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EFFECTS OF ZERO-VALENT IRON AND ENZYMES ON THE ANAEROBIC CO-DIGESTION OF SEWAGE SLUDGE AND CORN SILAGE

Anaerobic co-digestion of sewage sludge and corn silage with zero-valent iron powder (Fe^0), cellulase, and papain as reinforcement means was conducted. COD-based feeding ratio of sewage sludge to corn silage was set to 2:1, the solids retention time (SRT) 20 day, digestion temperature 35 °C, and mixing speed 60 rpm. Removal rates of total COD during the control group, and Fe^0 , papain, cellulase, and papain, Fe^0 , and the two kinds of enzyme-added tests were 38.04, 41.02, 34.62, 34.55, 35.42, and 48.21%, respectively. The corresponding biogas production was 2.12, 2.62, 2.22, 2.41, 2.25, and 2.81 dm^3/day , respectively. The results indicated the addition of cellulase, and papain could maximize the decomposition and hydrolysis of organic matter in sewage sludge and corn silage to volatile fatty acids. Fe^0 could reduce the redox potentials of the anaerobic co-digestion, optimize the circumstances of the methanogenesis stage, accelerate biogas production, and improve biogas components. Fe^0 and enzymes played a synergistic role in the anaerobic co-digestion system. Life cycle assessment indicated that the anaerobic co-digestion of sludge and corn silage co-substrates could benefit the economy, environment, and social development under the synergistic action of Fe^0 and enzymes.

1. INTRODUCTION

Concerns over the disposal of large quantities of organic wastes from domestic, industrial, and agricultural sources together with the need to reduce greenhouse gas emissions have been a major driver for further development of anaerobic digestion (AD) technology [1]. It has been widely used by wastewater treatment plants (WWTPs) to stabilize sewage sludge before land application or disposal and, at the same time, pro-

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duce biogas (which is a renewable fuel) to offset some of the energy input in the treatment process. During AD, nitrogen and phosphorus are liberated into the liquid phase in the form of ammonia and phosphate; thus, AD can also be an excellent platform for nutrient recovery [1].

A recent and notable trend in the development of AD is to co-digest two or more substrates together. Anaerobic co-digestion (AcoD) can overcome several inherent problems associated with single substrate digestion, such as the lack of micronutrients, imbalanced C/N ratio, and unfavorable (i.e., too high or too low) organic loading rates [2]. In the context of the water industry, the existing spare capacity of anaerobic digestion infrastructure at wastewater treatment plants allows for anaerobic co-digestion of sewage sludge with organic waste to generate supplementary revenue via gate fees or service charges, whilst producing electricity and heat [2]. Although successful co-digestion of sewage sludge and various organic wastes, such as food waste [1], and fat oil and grease [3], has been reported in many recent studies, several key aspects of the AcoD process remain poorly understood. In particular, little is known about the synergistic effect of co-digestion on anaerobic performance and the associated mechanisms responsible for such effect.

Co-digestion can enhance the degradation of each substrate [4]. In other words, co-substrate addition can result in synergistic effects, which result in either a boost in specific methane yield of the individual substrate in the mixture or an increase in biogas production kinetics, differing from the additive effect, where an increase in methane production is simply due to a higher mass of available biodegradable organic matter per unit volume from co-substrate addition. There has been some evidence that co-digestion can also result in some antagonistic effects [5]. However, in some cases, no obvious effects of co-digestion compared to mono-digestion have also been reported [6]. It is widely hypothesized that co-digestion can improve the process performance mainly because of a more balanced C/N ratio and sufficient macro- and micro-nutrients, a high buffering capacity, and a higher readily biodegradable organic fraction [7]. These factors attributed to the synergistic effects are inherently associated with co-substrate properties and composition. For example, sludge with a low C/N ratio can be co-digested with wastepaper with a high carbon content to achieve an optimum C/N ratio of 20–25 [8].

AD is an effective means of turning crop corn silage waste into treasure. Under anaerobic conditions, organic wastes such as corn silage can be decomposed and utilised by anaerobic microorganisms to produce methane. AD has many engineering applications because of its simple operation, low cost, and relatively mature technology. However, AD of the corn silage to produce biogas is facing many problems, such as long biogas production cycle and low biogas production, because it is not easily biodegradable. The pre-treatment of corn silage to improve its bioavailability has become a hot topic. Most physical, chemical, and thermal pre-treatments require high energy input and produce harmful effects, such as high temperature, high pH value, and inhibition of

by-products, all of which inhibit anaerobic digestibility. However, unlike these methods, biological pre-treatment is relatively economical, energy consumption and chemical costs are low, and it is safer because it does not produce inhibitory by-products [9]. Because lignocellulose-containing organisms are effective in degrading lignocellulose compounds, biological pre-treatment with microbial enzymes is considered suitable. However, the addition of enzymes can increase the volatile fatty acids (VFA) content in digestive juice and inhibit the methanogenesis stage [10]. On the other hand, zero-valent iron powder (Fe^0) can promote the conversion of VFA into biogas [11]. Enzymes and Fe^0 , as reinforcement, will improve the performance of anaerobic digestion.

This study aimed to systematically elucidate synergistic effects of enzyme and Fe^0 addition during AcoD of sludge with corn silage by applying methane production together with chemical oxygen demand (COD) balance calculations. The specific objectives of this study were: (i) to assess the process stability, and (ii) to quantify synergistic effects of the action of enzymes and Fe^0 on co-digesting sludge and corn silage through specific methane yields and the removal of volatile solid (VS) based on COD balance.

2. MATERIALS AND METHODS

Sludge and substrates. Sewage sludge from the sludge dehydrating unit of Eastern Water Treatment Plant, Shanghai, China was used. The sludge was diluted to a mixed liquid suspended solids (MLSS) concentration of 18 g/dm^3 . The corn silage was obtained from suburban farms of Zhengzhou, Henan province of China, which was dried and chopped to pieces of 1–2 cm. To maintain their stability, the sludge was stored at about $-4 \text{ }^\circ\text{C}$ while the corn silage was stored at $18\text{--}20 \text{ }^\circ\text{C}$ until experimental use.

Table 1

Characteristics of sewage sludge and corn silage used in the experiments

Parameter	Inoculum	Sludge	Corn silage
pH	6.8 ± 0.5	6.8 ± 0.5	–
TS, wt. %	1.0 ± 0.2	3.0 ± 0.2	87
VS, wt. %	–	1.8 ± 0.2	–
COD, g/g TS	1.8 ± 0.2	0.53 ± 0.02	1.12 ± 0.05
$\text{NH}_4^+\text{-N}$, mg/dm ³	40 ± 20	80 ± 20	–
TP, mg/dm ³	80 ± 30	110 ± 30	–
VFA, mg/dm ³	100 ± 30	120 ± 30	–
Cellulose, wt. %	–	–	33.87
Hemicellulose, wt. %	–	–	23.64
Lignin, wt. %	–	–	15.23

TS – total solids, VS – volatile solids, $\text{NH}_4^+\text{-N}$ – ammonium nitrogen, COD – chemical oxygen demand, VFA – volatile fatty acids, TP – total phosphorous.

Before the feeding, the frozen sludge was transferred to a cold room (4 °C) for one day and placed at room temperature for 1 h. To investigate the influence of feedstock on the characteristic of AD, the ratio of sludge and corn silage was adjusted to 2:1 (according to the mass of total solids (TS), g). Key properties of inoculum, sludge, and cornstalk are shown in Table 1.

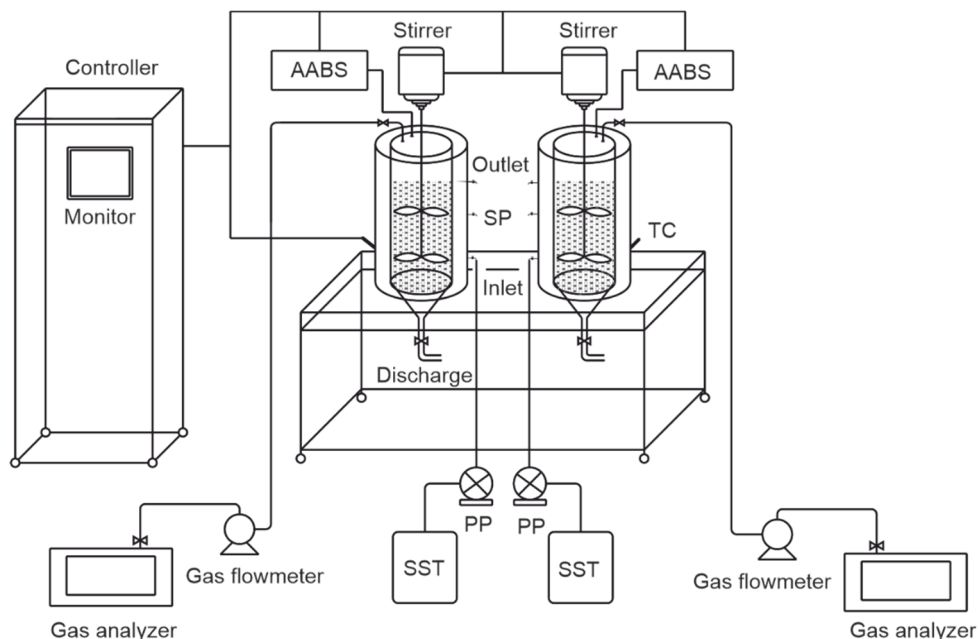


Fig. 1. Schematic diagram of the anaerobic digestion system: AABS – acid and passivity sensor, TC – temperature controller, SP– sampling port, PP – peristaltic pump, SST – substrate storage tank

Experimental equipment. The self-designed AD system (Fig. 1) consisted of four components: (a) digesters, (b) feeding system, (c) control panel, and (d) biogas measurement system. For the AD tests, two parallel oval-shaped anaerobic digesters were used made of stainless steel, with a total volume of 25 dm³ and a working volume of 20 dm³ each. Two propellers were installed for continuously homogenizing feedstock. The rotation (60 rpm) was controlled by an electric three-phase motor (220 V) operated by an inverter through the control panel. Two sampling ports were located in the middle and bottom of each digester to allow the collection of the samples for subsequent chemical analysis and to discharge the digestate. The feeding system comprised a pipe, peristaltic pump, and valve. The co-substrates were fed into each digester through a lower inlet by a peristaltic pump (BT300-2J, Longer, England), and discharged through the static pressure an upper outlet. Besides, nitrogen gas was introduced with a pressure-reducing valve (YQD-6, Shanghai, China) into the digester to eliminate oxygen in the headspace.

The movement of all mechanical devices and the operation sequence were controlled through a control panel situated within a protected and closed box. The temperature control was automated through a control unit connected to a built-in temperature probe and a heating rod to maintain a constant temperature of 37 °C. In the upper part, a liquid crystal display (LCD) monitor was mounted, connected to a pH probe and a temperature probe, both located in the midsection of the digester body.

The biogas measurement system consisted of biogas piping, a gas analyzer, and a biogas flow meter. The volume of biogas produced in the digester was measured with a volumetric flow meter (LML-1, Beijing, China). A gas analyzer (Gasboard-3200, Cubic Optoelectronics Co., China) was used to measure the composition of biogas.

Experimental procedure. The digesters must go through the start-up stage successfully before tests. The inoculum sludge 20 dm³ collected from the anaerobic digester of our lab was pumped into each digester. The procedure for the start-up has been described elsewhere [12]. Following the start-up, the digesters were fed with the co-substrates of sludge and the corn silage (the ratio of sludge and corn silage weight was adjusted to 2:1) based on the previous results [13]. Before feeding, the sludge was placed in a water bath to raise its temperature to that of the corresponding Ad; it was continuously stirred to obtain homogeneity. Solid retention times (SRTs) of mesophilic anaerobic digestion (MAD) were set at 20 day based on the previous results [13].

Based on the objectives of this study, three groups of batch tests were conducted, namely anaerobic co-digestion added with Fe⁰ (test F), cellulase (test C), and papain (test P) separately (test I); anaerobic co-digestion added with cellulase and papain together (test CP) (test II); and anaerobic co-digestion added with Fe⁰, cellulase, and papain together (test FCP) (test III). Co-substrates with additives were homogenized and fed into digesters to obtain an optimum dosage. According to previous reports [14], their concentrations during the tests were: Fe⁰ 800 mg/dm³, cellulase 100 mg/dm³, and papain 50 mg/dm³. ADs would run for 2–3 SRTs to be stabilized before a test began. The conventional indicators were also monitored for the confirmation of stabilization.

Samples of co-substrates were collected every 48 h during each test. Each time, 100-cm³ sample from a digester was taken in 250-cm³ flask and centrifuged immediately for 10 min at 1600 rpm to separate it into the soluble and biosolid fractions. The pre-treatment could ensure the accurate demonstration of the variations of the indicators during tests.

Analytical methods. COD of both soluble and biosolid fractions as well as corn silage were determined by the modified standard methods with HACH high-range COD kit (DRB200, HACH Company, USA). Ammonium nitrogen (NH₄⁺-N), total phosphorous (TP), total solids (TS) and volatile solids (VS) were performed according to standard methods [15]. The other following indicators were measured only in the soluble fraction. VFA was determined according to an 8-point titration method [16]. VFA was

converted to acetic acid. The volume of biogas was measured using a volumetric flow meter (FMA-1620A, Omega, UK). The value obtained was corrected to standard temperature and pressure conditions of 0 °C and 0.1 MPa. Biogas components including CH₄, CO₂, O₂ and H₂S were determined by a gas analyzer (Gasboard-3200, Cubic Optoelectronics Co., China). The moisture of corn silage was analyzed with a moisture meter (SH-02, Shengzhen Egrey Instruments Co., Ltd., China), and its cellulose, hemicellulose, and lignin were analyzed using an Ankom 2000 Fiber Analyzer System (Ankom Technology Corp., USA) as Yuan et al. [17] described. Fe in the samples was measured with an inductively coupled plasma mass spectrometry (ICP-MS) (FMA-1620A, Omega, UK). The reagents used were of analytical grade or better. Ultrapure water was used during all the tests and analyzes, obtained with the Aquapro Ultrapure Water System (China). All measurements were conducted in duplicate, and the results presented are the mean value. The statistics software Origin 2017 was used for data analyzes.

Calculations. Soluble COD removal efficiency was calculated as follows:

$$\text{SCOD removal} = \frac{\text{SCOD}_{c, \text{in}} - \text{SCOD}_{c, \text{out}}}{\text{SCOD}_{c, \text{in}}} \times 100\% \quad (1)$$

where SCOD_{c, in} is the soluble COD concentration of the feedstock and SCOD_{c, out} is the soluble COD concentration of the digestate.

Synergistic or antagonistic effects of the co-digestion of the additive are expressed by the difference between measured specific methane yield and weighted specific methane yield (WSMY), which is the sum of the individual contributions of each additive during the co-digestion (test I) [18]

$$\text{WSMY} = \sum_{i=1}^n \frac{M_i S_i}{S_0} \quad (2)$$

where n is the number of additive, M_i is the individual methane yield of the additive, dm³/g VS, S_i is the added VS of the individual additive in the mixture, g, and S_0 is the total VS of the co-substrates, g.

3. RESULTS AND DISCUSSION

3.1. PROCESS STABILITY

pH is one of the key operational factors that greatly affects the digestion process. In the biogas production process, there are multiple organisms of different optimal growth

pH values. The most favorable pH range to obtain maximal biogas production in AD is 6.8–7.2 [19]. pH decreased rapidly after the commencement of the experiment on the fifth day (Fig. 2). The decrease in pH may indicate the onset of hydrolysis and acidogenesis as the population of methanogens had not yet stabilized to maturity. pH increased to 6.8 from day 5 to day 35 and stabilized at around 6.8 after day 35. pH decreased most after adding Fe⁰ and enzymes. This suggests that both additives play a stronger role in the hydrolysis and acidogenesis stage than other groups. The effect of papain and Fe⁰ was not obvious. It is noteworthy that the system had low pH values and underwent a shorter hydrolysis stage than other groups after adding Fe⁰ and enzymes. Thus, the increased biogas resulted in a slight increase in the concentrations of VFA (up to 300 mg/dm³) within the digester.

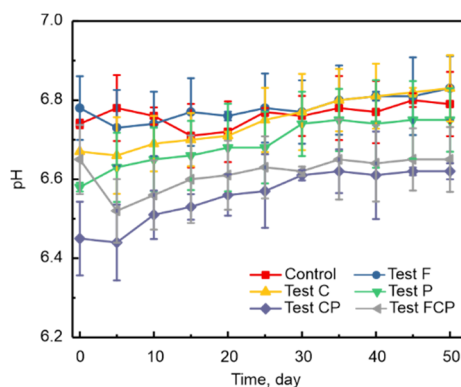


Fig. 2. Time dependences of pH during AcoDs of sludge and corn silage

Figure 3 represents the effects of various additives on the total COD (TCOD) and soluble COD (SCOD) during AcoD of the co-substrates. No remarkable differences are visible. SCOD was mostly affected in the C and CP tests, and the concentration in the supernatant increased. Compared with the control test, the increase in SCOD in the tests C and CP was 17.6% and 21.63%, respectively.

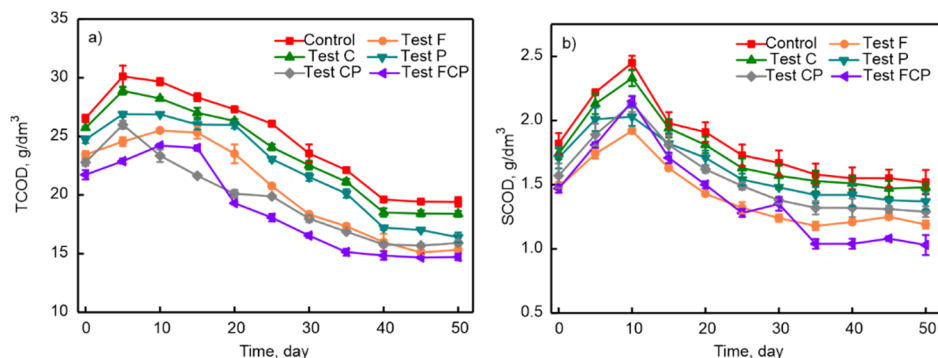


Fig. 3. Time dependences of a) TCOD and b) SCOD during AcoDs of sludge and corn silage

This might be because cellulase or papain can hydrolyse cellulose, hemicellulose, and lignin in corn silage to water-soluble small-molecule organic matter, resulting in an increase in SCOD concentration in the supernatant. However, the SCOD content of the test FCP was the lowest, mainly because under the action of Fe^0 , SCOD was converted into biogas by anaerobic microorganism consumption. In summary, the highest TCOD removal rate of anaerobic digestion of co-substrates of sludge and corn silage was 48.21% in the presence of Fe^0 and enzymes, which indicated that under certain conditions, iron and enzymes could promote COD consumption in co-matrix mixtures [20].

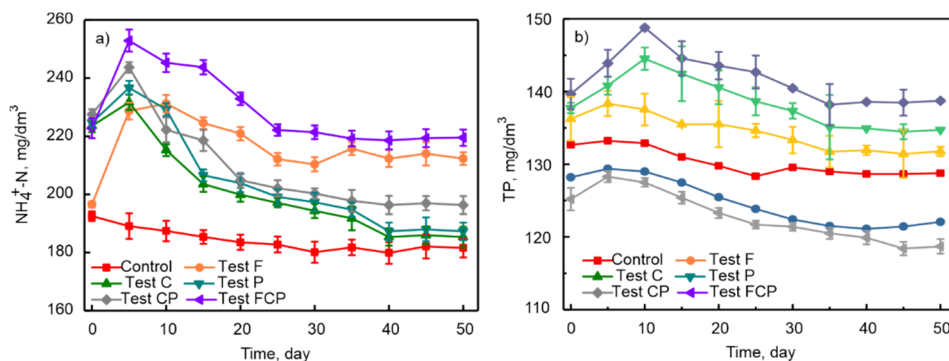


Fig. 4. Time dependences of a) N-NH_4^+ , b) TP concentration during AcoDs of sludge and corn silage

Figure 4a shows the effects of different additives on N-NH_4^+ concentration during AcoD of sludge and corn silage co-substrates. The concentration of N-NH_4^+ increased with the addition of different additives in the first 5 days. The highest N-NH_4^+ concentrations, corresponding to the control group, tests F, P, C, CP, and FCP, were 195.92, 228.62, 236.68, 231.71, 243.68, and 252.26 mg/dm^3 , respectively. Compared with the control group, the corresponding increases in the concentration of N-NH_4^+ were 16.69, 20.81, 18.33, 24.36, and 28.76, respectively, which indicates that both Fe^0 and enzyme promote the production of N-NH_4^+ , mainly because of the reaction of iron with nitrate and nitrite in the co-substrate anaerobic digestion system to produce N-NH_4^+ . Cellulase and papain promote the hydrolysis of nitrogen-containing organic matter in sludge and corn silage, which results in the increase in N-NH_4^+ concentration in the co-substrate anaerobic digestion system. The decomposition of enzymes can also produce part of N-NH_4^+ . After 20 days, the anaerobic digestion system gradually stabilized and the concentration of N-NH_4^+ gradually became constant. It was ca. 219 mg/dm^3 , and basically did not inhibit the anaerobic microorganisms [21].

Figure 4b shows the effects of different additives on TP concentration during AcoD of sludge and corn silage co-substrates. TP concentration increased gradually in the first 5 days. This is mainly because the phosphorus-containing organic matter in sludge and corn silage was gradually decomposed and released into the digestive juice by anaerobic

microorganisms, resulting in the increase in TP concentration in the co-substrate anaerobic digestion system. Different additives have different effects on TP concentration. Test P, test C, and test CP can increase the TP concentration in the system to a certain extent in the first 20 days. This is mainly due to the accelerated degradation of phosphorus-containing organics by cellulase and papain, while in tests F and FCP on TP concentration the effects of co-substrate anaerobic digestion are less substantial. After 5 days, with the stabilization of the anaerobic digestion system, the TP concentration gradually stabilized. After stabilization, the corresponding TP concentrations of the control group, and tests F, P, C, CP, and FCP were 128.66, 121.78, 134.71, 131.52, 138.62 and 118.41 mg/dm³, respectively. It can be concluded that compared with the control group, test P, C, and CP, the TP concentration in the anaerobic digestion system of sludge and corn silage co-substrates increased by 4.71, 2.22, and 7.74%, respectively, but the effect is relatively small. The TP concentration can be reduced in tests F and FCP, with removal rates of 7.97 and 13.09%, respectively. According to the above analysis, the combined action of Fe⁰ and enzymes on AcoD of sludge and corn silage is conducive to the removal of TP in the system, stabilizing the content of TP in the system and indicating that there is a certain synergistic effect between Fe⁰ and enzymes [4].

VFA concentration is meaningful to anaerobic digestion, especially for co-digestion of corn silage because of the high content of carbohydrates. VFAs can also be used as an indicator for the evaluation of fermentation status [22]. It is well known that VFA originates from hydrolysis acidification and then it is converted to methane and carbon dioxide by methanogenic bacteria. However, different acids have different degradation rates; for example, propionic acid degrades more slowly than other acids [23]. High VFA concentrations in anaerobic digestion could cause the inhibition of methanogenesis. In a study, the fermentation process was slightly inhibited when the VFA concentration was above 4 g/dm³, and the composition of biogas changed when the VFA concentration was over 6 g/dm³ [24].

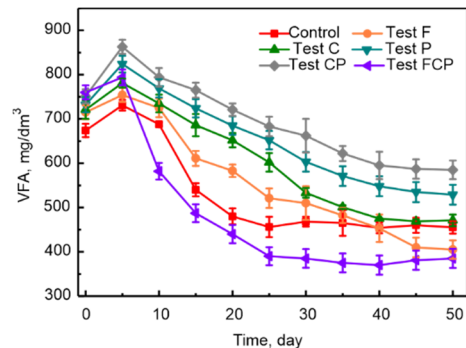


Fig. 5. Time dependences of VFA concentration during AcoDs of sludge and corn silage

Figure 5 time dependences of VFA concentration during AcoD of sludge and corn silage co-substrates by different additives during three consecutive SRT operations.

Compared with the Fe^0 test and the enzyme test, the change in VFA content could demonstrate the synergistic action of the iron enzyme.

In the first 5 days, the VFA concentration of various additives increased. The highest VFA concentrations of tests F, P, C, CP, and FCP were 754, 781, 824, 863, and 794 mg/dm^3 , respectively, which were higher than in the control group (731 mg/dm^3). This indicated that the additives could promote the hydrolysis of organic matter in sludge and corn silage. In the test group, the lowest VFA concentration of test F was 754 mg/dm^3 , and Fe^0 might promote the transformation of VFA during the anaerobic digestion stage. Five days later, with the rapid propagation of methanogenic bacteria, the anaerobic digestion system of sludge and corn silage co-substrates gradually stabilized. Under the action of different additives, VFA was gradually consumed. Figure 5 shows that the concentration of VFA decreased fastest in the test FCP. After stabilization, the corresponding VFA concentrations of tests F, P, C, CP, and FCP were 408, 470, 529, 580, and 382 mg/dm^3 , respectively. The corresponding VFA consumption rates were 47.74%, 39.82%, 35.8%, 32.79%, and 52.72%. The above results indicate that the highest consumption rate of VFA is achieved in the test FCP. Fe^0 may promote the conversion of some organic acids of high concentration VFAs to acetic acid, reduce the redox potential in the anaerobic digestion system, and optimise the anaerobic environment, resulting in faster consumption of VFA.

3.2. BIOGAS PRODUCTION AND SOLUBLE COD REMOVAL RATE

Figure 6 shows the effects of different additives on methanogenesis during AcoD of sludge and corn silage co-substrates. The anaerobic digestion system is in the adaptive period in the first 10 days. At this stage, compared with the control group, different additives increased the gas production rate but the effect of different additives on the biogas production rate is not significant, probably because lower pH and higher VFA concentration inhibit the growth of methanogens. Ten days later, with the consumption of VFA, the pH value gradually increased, methanogens multiplied in large quantities, and the biogas production of the anaerobic digestion system gradually stabilized.

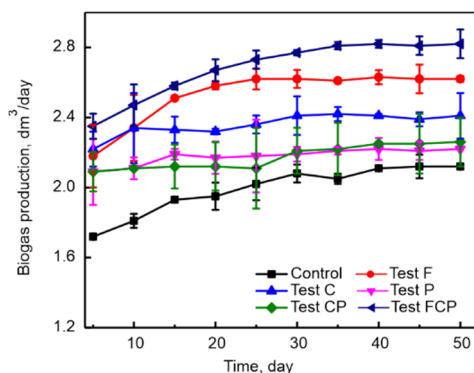


Fig. 6. Changes in biogas production during AcoD of co-substrates with various additives

After stabilization, the corresponding biogas production of in tests F, P, C, CP, and FCP was 2.62, 2.22, 2.41, 2.25, and 2.81 dm³/day, respectively. It can be seen that the biogas production in test FCP was much higher than that in other tests without Fe⁰. Tests F and FCP showed that Fe⁰ could increase the biogas production of the anaerobic digestion system mainly because iron [11, 21, 25]: (1) was a necessary trace element for methanogenesis bacteria; (2) reduced the redox potential of the anaerobic digestion system; (3) was corroded by hydrogen evolution under acidic conditions, which directly participated in methane formation and (4) could synthesize and activate acid production and methane production. A variety of enzymes were involved in this stage.

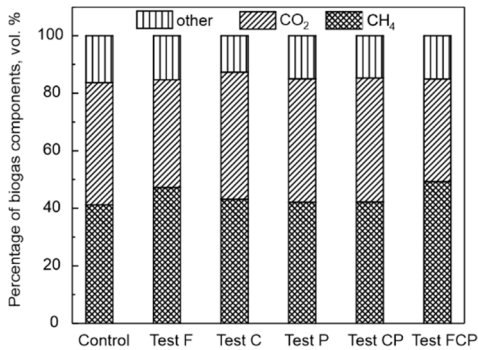


Fig. 7. Changes in biogas components on average during AcoD of co-substrates with various additives

Figure 7 shows changes in biogas components during AcoD of co-substrates with different additives. The methane proportion corresponding to the control group, tests P, C, and CP is less than that of CO₂. When Fe⁰ is added to the co-matrix anaerobic digestion system, the methane proportion of test F and test FCP (is 47.21 and 49.35%, respectively) is larger than that of CO₂. The methane proportion of test FCP is the largest, and the carbon dioxide proportion is the smallest, which shows that the combined action of iron powder, vitaminase and papain can promote the conversion of organic matter into methane in the co-substrate anaerobic digestion system and promote the reduction of CO₂ to methane, resulting in an increase in methane components. The H₂S concentrations of the control group, tests F, P, C, CP, and FCP were 325, 133, 480, 434, 627, and 121 mg/m³, respectively. Compared with other test groups, the H₂S concentration in the FCP was the smallest and the removal effect was the best. This indicated that the combined action of Fe⁰, cellulase, and papain could enhance methane production and decrease CO₂ ratio and H₂S content in the co-substrate anaerobic digestion system.

Removal of COD during AcoD of sludge and corn silage with different additives were calculated (Fig. 8). The COD removal rates of the control group, tests F, P, C, CP, and FCP were 38.04, 41.02, 34.62, 34.55, 35.42, and 48.21%, respectively. The weighted specific methane yield in the control group, and particular tests were 1.00, 1.41, 0.92, 0.95, 0.81, and 1.57%, respectively. The above data showed that the COD removal rates of test FCP were the highest. According to the data analysis, the removal rate of COD in

the test CP was relatively lower, indicating that cellulase and papain could not effectively promote the removal of COD. When Fe^0 was added to the CP, the removal rate of COD increased greatly. Thus, the lower monetary cost can be expected during the downstream processes of the digestate in terms of digestate dewatering ability and bio-solids production.

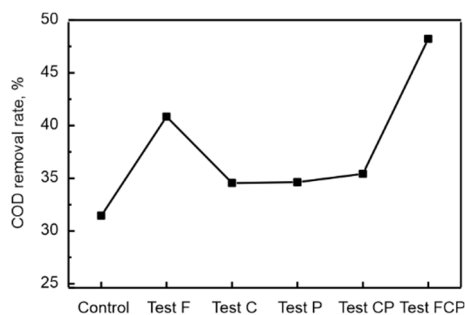


Fig. 8. Removal of COD during AcoD of sludge and corn silage with various additives

The efficiency of anaerobic co-digestion in terms of methane yield can be expressed by the synergistic or antagonistic effect. Measured specific methane yield was calculated based on the results obtained in test III, and WSMY was achieved through equation (2). The synergistic or antagonistic effects of the co-digestion substrates can be determined by the difference between the specific methane yields (obtained in tests I–III). There is a synergistic effect when the differential is positive, otherwise an antagonistic effect. As shown in Fig. 6, all treatments in the co-digested tests showed synergistic effects. However, the effects increased significantly with the addition of Fe^0 and enzyme in test III.

Life cycle assessment (LCA) was based on AcoD of sludge and corn silage. The anaerobic digestion reactor under these experimental conditions means that the operating conditions of anaerobic digestion of sludge and corn silage are unchanged. The volume of the anaerobic reactor was expanded to 300 m^3 , and the volume of the original anaerobic digestion tank was expanded $10\,000\times$. This assessment assumed that there were sufficient raw materials for anaerobic digestion of sludge and corn silage co-substrates (mainly sludge, corn silage, and Fe^0), that the equipment of the anaerobic digestion reactor was in good condition and there was no malfunction during the evaluation cycle, that the relevant costs incurred by personnel were not taken into account, and that the digestive juice produced in this test was directly used or processed to be used as crop fertilizer. The purpose of this evaluation was to explore the environmental impact of anaerobic digestion of sludge and corn silage co-matrix technology under the synergistic effect of the iron enzyme and the economic rationality of its practical application in engineering.

The process used in this evaluation was as follows:

1. According to the price of corn silage, cellulase, papain, and Fe^0 in the current market (Table 2), the cost of consuming these additives in one year was calculated. The

cost of electricity consumed by anaerobic digestion, that is, the total cost of the experiment (not the cost caused by labor and other external conditions), was calculated.

Table 2

Basic parameters of sludge, corn silage, iron powder, enzymes, and biogas production for the calculation

Item	Parameter	Value
Sewage sludge	TS, g/dm ³	31±3
	VS, g/dm ³	15.6±2
	COD, g/dm ³	18±2
	N-NH ₄ ⁺ , mg/dm ³	123±10
Corn silage	COD, mg/g	1170
	Cellulose, wt. %	37.2±0.4
	Hemicellulose, wt. %	25.7±0.3
	Lignin, wt. %	7.8±0.4
	Price, US \$/kg	0.3
Additive	Iron powder, US \$/kg	1.0
	Cellulase, US \$/kg	18.9
	Papain, US \$/kg	14.4
Biogas production	Calorific value of methane, kW·h/dm ³	7.66
	Methane power-generating efficiency, %	55
	Methane heating efficiency, %	45
	Rate, dm ³ /day	2.81
	Methane content, %	49.3
	CO ₂ content, %	35.6
Others	Electricity price, US \$(kW·h)	0.14
	Sludge disposal cost, US \$/ton	82.0

2. The net value of methane produced in this experiment was converted into corresponding electricity and heat, and the energy and heat generated in one year under the synergistic action of the ferric enzyme were calculated. The results were compared with those of the control group. Then, according to the current market price, the cost could be calculated. At the same time, the environmental benefits caused by the reduction of carbon dioxide were analyzed.

3. The cost calculated in the first two steps was subtracted. If the value is positive, the economic benefit is better. If the value is negative, the cost of the experiment is larger, and still needs to be reduced.

The basic parameters of sewage sludge, corn silage, additives, biogas production, etc., used for the calculation (Table 2) are collected and quantified, mainly based on the data from these tests concerning literature data [26]. The parameters as the input and output for the control and pilot groups as well as the assessment results are shown in Table 3. Compared with the control group, each 300-m³ sludge and corn silage anaerobic digestion tank in the experimental group can save about 45 000 US \$ per year and

reduce CO₂ emissions by 492.86 m³. This indicated that the anaerobic digestion technology of sludge and corn silage co-substrates under the synergistic action of the Fe⁰ and enzymes can effectively achieve the unity of economic, environmental, and social benefits.

Table 3

Parameters used as the annual input and output for control and pilot groups as well as the LCA results of AcoD of sewage sludge and corn silage

Item	Parameter	Control group	Pilot group	Life cycle assessment [kUS \$/year]		
				Cost of control group	Cost of pilot group	Saving
Input	Sludge	3394.5 t	3394.5 t	–	–	–
	Corn silage	876 t	876 t	172.33	172.33	0
	Fe ⁰		87.6 t	0	93.15	–93.15
	Cellulase		10.95 t	0	110.92	–110.92
	Papain		5.475 t	0	89.67	–89.67
	Electric energy	29 200 kWh	29 200 kWh	2.79	2.79	0
Output	Biogas	7701.5 m ³	10256.5 m ³	–	–	–
	Methane	3173.02 m ³	5056.45 m ³	349.08 (power generation)	542.18 (power generation)	193.10
				299.10 (heat energy)	397.72 (heat energy)	98.62
	CO ₂	3273.14 m ³	3651.31 m ³	59.85	52.84	7.01
Sludge	3302.1 t	2812.6 t	270.66	230.54	40.12	
Total						45.11

4. CONCLUSIONS

The characteristics of co-substrate anaerobic digestion (AcoD) technology was studied through a series of tests. The feasibility of enhancing its performances of co-digestion of sludge and corn silage under the synergistic action of the ferric enzyme was analyzed through life cycle assessment. The effects of Fe⁰, cellulase, and papain on biogas production and COD removal rates during AcoD of sewage sludge and corn silage co-substrates under the synergistic action of the iron and enzymes were studied. After stabilization of the co-substrate anaerobic digestion system, the TCOD removal rate was 48.21%, the VFA consumption rate was 52.72%, and the biogas production was 2.81 dm³/day, according to the optimal ratio of Fe⁰, cellulase, and papain. When all these additives were added at the same time, TCOD removal rate, VFA concentration, and biogas production were greatly increased, which indicated that Fe⁰ and enzymes could not only strengthen the hydrolysis but also enhance the methanogenesis. Thus, Fe⁰ and enzymes played a synergistic role in the process of co-substrate anaerobic digestion. Life cycle assessment (LCA) was used to evaluate the environmental impact of anaerobic co-digestion of sewage sludge

and corn silage co-substrates under the synergistic action of ferric enzymes and the economic rationality of its practical application in engineering. The results showed that compared with the control group, each 300-m³ sewage sludge and corn silage anaerobic digestion tank in the experimental group could save about 45 000 US \$ per year, and the CO₂ emission reduction reached 492.86 m³ per year. This indicated that the anaerobic co-digestion of sludge and corn silage co-substrates could benefit the economy, environment, and social development under the synergistic action of Fe⁰ and enzymes.

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