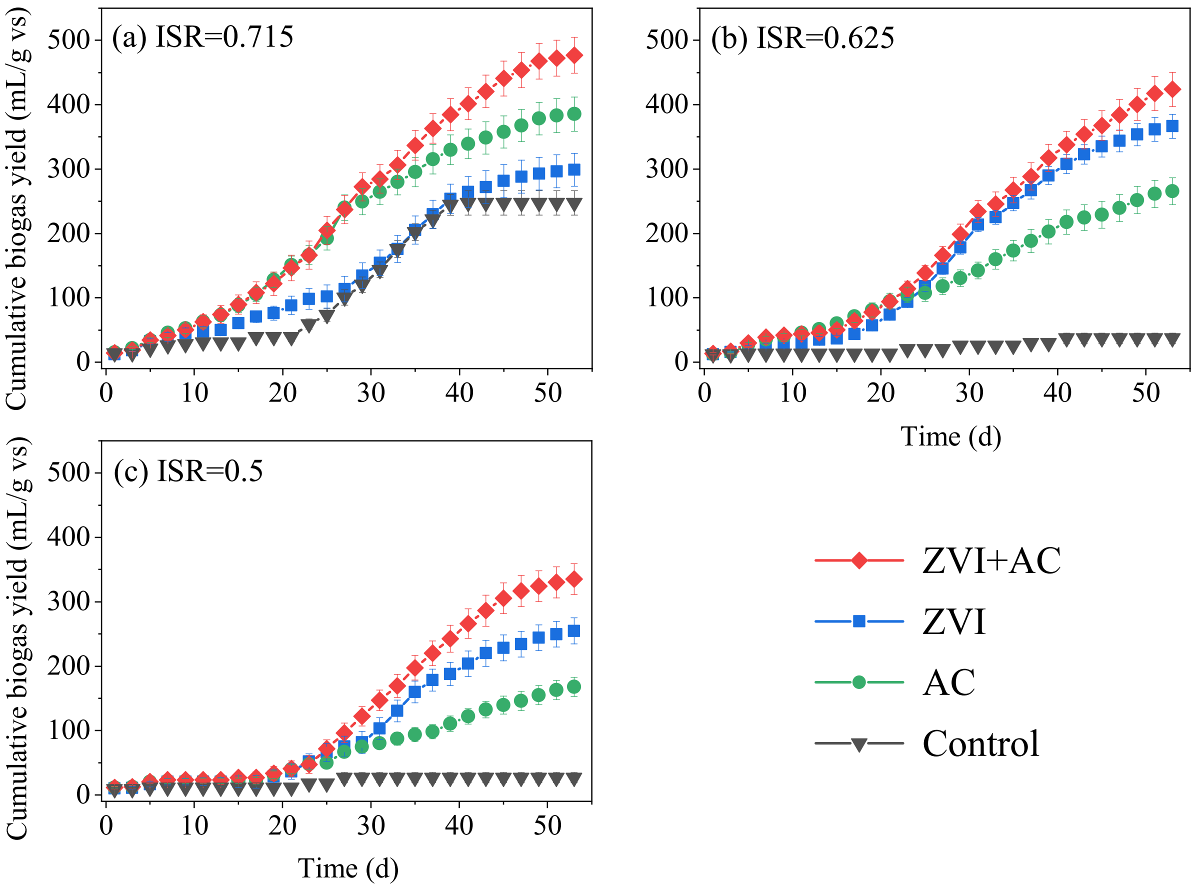

Figure 1. Variation in cumulative biogas yield with time for each group at different ISRs.

Figure 1a showed that there was a lag time of up to 17 days for AD of FW at an ISR of 0.715, and adding ZVI and AC effectively reduced this lag time. In contrast, the lag time of the AC and ZVI + AC groups was shorter than that of the ZVI group, and AC had a more obvious advantage in shortening the lag time. A previous study also reported that the coupled addition of ZVI and AC shortened the time to reach maximum daily methane yield by 18.2% compared to ZVI groups [34]. The reason may be that the iron ions produced by ZVI combined with the activated radicals and produced stabilized complexes, thus inhibiting the hydrolyzation in the sludge [35]. The shortening of the lag time by AC is due to the fact that its richer microporous–mesoporous structure creates a suitable microbial environment. This facilitates the enrichment of methanogens at the initiation of AD [33] and thus facilitates the degradation and utilization of soluble organic matter. In addition, AC has an adsorption effect on VFAs produced by acidification. When the activity of methanogens and syntrophic acetogenic bacteria increases, the VFAs adsorbed by AC are gradually utilized, which corresponds to a slow release of VFAs. Therefore, ZVI coupled with AC in the low ISR system not only alleviated acidification and increased cumulative gas yield, but also improved AD efficiency.

Methane concentration is the percentage by volume of methane in biogas. It is an important indicator of the quality of biogas and is usually 50–70% [36]. Figure 2 shows the average methane concentration of each group at different ISRs. The results showed that all three groups with the addition of ZVI or AC had higher average methane concentrations than the control group. At ISR = 0.715, the mean methane concentration in the ZVI + AC group reached 62.0%, which was 2.5, 2.8, and 12.3 percentage points higher than that in the ZVI group (59.5%), the AC group (59.2%), and the control group (49.7%), respectively. At ISR = 0.625, the mean methane concentration in the ZVI + AC group (57.6%) was still higher than that in the ZVI group (56.0%), the AC group (57.0%), and the control group (31.1%). At ISR = 0.5, the mean methane concentration in the ZVI + AC group (56.4%) was higher than that in the ZVI group (51.1%), AC group (51.6%), and control group (30.6) by 5.3, 4.8, and 25.8 percentage points, respectively. Therefore, ZVI coupled with AC significantly increased the methane concentration in the system under each ISR.

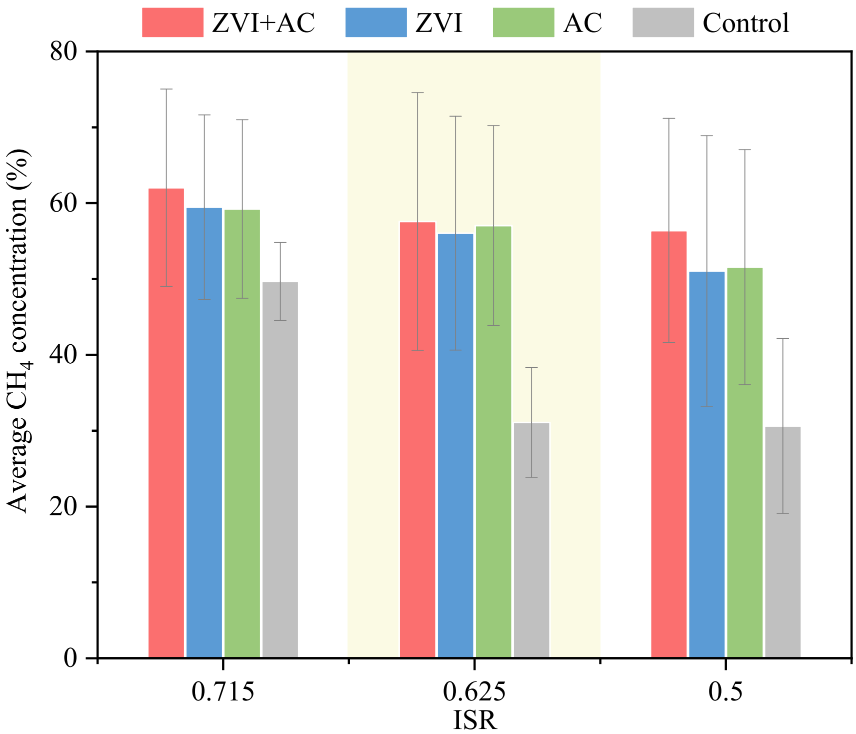

Figure 2. Mean methane concentration in each group at different ISRs.

3.2. System Stability Indexes

pH, alkalinity, and TAN concentration are key indicators that show the stabilization in the system [37]. Figure 3 showed that the pH for each group was within the suitable range of 6.5 to 8.2. The reason that the system acidified and stopped gas production in the low ISR (0.5) system and the pH did not decrease to acidic may be due to the high concentration of TAN, which increased the alkalinity. This is due to the fact that TAN can promote the dissolution of CO_2, which can raise the bicarbonate alkalinity [38]. The alkalinity of each group decreased with the decrease in the ISR and was maintained in the range of 9.34 to 15.8 g/L. As can be seen in Figure 4, the TAN concentration of each group increased with the degradation of proteins during AD. When ISR = 0.5, the final TAN concentration in the ZVI + AC group was 26.0%, 8.82%, and 9.29% lower than that of the ZVI, AC, and control groups, respectively. Therefore, ZVI coupled with AC was more beneficial in alleviating ammonia inhibition at lower ISRs.

3.3. Organics Degradation

During AD, the concentration of SCOD in each group generally showed a decreasing trend, which was attributed to the degradation and consumption of soluble organic matter with the progress of fermentation [17,33]. The SCOD degradation rates of the ZVI + AC, ZVI, and AC groups were all greater than those of the control group at three ISRs (Figure 5). At ISR = 0.715, the SCOD degradation rate of the ZVI + AC group was 8.2%, 9.1%, and 34.4% higher than that of the ZVI, AC, and control groups, respectively. At ISR = 0.625, the SCOD degradation rate of the ZVI + AC group was 8.1%, 8.1%, and 18.2% higher than that of the ZVI, AC, and control groups, respectively. At ISR = 0.5, the SCOD degradation rates were 50.0%, 20.1%, 56.9%, and 16.1% of the ZVI + AC, ZVI, AC, and control groups, respectively. The results showed that the addition of ZVI or AC enhanced the degradation of soluble organic matter. The coupled addition of ZVI and AC could further promote the degradation of soluble organic matter, which is consistent with the conclusion that the cumulative biogas production was higher in the ZVI + AC group in Figure 1. Other studies have also found that the addition of AC loaded with nano-ZVI increased the degradation of organic matter from 37.49% to 66.56%, thus facilitating the methanogenic process [39].

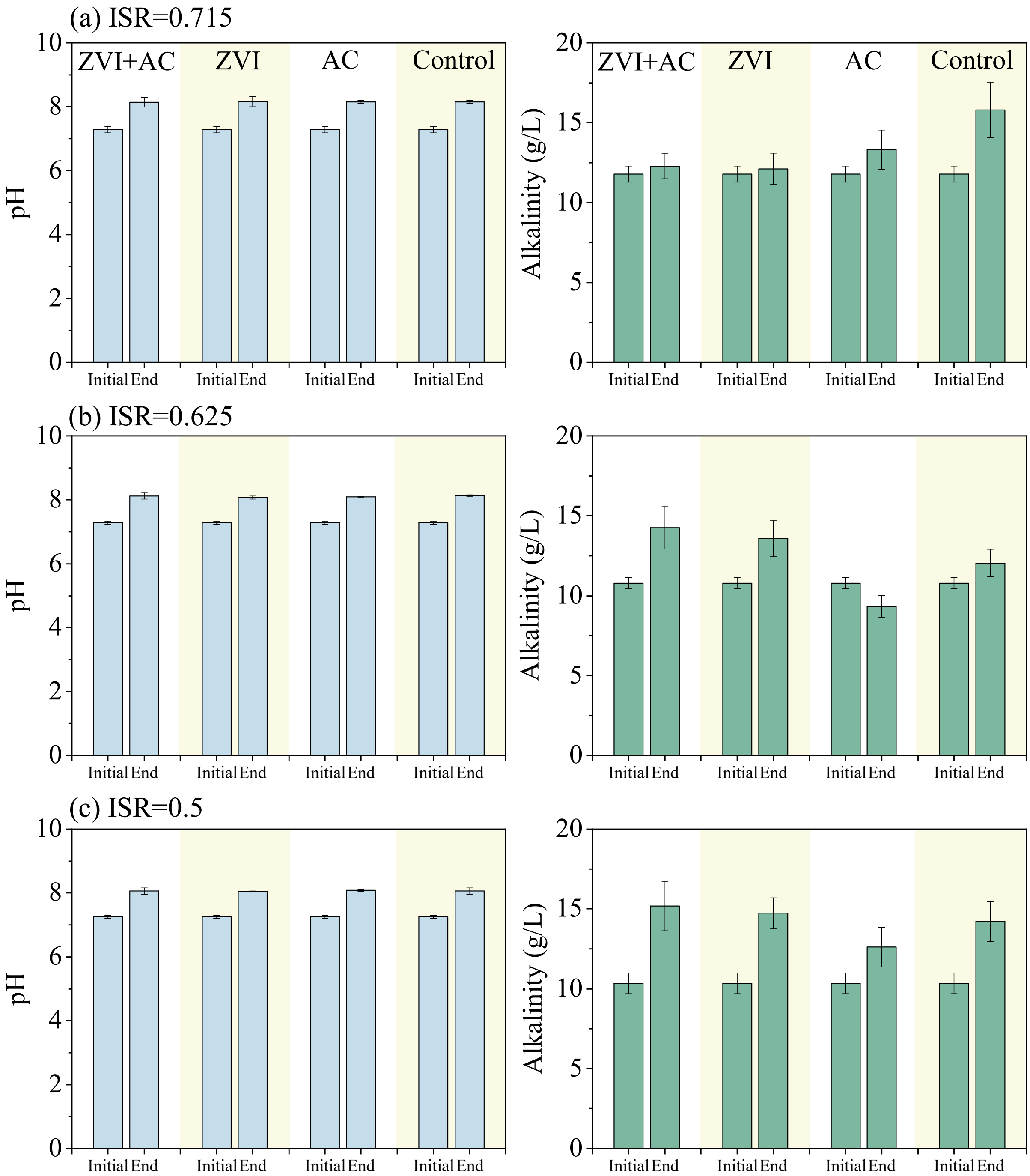

Figure 3. Variation in pH and alkalinity in different ISRs for each group.

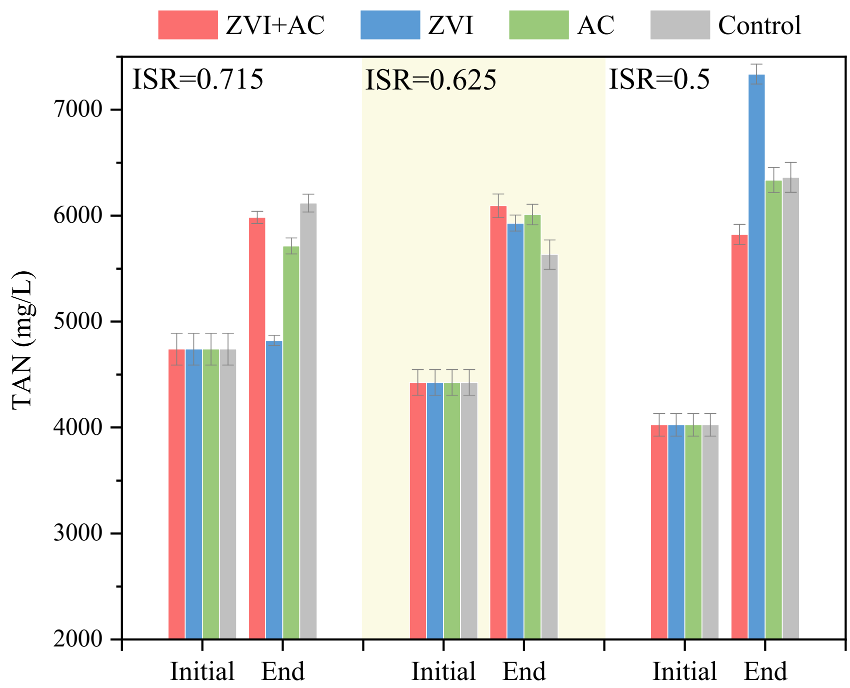

Figure 4. TAN concentration in each group under different ISRs.

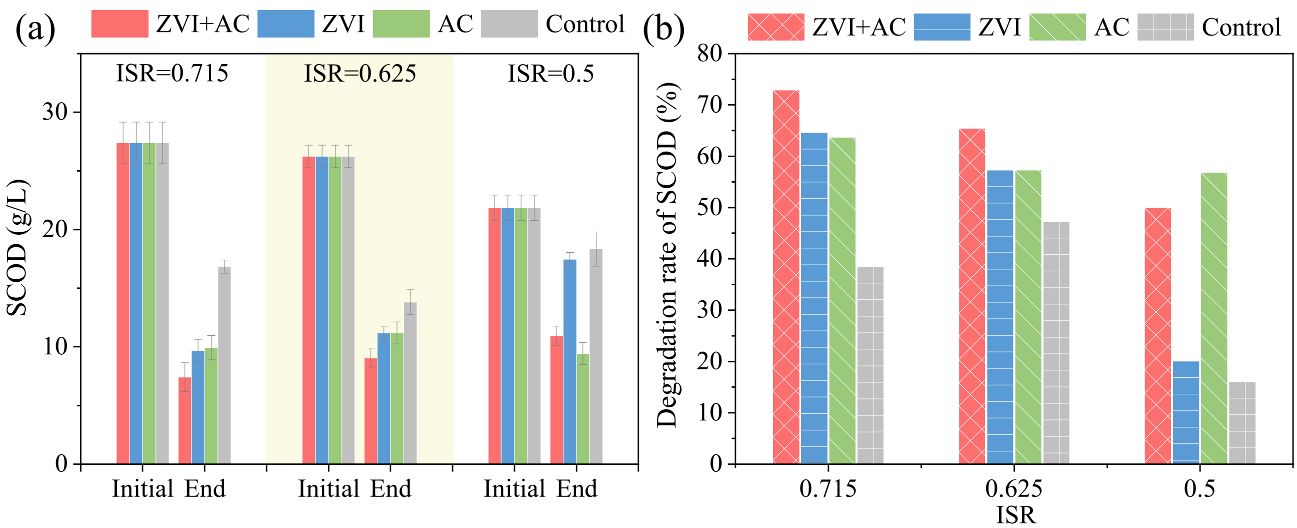

Figure 5. (**a**) SCOD and (**b**) degradation rate of each group under different ISRs.

VFAs are essential meso-products during AD [40,41]. Figure 6 shows the changes in the composition of VFAs in each group at the initiation and end of AD. The TVFA concentration of the control group at the end increased significantly as the ISR decreased. This is due to the higher amount of soluble organic matter at low ISRs, indicating that the system tends to accumulate VFAs at low ISRs. In particular, when the ISR = 0.715, the final TVFA concentration in the control group was higher than that in the other three groups by 49.9–94.8%. The degradation rate of VFAs in the ZVI + AC group (84.4%) was 4.67, 5.29, and 14.8 percentage points higher than that of the ZVI, AC, and control groups, respectively. At ISR = 0.625, the final TVFA concentration in the control group was 23.6–32.3% higher than those in the other three groups. The degradation rate of VFAs in the ZVI + AC group (76.3%) was 0.72 to 7.67 percentage points higher than that of the ZVI, AC, and control groups. At ISR = 0.5, the final TVFA concentration in the control group was 7.73–68.0% higher than those in the other three groups. The degradation rate of VFAs in the ZVI + AC group (70.5%) at ISR = 0.5 was 15.4, 15.7, and 19.1 percentage points higher than that in the ZVI, AC, and control groups, respectively. It can be seen that ZVI coupled with AC enhanced VFA degradation and thus increased the methane production more than adding ZVI or AC alone. This might be because ZVI and AC can stimulate fermentation products such as VFAs degraded to methane by promoting DIET [25].

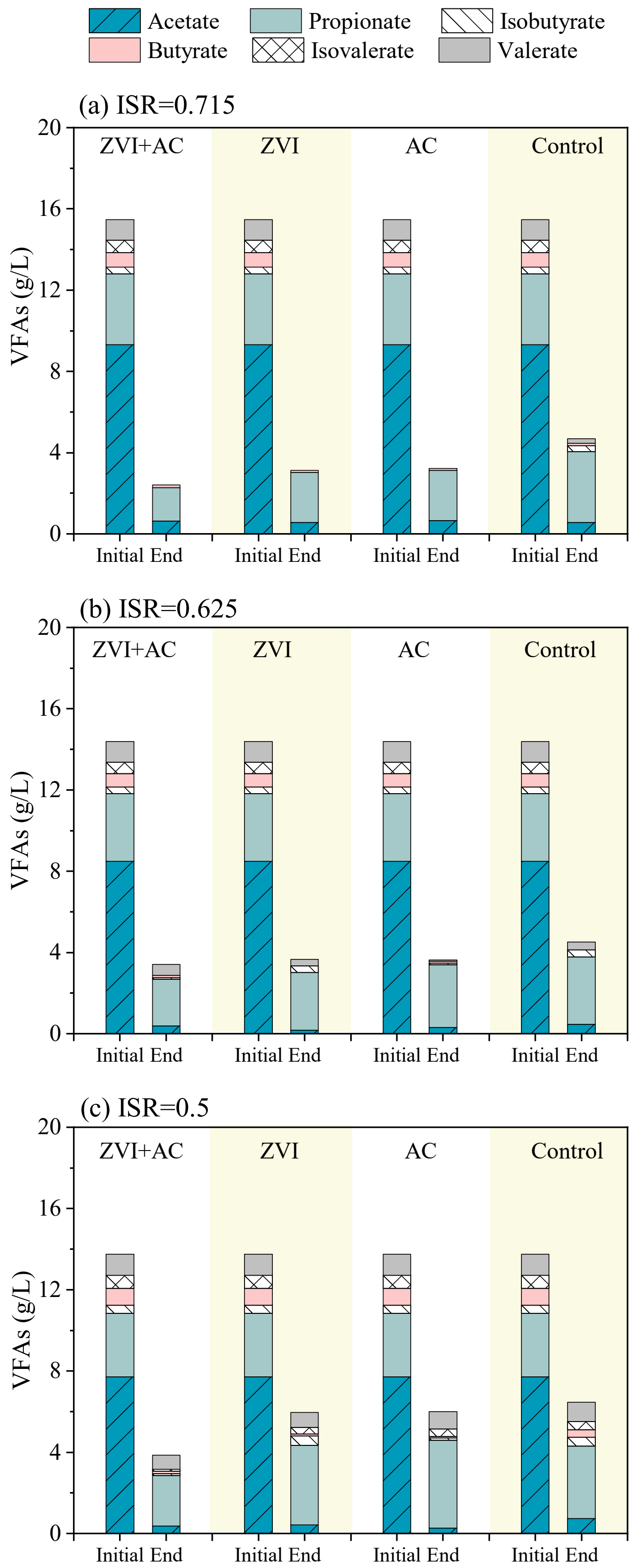

Figure 6. Variations in volatile fatty acids concentration in each group under different ISRs.

It can also be seen from Figure 6 that acetate and propionate accounted for the highest percentage of TVFA during AD. Among them, acetate can be directly utilized, while propionate needs to be converted to acetate before producing methane [37]. When the concentration of propionate is too high in the system, acid accumulation will inhibit the methanogenic process [42,43]. At the end of AD, the control group at all three ISRs showed propionate accumulation compared to the ZVI + AC, ZVI, and AC groups, with the final concentrations of propionate ranging from 3.32 to 3.58 g/L, accounting for up to 55.3–74.5%. While the ZVI + AC group had the lowest final propionate concentrations, ranging from 0.63 to 2.50 g/L. The above result indicated that ZVI coupled with AC promoted the metabolism of propionate to acetate and avoided the accumulation of propionate, which ensured the successful operation of AD.

3.4. Substance Balance Analysis Based on COD

Material balance analysis at the initiation and end of AD can provide a more intuitive explanation of the organic matter degradation process. The COD mass balance of the groups at the initiation and end was analyzed according to a previous study [44]. All COD in AD systems comes from the substrate, usually in the form of gas (CH_4-COD), supernatant (S-COD), and particle (P-COD) [45,46]. According to the principle of AD, it can be seen that all COD basically exists in the particle phase (P-COD) and supernatant phase (S-COD) at the time of feeding (Figure 7). After the hydrolysis and acidification process, the particle-phase COD is transferred to the supernatant phase (S-COD), which exists in the form of VFAs, etc.; then, the methanogenesis process occurs, with the methane produced by the degradation of VFAs, the supernatant-phase COD is transferred to the gas phase (CH_4-COD).

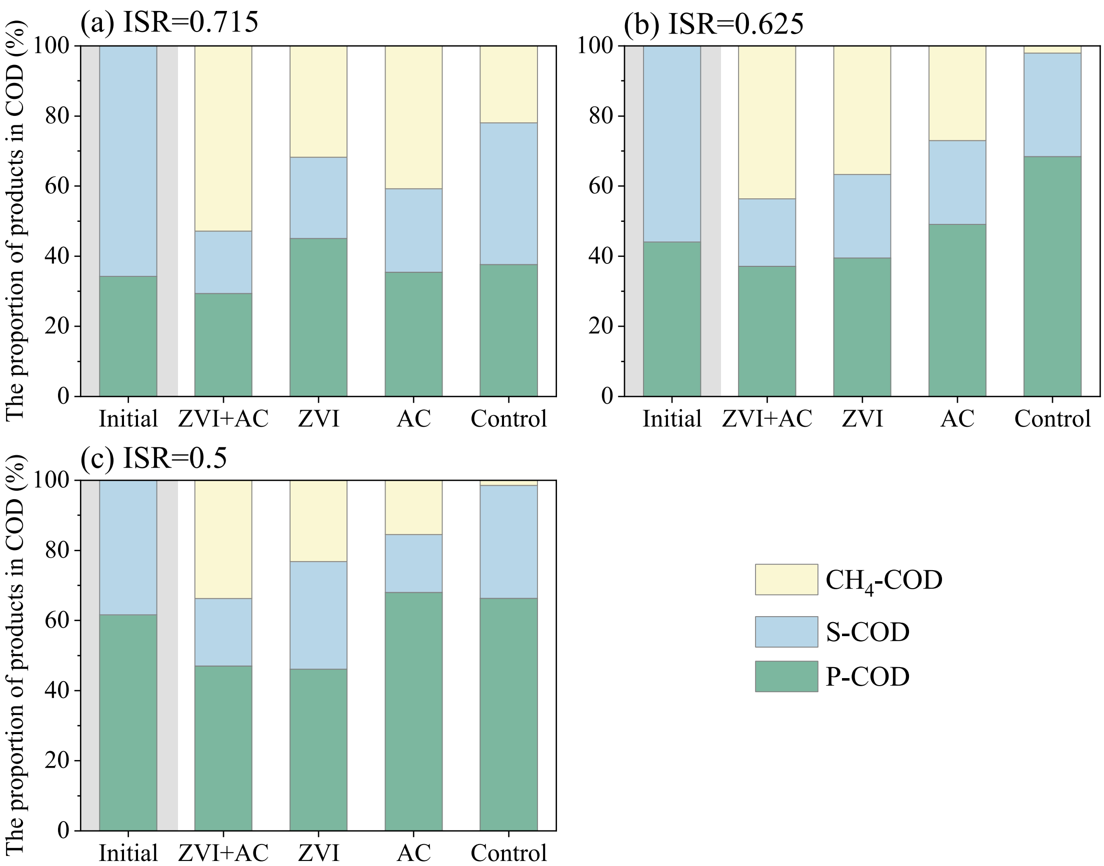

Figure 7. COD balance of each group at the initial and end stages of the AD process.

At the initial state of the three ISRs, organic matter existed in the form of particles and supernatants, and the proportion of P-COD increased from 34.24% to 44.07% and 61.62% as the ISRs decreased. Usually, soluble organic matter is preferentially utilized in AD and particulate organic matter is not easily degraded, therefore, a low ISR is not conducive to methane production. As AD proceeded, S-COD decreased substantially and was utilized for methane production, resulting in a relative increase in the proportion of P-COD and a substantial increase in CH_4-COD. The ZVI + AC group had the highest proportions of CH_4-COD (33.7–52.8%) and lower proportions of S-COD (17.80–19.29%), which intuitively indicated that ZVI coupled with AC increased the conversion rate of carbon sources to methane. The higher proportions of S-COD and P-COD in the control group under low ISR indicated that the activities of hydrolyzing bacteria and methanogens were inhibited under high loading conditions, and could not efficiently hydrolyze organic matter and utilize it for methane production. The relative abundance of hydrolyzing bacteria, such as *Clostridium*, was also found to be lower at low ISR in previous studies, while the addition of ZVI increased the abundance of hydrolyzing bacteria in the system [21]. Yang et al. found that the addition of AC-enriched hydrolyzing and methanogenic bacteria in the system, and accelerated substrate consumption and methane production [47]. Therefore, ZVI coupled with AC can fully utilize the advantages of both to maintain gas production under high loading conditions and improve the hydrolysis efficiency and degradation rate of organic matter, thus promoting AD.

4. Conclusions

To solve the problems of acid inhibition during high-load AD of FW, this study investigated the effects of coupled addition of ZVI and AC under three low ISR conditions of 0.715, 0.625, and 0.5, from the perspective of engineering applications. The results showed that the TVFA concentration in the control group increased significantly, the system acidified and stopped gas production as the ISR decreased from 0.715 to 0.625 and 0.5, while adding ZVI or AC alone effectively alleviated acidification and increased biogas production. Moreover, the coupled addition of ZVI and AC had the highest cumulative biogas production and the shortest lag time under the three ISRs, which effectively improved the anaerobic digestion efficiency. The ZVI + AC group had the highest SCOD degradation rates, VFAs degradation rates, and lowest propionate concentrations under the three ISRs, as well as reducing the TAN concentration when ISR = 0.5, which effectively alleviated acidification and ammonia inhibition under high-load conditions. COD mass balance analyses indicated that the coupled addition of ZVI and AC promoted the conversion of particulate organic matter to soluble organic matter and increased the conversion of carbon sources to methane.

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