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ORIGINAL PAPER

Effect of Zinc Supplementation on Biogas Production and Short/Long Chain Fatty Acids Accumulation During Anaerobic Co-digestion of Food Waste and Domestic Wastewater

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Abstract
This work evaluated the stimulatory effect of zinc (provided as $ZnSO_4$ and $ZnCl_2$; 50, 70 and 100 mg/L Zn^{2+}) supplementation on biogas (methane) production, while co-digesting a mixture of food waste and domestic wastewater (0.183, v/v) in an upflow anaerobic sludge blanket reactor operated under mesophilic condition at pH 7.6 and 10 days of hydraulic retention time. The intermittent feeding mode (48 h feed and 48 h feedless) was applied to avoid the reactor failure due to the accumulation of short and long chain fatty acids (SCFAs and LCFAs). With the increasing zinc supplementation from 50 to 100 mg/L Zn^{2+}, chemical oxygen demand removal efficiency and methane yield increased by 10 and 30–65%, respectively, compared to the control without zinc supplementation. This improvement was considered mainly attributed to the higher conversion of organic matter into methane since this microelement is essential to many enzymes involved in the anaerobic reactions. Regardless of the Zn^{2+} concentration, the total SCFAs accumulation was decreased, and together with the decrease of acetate concentration with the increase of zinc supplementation, SCFAs other than acetate might have been converted directly to biogas (methane) through pathways different from ordinary hydrogenotrophic and acetotrophic methanogenesis. There were statistically significant differences ($p<0.05$) in the effluent total LCFAs concentration, regardless of the influent supplemented with different zinc concentrations. The disappearance of the unsaturated ones (oleate and linoleate) after the microelement supplementation could be related to the contribution of biological and physical (precipitation) removal.

Keywords Anaerobic co-digestion · Biogas production · Domestic wastewater · Food waste · Zinc supplementation

Introduction

Annually, 1.3 billion tons of food produced for human consumption are wasted or lost worldwide [1]. In China, approximately 600 million Mg of food waste are generated annually [2] and are mainly incinerated or landfilled [3]. In Macau Special Administrative Region (SAR) of China, incineration has been used as a waste management method due to the limited territory (30 km^2). However, the incineration-based technologies have been a subject of intense debate in the environmental area and the adoption of alternative cleaner methods for the waste disposal and management is necessary [4]. The increasing amount of food waste-to-biogas projects shows that anaerobic digestion (AD) technology is the most attractive technique for the food waste treatment, even though some are still suffering from the technical and food waste collection issues [5]. Considering the concept of 'circular economy', the AD technology has been recognized as a promising option to treat food waste while producing biogas as energy and compost as soil fertilizer [6]. The potential use of AD as an energy recovery process would play a considerable role in the organic waste energy utilization taking into account that 248 MWe of energy could be recovered from AD of 4 million dry metric tons of landfilled food waste per year [7].

Food waste is mostly composed of lipids, carbohydrates, and proteins and their proportions are mainly related to the season and local cultural habits. In China, food is generally rich in oil (22–31% of the food waste dry matter), which would be an ideal and favorable substrate for AD due to the higher theoretical methane yield (0.99 L CH_4/g) of lipids

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[2]. However, the AD efficiency of treating food waste, especially lipid-rich one, is generally low, resulted from the accumulation of inhibitors such as ammonia nitrogen, short chain fatty acids (SCFAs), and long chain fatty acids (LCFAs) [8, 9]. To overcome this problem, the co-digestion of food waste with other substrates has been carried out to improve the biogas production performance [10–12]. Other strategies commonly applied to the lipid-rich substrates include the addition of adsorbents [13], microbial consortium adaptation [14], and intermittent feeding [15]. Our previous study [16] showed the successful co-digestion of food waste and domestic wastewater by using the intermittent feed mode strategy (48 h feed/48 h feedless). The degradation of fat matters was more effective during the intermittent mode and the inhibition observed in the continuous mode could be recovered accordingly.

AD is a complex multi-stage biochemical process catalyzed by different types of enzymes provided by diverse microorganisms, mainly including acid-forming bacteria and methane-forming archaea, with different nutritional requirements, sensitivity to environmental changes (e.g., temperature, pH), and growth kinetics [17]. The AD activity and stability is mainly associated with the relationship (balanced growth) between acid-forming bacteria and methane-forming archaea. For the food waste AD, SCFAs generally accumulate during acidogenic stage, followed by pH decline and reactor deterioration [8]. The scarcity of essential microelements in food waste is also an important factor limiting the AD process since micronutrients play major roles in many related metabolic pathways as growth factors to methanogens and being vital co-factors of such enzymes as carbon monoxide dehydrogenase, methyl-coenzyme M, and coenzyme M methyl-transferase [18, 19]. Consequently, the deficiency of microelements would cause limitation of the activity of the microbial consortium [20]. When Menon et al. [17] evaluated the influence of adding four microelements (Ca, Mg, Co, and Ni) in the methanogenic phase of two-phase thermophilic anaerobic digestion using food waste as the primary substrate, the optimal concentrations of 303, 777, 7 and 3 mg/L for Ca, Mg, Co, and Ni, respectively, increased the biogas productivity by 50% and significantly reduced the processing time. Tampio et al. [21] found out the mono-digestion of food waste failed at the organic loading rates (OLRs) of 3–6 kg VS/m^3/day due to the SCFAs accumulation. However, a stable digestion of untreated and autoclaved food waste was possible at the OLRs up to 6 kg VS/m^3/day when the reactor was weekly supplemented with the microelements solution (Al 0.1; B 0.1; Co 1.0; Cu 0.1; Fe 5.0; Mn 1.0; Ni 1.0; Zn 0.2; M 0.2; Se 0.2; and W 0.2 mg/L). In general, adding adequate concentrations of microelements would accelerate the degradation of SCFAs and LCFAs and would be beneficial for the anaerobic mono-digestion of food waste. Zhang et al. [22] observed the AD of food waste was not feasible even with the pH control, but the co-digestion of food waste with piggery wastewater showed a high methane production rate without the SCFAs accumulation and the microelement supplemented from piggery wastewater was suggested the key factor enhancing the co-digestion performances. Zhang and Jahng [23] further confirmed the food waste was usually deficient in microelements but the long term (368 days) AD of food waste was possible and stable without significant accumulation of SCFAs, due to the supplementation of micronutrients (2 mg/L Co, 100 mg/L Fe, 5 mg/L Mo, and 10 mg/L Ni). Facchin et al. [24] also observed the supplementation of 10 mg/kg TS Co and Ni, 1 mg/kg TS Se and W, and 6 mg/kg TS Mo increased the methane production to the range of 45–65% and suggested the performance stability of food waste AD could be reached by the microelement supplementation or even by the implementation of a co-digestion option. The impact of microelement supplementation (Co and Ni, both at 0.2 mg/L/day) on biogas production when co-digesting ammoniated rice straw and food waste was evaluated, and the simultaneous supplementation of Co and Ni increased the methane content significantly (68.9%) compared to the control without micronutrient addition (59.2%) while Ni was superior to Co on the VS removal rate [25]. Methanogenesis is considered one of the most metal enriched enzymatic pathways, and depending on the pathway adopted, different microelements requirements are necessary. However, in general, Fe is the most required microelement, followed by Ni, Co, and traces of Mo, W, and Zn [26]. Therefore, even though the supplementation of microelements has been extensively studied, there are still questions to be answered and rooms to improve, and the results obtained in this work would help to solve those issues related to the AD of a mixture of food waste and domestic wastewater. Optimizing the best microelements combination and their respective concentrations can be used for many substrates in full-scale applications for the improved biogas production.

The concentration of zinc commonly found in food waste varies (7.8–75 mg/L) [23, 27, 28]. This microelement is considered an essential nutrient and a cofactor of several methanogenic enzymes [29]. Previous works suggest the stimulatory/inhibitory effects of zinc supplementation on biogas production not conclusive. At the concentration higher than 40 mg/L, zinc inhibited 50% of methanogens using whey as substrate [30], while lower concentration (7.5 mg/L) toxic for the methane-producing anaerobic granular sludge treating yeast factory wastewater [31]. On the other hand, the zinc concentrations in the range of 125–1250 mg/L greatly improved the microbial activity during the swine manure AD [29]. The objective of current work was to supplement Zn^{2+} (as $ZnSO_4$ and $ZnCl_2$) at different concentrations (50, 70, and 100 mg/L), while co-digesting a mixture of food waste and domestic wastewater, to further find out the existence of stimulatory/inhibitory effects of this microelement on biogas production, methane content, and SCFAs and LCFAs accumulation.

Materials and Methods

Chemicals, Substrate Preparation, and Seed Culture

All the chemicals used were of analytical grades (Sigma-Aldrich). The effect of Zn^{2+} was first evaluated by adding zinc sulfate ($ZnSO_4$) at different concentrations (50, 70, and 100 mg/L Zn^{2+}) in the influent. To further confirm the stimulatory/inhibitory effect was attributed to Zn^{2+} and not to SO_4^{2-} addition, the experiment was repeated by supplementing the influent with zinc chloride ($ZnCl_2$) at the same concentration levels. The influent consisted of a mixture of food waste and domestic wastewater (at 0.183, v/v), collected from local university canteen and wastewater treatment plant, respectively. Table 1 shows the physicochemical composition of food waste, domestic wastewater, food wastewater, and sludge used as seed for the reactor. The food waste, consisted of rice (58.4%), vegetables (30.2%), and meat (11.4%) (w/w), was pretreated by the manual removal of impurities such as bones, papers, and plastics, followed by crushed in a blender and sieved through 3 mm. The resultant was stored at − 20 °C until use. For the influent preparation, this resultant was mixed with domestic wastewater at the ratio of 0.183 (v/v). More details about the food wastewater preparation can be found elsewhere [16]. The inoculum (activated digested sludge, 10 L) was taken from a local wastewater treatment plant between filter pressing and dewatering processes.

Table 1 Physicochemical characteristics of domestic wastewater (DWW), food waste (FW), food wastewater (FWW), and sludge

Physicochemical parameter	DWW	FW	FWW	Sludge
COD (mg/L)	510	220,100	42,700	18,360
TN (mg/L)	38.2	3600	450	1285
TP (mg/L)	7.9	720	76	310
COD:TN:TP	65:4.8:1	305:6.1:1	561:6:1	–
C/N ratio	5.3	24.1	29.4	–
pH	7.1	5.1	6.9	–
Total solids (%)	–	22.3	–	–
Volatile solids (%)	–	21.1	–	–
TSS (mg/L)	2580	2988	–	–
VSS (mg/L)	1398	1463	–	–

FWW mixture of food waste and domestic wastewater, *COD* chemical oxygen demand, *TN* total nitrogen, *TP* total phosphorus, *TSS* total suspended solids, *VSS* volatile suspended solids

UASB Reactor Setup and Operation

The co-digestion experiments were carried out in an upflow anaerobic sludge blanket (UASB) reactor operated at the intermittent mode (48 h feed/48 h feedless) [16]. The cylindrical reactor (Fig. 1) had a working volume of 38 L (1.6 m height and 0.15 m internal diameter) and was operated under mesophilic condition (35 ± 1 °C) by using a water jacket. The reactor was first seeded with the sludge (10 L) and then purged with nitrogen for approximately 5 min to guarantee the anaerobic environment inside the reactor (dissolved oxygen concentration at ~ 0.1 mg/L). Synthetic domestic wastewater (chemical oxygen demand, COD, 500 mg/L; total nitrogen, TN, 40 mg/L; total phosphorus, TP, 10 mg/L) was continuously fed into the reactor at the hydraulic retention time (HRT) of 10 days for the sludge maturation and granulation. The process was carried out for 40 days until a stable biogas was produced. Then, the reactor was fed with the mixture (as described above) of food waste and domestic wastewater (at 0.183, v/v) under the intermittent mode (48 h feed/48 h feedless), 10-day HRT, and the OLR of 3.8 g COD/L/day. In this first cycle, no zinc was added into the influent and used as the control. The zinc supplementation (as $ZnSO_4$ and $ZnCl_2$) at different concentrations (50, 70 and 100 mg/L Zn^{2+}) was then carried out in the following cycles of 10-day HRT each. Table 2 summarizes the zinc supplementation experiments. Biogas production, COD removal, methane content, SCFAs and LCFAs accumulation, and ammonia nitrogen were monitored daily during both feed and feedless periods. A stable pH during the reactor operation was obtained by adding alkalinity as $CaCO_3$ (3,500 mg/L) daily.

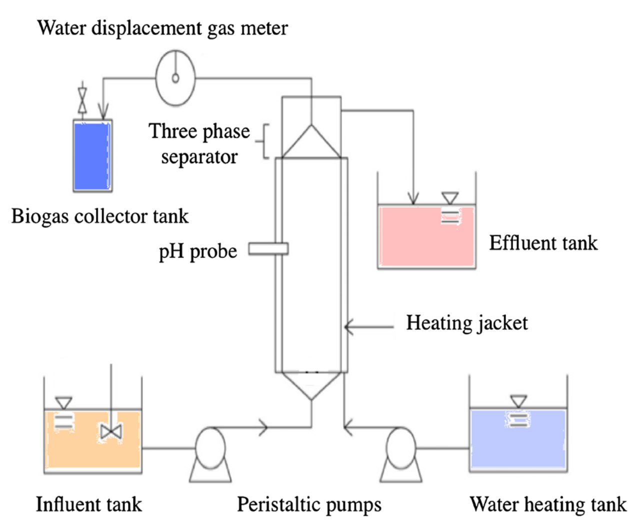


Fig. 1 Schematic of UASB reactor

Table 2 Summary of experiments carried out during zinc supplementation

Supplementation	Concentration (mg/L Zn^{2+})	Period (days)	Parameters measured daily (feed and feedless periods)
Control	0	1–20	Biogas production (L/day), methane content (%), COD (mg/L), SCFAs (mg/L), LCFAs (mg/L), ammonia nitrogen (mg/L), alkalinity (mg/L $CaCO_3$)
$ZnSO_4$	50	21–40	
	70	41–60	
	100	61–80	
$ZnCl_2$	50	81–100	
	70	101–120	
	100	121–140	

Analytical Methods

The COD, TN, TP, and ammonia nitrogen concentrations were measured by HACH methods (Hatch, Loveland, CO, USA). Alkalinity, total suspended solids (TSS), and volatile suspended solids (VSS) were checked according to the Standard Methods (2320D, 2540B, and 2540E method, respectively) [32]. The volume of daily biogas produced was monitored by a gas meter using a 2-L water-displacement gas collector. The gas sample was collected in a Tedlar® gas sampling bag and the composition of biogas (CH_4+CO_2) was analyzed by gas chromatography (GC) equipped with a thermal conductivity detector (TCD) (Agilent, U.S.A.) and a HP-PLOTQ column (30 m × 0.53 mm × 40 µm). The concentrations of LCFAs (oleate, linoleate, and palmitate) and SCFAs (acetate, propionate, butyrate, and valerate) were determined by GC equipped with a flame ionization detector (FID) (Agilent, U.S.A.) and a DB-FFAP column (30 m × 0.32 mm × 0.5 µm). Among the LCFAs commonly generated during AD, the ones chosen to monitor in this work were directly related to their contribution to the reactor deterioration as well as generally found in raw wastewater [33, 34]. The detailed information about the GC-TCD and GC-FID analytical methods for the analyses of biogas composition, LCFAs, and SCFAs can be found elsewhere [33, 35, 36]. The effluent and gas samples were collected daily and analyzed in duplicates. The one-way analysis of variance (ANOVA) at 95% confidence was used for the statistical significances of zinc supplementation in the anaerobic co-digestion of food waste and domestic wastewater.

Results and Discussion

Reactor Operation Without Zinc Supplementation

The first stage of reactor operation consisted of evaluating the AD performance in terms of methane production rate, COD removal, methane content, and accumulation of SCFAs and LCFAs with the food wastewater (mixture) influent without microelement addition as the control. As shown in Fig. 2, at 10-day HRT, 3.8 g COD/L/day OLR, and intermittent feeding strategy of 48 h feed/48 h feedless, the reactor operation was stable and the methane production rate increased progressively from 0.2 to 0.5 L CH_4 /L/day with 76 ± 1.2% COD removal efficiency, and methane content of 61%. Compared to the previous experiments where the ratio of food waste to domestic wastewater was 0.09 (v/v) [16], the AD system in this study could be operated under a relatively stable condition even though the ratio was doubled to 0.183 (v/v), further confirming the intermittent feeding strategy was crucial to avoid the reactor failure due to the accumulation of SCFAs and LCFAs.

Figure 3a shows the accumulation of total SCFAs in the reactor during 20 days. Although the SCFAs accumulation sharply increased after 10 days of reactor operation, the pH was within the acceptable values (7.7 ± 0.2) to ensure

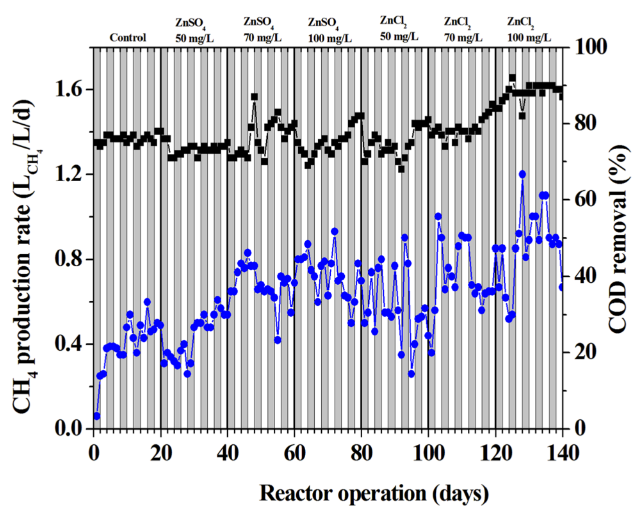


Fig. 2 Effects of different zinc supplementations (50, 70, and 100 mg/L Zn^{2+}; as $ZnSO_4$ and $ZnCl_2$) on methane production rate (blue dashed filled circle line) and COD removal efficiency (black dashed filled square line). Gray bars represent 48 h feed period and white bars represent 48 h feedless period. Control: no addition of zinc. (Color figure online)

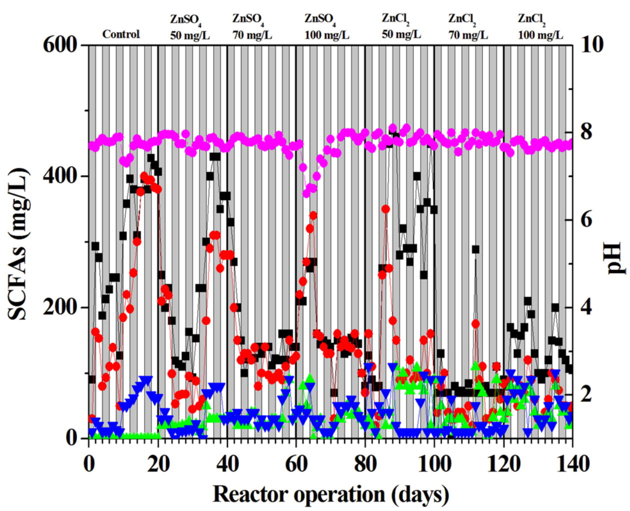
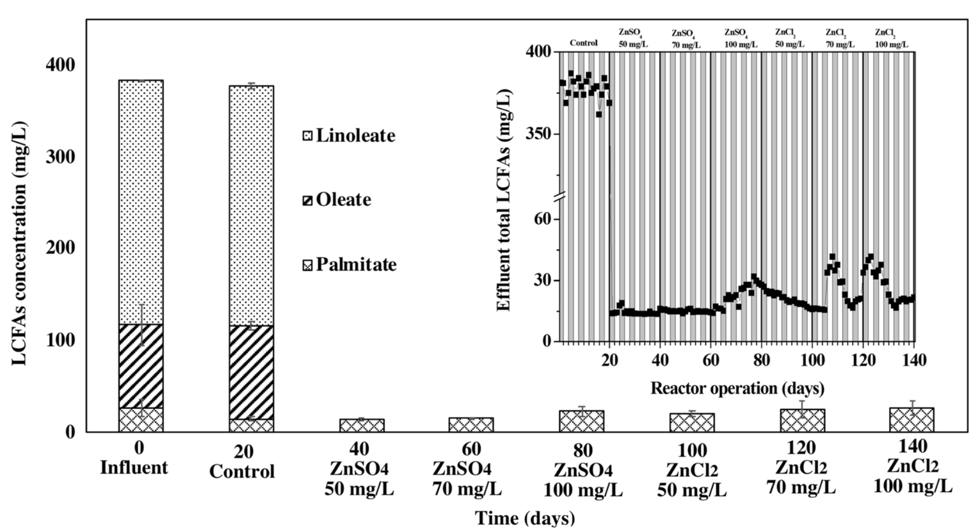


Fig. 3 Effects of different zinc supplementations (50, 70, and 100 mg/L Zn^{2+}; as $ZnSO_4$ and $ZnCl_2$) on SCFAs: (black dashed filled square line) acetate; (blue dashed filled circle line) propionate; (green dashed filled inverted triangle line) butyrate; (blue dashed filled triangle line) valerate; pH (pink dashed filled circle line). Gray bars (feed period, 48 h); white bars (feedless period, 48 h). Control: no addition of zinc. (Color figure online)

a stable performance and activity of different groups of microorganisms involved in the AD biochemical reactions. Acetate (303 ± 99 mg/L) and propionate (220 ± 129 mg/L) were the main SCFAs accumulated (Fig. 3b). According to Zhou et al. [37], the composition of food waste, in terms of carbohydrates, lipids, and proteins, usually determines the proportion of fermented products and a considerable percentage of carbohydrates would favor the formation for acetate. In addition, the neutral pH would also be beneficial to the formation of acetate instead of butyrate. Those findings are in agreement with the present study, considering the high percentage of carbohydrate (58.4%) present in the collected food waste and the pH monitored (7.7 ± 0.2) during the reactor operation. Propionate is also considered a common intermediate formed during the AD of food waste and is usually generated from the reduction of pyruvate with lactate as the intermediate [38]. When Liu et al. [39] studied the effect of salt and oil concentrations on SCFAs generation during food waste fermentation, the addition of oil (5–35%) resulted in a great proportion of propionate (8.9–20.2%) due to the hydrolysis of oil into glycerol and LCFAs, followed by the conversion of glycerol to pyruvate. The amount of lipids in the food waste used in this study may also play a major role in generation of propionate since the amount of oil present in the substrate was the primary reason for the reactor failure due to the adsorption of LCFAs on the sludge bed [16]. The propionate accumulation is often associated with the low efficiency of the methanogenic phase [40] and the ratio of propionate to acetate greater than 1.4 would suggest an imminent digester failure. During the control cycle (days 1–20), this ratio was around 0.70, within the acceptable limit for a stable reactor operation.

Figure 4 shows the effluent total LCFAs concentration monitored (oleate, linoleate, and palmitate) during 20 days of reactor operation. Compared to our previous results [16], the concentrations of LCFAs changed considerably, which was expected due to the influent used in this study, which contained a higher proportion of food waste and consequently more lipids to be hydrolyzed to glycerol and LCFAs. The palmitate concentrations (14.8 ± 2.2 mg/L) were always below the toxic concentration level (over 1100 mg/L) [41], not considered a risk to the reactor stability. In comparison, although the concentrations of linoleate (261.0 ± 3.5 mg/L) and oleate (101.4 ± 4.9 mg/L) were above the concentrations considered toxic to anaerobic microorganisms (50 mg/L for oleate and 75 mg/L for linoleate) [41], the reactor could still be operated with a relative stability during 20 days. One possible explanation for this would be the gradual adaptation of

Fig. 4 LCFAs concentrations (linoleate, oleate, palmitate) in effluent, control, and with different concentrations of zinc supplementation. Inset: effects of different zinc supplementations (50, 70, and 100 mg/L Zn^{2+}; as $ZnSO_4$ and $ZnCl_2$) on effluent total LCFAs concentration. Gray bars (feed period, 48 h); white bars (feedless period, 48 h). Control: no addition of zinc



biomass to adsorb/degrade higher concentrations of LCFAs. This behavior was also observed by Gonçalves et al. while treating the olive mill wastewater [42]. Since LCFAs are usually adsorbed on the sludge surface and limit the transportation of nutrients to/out of the microbial cells to some extent, they could hinder the oxidation of propionate into acetate. This aspect was also reported by Liu et al. [39], further explaining the accumulation of propionate when the substrate with a high oil content used.

Reactor Operation with Zinc Supplementation

After zinc sulfate ($ZnSO_4$) was used for the effect of zinc supplementation at different concentrations (50, 70, and 100 mg/L Zn^{2+}) on methane production rate, COD removal, methane content, and accumulation of SCFAs and LCFAs, zinc chloride ($ZnCl_2$) was supplemented as a substitute for zinc sulfate to further confirm whether the effect observed during biogas production was due to the zinc ion and not the sulfate ion. The range of zinc concentration was chosen based on the previous literature about the usual content of this microelement in food waste (7.8–75 mg/L) [23, 27, 28]. Table 3 summarizes the effects of zinc ($ZnSO_4$ and $ZnCl_2$) supplementation on COD removal efficiency, CH_4 content and yield, and accumulation of total SCFAs and LCFAs and ammonia nitrogen during the anaerobic co-digestion of food waste and domestic wastewater (0.183, v/v). Although a stable performance was obtained during the control cycle, the obtained methane yield was low (0.17 L CH_4/g $COD_{removed}$), compared to when zinc was supplemented into the influent at different concentrations (0.28±0.02 L CH_4/g $COD_{removed}$ for 50 mg/L Zn^{2+}, 0.36±0.01 L CH_4/g $COD_{removed}$ for 70 mg/L Zn^{2+}, and 0.37±0.01 L CH_4/g $COD_{removed}$ for 100 mg/L Zn^{2+}), further implying the zinc supplementation enhanced the conversion of organic matter to methane to some extent. The statistical analysis also showed the methane yield obtained, regardless of the zinc supplementation concentration, was significantly different from the control ($p < 0.05$). However, there were no significant differences in methane yield among the cycles with different zinc supplementation levels ($p = 0.243$). The daily biogas production rates (L/day) generated in each cycle also accounted for the stimulatory effect of zinc. While the control period generated 30.35 L/day, 38.18, 48.80, and 54.10 L/day were produced during 50, 70, and 100 mg/L Zn^{2+} supplementation period, respectively. The obtained results agreed with Zhang et al. [29] who evaluated the influence of zinc (0, 125, and 1215 mg/L Zn^{2+}) on biogas production from swine manure and reported the zinc supplementation greatly improved the microbial activity during AD. On the other hand, Bhattacharya et al. [43] pointed out 20 mg/L Zn^{2+} caused a total inhibition of the acetate degradation due to the zinc toxicity to methanogenesis. The variations of zinc concentration which can stimulate or inhibit the AD process may be associated with the different tolerance and resistance of microbial communities to this microelement, the synergistic inhibition of other intermediates (SCFAs, LCFAs, and ammonia nitrogen) usually coexisting in the AD system, and/or pH and type of salt used. The supplementation of increasing concentrations of Zn^{2+} generally followed a similar trend regardless of the counter ions used (SO_4^{2-} and Cl^-), further confirming the stimulation observed during biogas production was attributable to Zn^{2+} ions (Table 3). The COD removal, methane production rate (Fig. 2), and methane content of the biogas (Table 3) increased with increasing Zn^{2+} supplementation concentrations during 140 days of reactor operation. This improvement is mainly attributed to the higher conversion of organic matter into methane since this microelement is essential to many enzymes involved in the anaerobic reactions, such as hydrogenases, formate dehydrogenase, and superoxide dismutase [29].

Wu et al. [44] reported zinc is a microelement related to the high productivity of methane fermentation with H_2/CO_2 culturing methanogens. In addition, Yenigun et al. [45] suggested zinc can be inhibitory to acidogenic bacteria in the concentration range of 5–40 mg/L and among the SCFAs

Table 3 Effect of zinc ($ZnSO_4$ and $ZnCl_2$) supplementation, at different concentrations (50, 70, and 100 mg/L Zn^{2+}), on COD removal, CH_4 content and yield, total SCFAs, acetate, effluent total LCFAs, and ammonia nitrogen during the anaerobic co-digestion of food waste and domestic wastewater (0.183, v/v)

Parameter	Control	50 mg/L		70 mg/L		100 mg/L	
		$ZnSO_4$	$ZnCl_2$	$ZnSO_4$	$ZnCl_2$	$ZnSO_4$	$ZnCl_2$
COD removal %	76.0 ± 1.2	75.7 ± 3.7	81.3 ± 1.4	76.4 ± 4.7	78.8 ± 2.8	82.1 ± 3.7	88.2 ± 2.2
CH_4 content %	61.0	63.0	64.0	63.8	63.5	64.5	65.0
CH_4 yield (L CH_4/g COD)	0.17	0.29	0.28	0.36	0.36	0.36	0.37
Total SCFAs (mg/L)	572 ± 253	513 ± 135	545 ± 120	302 ± 104	206 ± 80	316 ± 110	307 ± 94
Acetate (mg/L)	303.0 ± 99.4	242.4 ± 114	151.9 ± 55.8	160.5 ± 56.5	294.2 ± 125	85.5 ± 53.1	138.1 ± 37.2
Effluent total LCFAs (mg/L)	377.7 ± 60.3	14.6 ± 1.4	15.9 ± 0.5	22.9 ± 5.4	21.1 ± 3.1	24.8 ± 8.8	26.9 ± 8.2
Ammonia nitrogen (mg/L)	835 ± 101.2	818 ± 50.6	858 ± 36.6	738 ± 44	795 ± 81.9	659 ± 66.9	564 ± 57.8

monitored, the production of acetate was more severely inhibited while the propionate production inhibition started at concentrations higher than 20 mg/L Zn^{2+}. The results obtained during the whole experimental period (Table 3) show the Zn^{2+} supplementation could improve the methane-producing microbial community to some extent, compared to no supplementation (control), while it could inhibit (or even stimulate) the generation of SCFAs. The statistical analysis showed the total SCFAs accumulation, regardless of the zinc supplementation concentration, was significantly different from the control ($p < 0.05$) and among different zinc supplementation levels ($p < 0.05$). An increase in Zn^{2+} concentration resulted in a decrease of total SCFAs accumulation, especially when 70 mg/L Zn^{2+} was supplemented in the influent (Fig. 3a; Table 3). Especially, the accumulation of acetate and propionate was reduced (Fig. 3b) at higher concentrations of Zn^{2+} (70 and 100 mg/L). During this period, the pH value was relatively stable (7.7 ± 0.2) with a satisfactory low level of SCFAs, confirming the addition of zinc accelerated the SCFAs consumption. Karlsson et al. also observed the addition of microelements (Fe, Ni, and Co) had a positive effect on the ability of the microbial community to degrade intermediates and resulted in a higher degradation rates for acetate and propionate [46]. Compared to the total SCFAs accumulated, the concentration of acetate decreased with the zinc supplementation (Table 3) while the methane production rate increased (Fig. 2), further suggesting the SCFAs other than acetate might have been converted directly to methane and not going through to acetate or H_2/CO_2 [48]. On the other hand, it would also be possible that the methane-producing bacteria have the ability to directly use other volatile acids and organic end compounds [47, 48] to generate methane, further suggesting methane may be formed from other route(s) than hydrogenotrophic and acetotrophic methanogeneses.

In the present study, two parameters that would increase the methane production rate, the intermittent feed mode (48 h feed/48 h feedless, especially the feedless/stabilization period) and the organic loading rate (3.8 g COD/L/d), were fixed throughout the reactor operation. It was considered that the improvement of methane production rate observed could be associated not only with the intermittent feed strategy but also with the micronutrient supplementation. As shown in Table 3 below (including results for controls), the relative decrease of SCFAs concentrations by zinc supplementation with the concomitant increase of methane yield and methane production rate could also support the zinc addition provided the synthesis of enzymes required for both acetoclastic and hydrogenotrophic methane production, which was also reported by Banks et al. [28].

The effect (inhibitory or stimulatory) of zinc on the LCFAs degradation is relatively scarce while selenium and tungsten have been reported involved in the fat and LCFAs degradations [49]. In the current work, the zinc supplementation was shown efficient on the LCFAs removal (Fig. 4; Table 3). There are statistically significant differences ($p < 0.05$) in the effluent total LCFAs concentration, regardless of the influent supplemented with different zinc concentrations, suggesting the microelement supplementation improved the removal of LCFAs to some extent. The LCFAs removal can be achieved by at least two different mechanisms, biological and precipitation by divalent ions. When $ZnSO_4$ was supplemented at 50 and 70 mg/L, the concentration of palmitate, a saturated LCFA, remained low (14.8 ± 1.1 mg/L) and relatively constant during days 21–60 (inset in Fig. 4). However, when the influent was supplemented with $ZnCl_2$, at the same concentrations of Zn^{2+}, the palmitate concentrations fluctuated (22.9 ± 6.8 mg/L) and did not follow the same trend (days 81–120), further suggesting the sulfate ion might have played a significant role in degrading this LCFA. The sulfate reducing bacteria (SRB) has been reported to outcompete the syntrophic acetogens for fatty acids and to partially oxidize the saturated LCFAs to acetate or acetate plus propionate [50]. Palmitate has been detected as the main accumulator during the anaerobic digestion [51–53] and the possible reason for its accumulation was suggested by Wu et al. [54]. According to them, at the mesophilic fermentation condition (37 °C), palmitate is mainly in the solid form (melting point, 61–62.5 °C) and the heterogeneity between this LCFA and sludge blanket would limit the mass transfer substantially, resulting in the palmitate accumulation. In addition, the saturated LCFAs such as palmitate are known to be degraded five times slower than the unsaturated ones and consequently the slow β-oxidation kinetics may also contribute to the LCFAs accumulation [55]. Another important route for the LCFAs removal is their precipitation by divalent cations [56]. This process is known to alleviate the LCFAs toxicity substantially by decreasing the LCFAs adsorption onto the sludge surface through the formation of LCFAs-M^{2+}precipitates with less bioavailability to microorganisms. When the LCFAs concentrations in the effluent with and without zinc supplementation were compared (Fig. 4), it is clear that the disappearance of the unsaturated ones (oleate and linoleate) after the microelement supplementation could be associated with the contribution of biological and physical (precipitation) removal. However, the exact role of each mechanism in the LCFAs removal still warrants further study. In the current study, the application of intermittent feeding and zinc supplementation strategies alleviated the toxic effects of LCFAs to some extent and the reactor could be operated under stable condition during the whole AD period.

Another parameter monitored during the reactor operation was the accumulation of ammonia nitrogen which can be considered an inhibitor during the AD, but its inhibitory concentrations are reported varying greatly (from 1600 to

5000 mg/L) under the mesophilic conditions, mainly associated with the microbial community adaptation [57]. Figure 5 shows the ammonia nitrogen concentration (mg/L) and the alkalinity (mg/L $CaCO_3$) during 140 days of reactor operation. There were statistically significant differences between control and zinc supplementations ($p < 0.05$), and the concentration of ammonia decreased from 835 ± 101.2 mg/L (control) to 564 ± 57.8 mg/L when the system was supplemented with the higher concentration of Zn^{2+} (100 mg/L). The decrease of ammonia nitrogen concentration during the microelements supplementation during the AD was also observed by Banks et al. [28]. They reported the reason for the ammonia nitrogen concentration reduction is unknown but there is a relationship between the microelements supplementation and the fixation of nitrogen for biomass production in the reactor. In the current study, since the percentage of protein in the collected food waste was not significant (only 11.4%), the ammonia nitrogen concentration was not considered as a directly relevant parameter which would interfere the stability of the reactor operation.

The natural alkalinity produced during the co-digestion of food waste and domestic wastewater was not enough to maintain an ideal pH for the microbial community as well as to buffer the SCFAs generated in the acidogenic phase [16]. Therefore, alkalinity was added daily at 3,500 mg/L $CaCO_3$ to avoid the reactor instability. The ratio of total SCFAs to total alkalinity (TA) is a parameter usually adopted to assess the AD stability and if the ratio is less than 0.4, the system is considered stable [58]. The ratios of SCFAs/TA during the control and the zinc supplementations (at 50, 70, and 100 mg/L Zn^{2+}) were 0.12, 0.11, 0.05, and 0.06, respectively, suggesting the reactor was operated under the stable condition during the whole AD operation (140 days). The improvement of reactor stability and the consequent consumption of SCFAs to generate methane gas are clearly evident at higher zinc supplementations (70–100 mg/L Zn^{2+}) and confirm the food waste used in this study is deficient in this microelement crucial for the activity of methane-producing microbial community. Figure 5 shows the trend of alkalinity was relatively stable after 20 days of reactor operation and was within the desirable values required for a well-buffered digestion process (2.0–5.0 g/L as $CaCO_3$) [59]. The pH-buffer capacity was improved considerably when zinc was supplemented to the influent, further confirming the important role of this micronutrient to enhance the SCFAs conversion to methane.

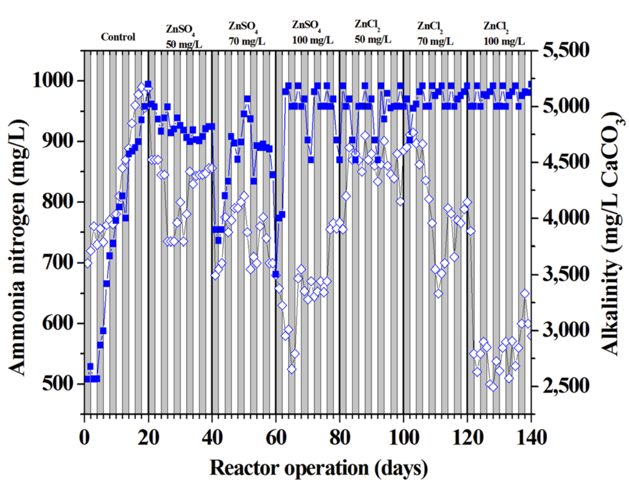


Fig. 5 Effects of different zinc supplementations (50, 70, and 100 mg/L Zn^{2+}; as $ZnSO_4$ and $ZnCl_2$) on: (blue dashed filled square line) alkalinity and (white dashed open diamond line) ammonia nitrogen. Gray bars (feed period, 48 h); white bars (feedless period, 48 h). Control: no addition of zinc. (Color figure online)

Our previous results showed the best anaerobic co-digestion performance for a mixture of food waste and domestic wastewater was obtained with the application of intermittent feeding (48 h feed/48 h feedless) which avoided the accumulation of LCFAs on the sludge bed. The influent supplementation with 100 mg/L Zn^{2+} further improved the conversion of organic matter to methane substantially, even though further studies are still warranted to establish the maximum zinc concentration to be used before its inhibition of microbial communities occurs as well as for the possible synergistic effects eventually present when the influent is simultaneously supplemented with other microelements commonly found in food waste. Further characterization and identification of microbial communities involved during co-digestion and how they would shift over time with the microelements supplementation and/or the intermittent feeding strategy would also be necessary to further find out the microbial mechanisms to maintain the reactor stability. In addition, the microelement speciation and bioavailability studies in AD still need to be further clarified due to their substantial influence on toxicity and digester performance optimization.

Conclusion

The zinc supplementation during the co-digestion of food waste(water) and domestic wastewater (at 0.183, v/v) was carried out at different concentrations (50, 70, and 100 mg/L Zn^{2+}) to mainly maximize the conversion of organic matters to biogas (methane), with the following conclusions.

1. Although a stable performance was obtained during the control cycle, the obtained methane yield was low (0.17 L CH_4/g $COD_{removed}$), compared to when zinc was supplemented into the influent at different concentrations (0.28 ± 0.02 L CH_4/g $COD_{removed}$ for 50 mg/L Zn^{2+}, 0.36 ± 0.01 L CH_4/g $COD_{removed}$ for 70 mg/L Zn^{2+}, and 0.37 ± 0.01 L CH_4/g $COD_{removed}$ for 100 mg/L

Zn^{2+}), suggesting the zinc supplementation can enhance the conversion of organic matter to methane to some extent.

2. The COD removal and methane yield increased by 10 and 30–65%, respectively, compared to the control without supplementation.
3. The supplementation of increasing concentrations of Zn^{2+} generally followed a similar trend regardless of the counter ion used (SO_4^{2-} or Cl^-), further confirming the stimulation observed during biogas production was attributable to Zn^{2+} ions.
4. The statistical analysis showed the total SCFAs accumulation, regardless of zinc supplementation concentration, was significantly different from the control ($p < 0.05$) as well as among different zinc supplementation levels ($p < 0.05$). The increase in Zn^{2+} concentration resulted in a decrease of total SCFAs accumulated, especially when 70 mg/L Zn^{2+} was supplemented in the influent.
5. The zinc supplementation was also shown efficient on the LCFAs removal. There are statistically significant differences ($p < 0.05$) in the effluent total LCFAs concentration, regardless of the influent supplemented with different zinc concentrations. The disappearance of the unsaturated ones (oleate and linoleate) after the microelement supplementation could be related to the contribution of biological and physical (precipitation) removal.
6. The SCFAs/TA (total alkalinity) ratios during the control and the zinc supplementations (at 50, 70, and 100 mg/L Zn^{2+}) were 0.12, 0.11, 0.05, and 0.06, respectively, suggesting the reactor was operated under the stable conditions during the whole AD operation (140 days).
7. The improvement of reactor stability and the consequent consumption of SCFAs to generate methane gas are clearly evident at higher zinc supplementations (70–100 mg/L Zn^{2+}) and confirm the food waste used in this study is deficient in this microelement crucial for the activity of methane-producing microbial community.
8. The influent supplementation with 100 mg/L Zn^{2+} further improved the conversion of organic matters to methane but additional studies are still warranted to establish the maximum zinc concentration to be used before its inhibition of microbial communities involved occurs.
9. The simultaneous supplementation of Ni^{2+}, Co^{2+}, and Zn^{2+} (and even other microelements) to improve the microbial community's nutrient balance would definitely be a part of future investigation to find out the possible synergistic and antagonistic effects of microelements addition on maintaining a stable reactor performance and improving biogas production. The effects of Zn^{2+} and Cu^{2+}, present singly or in a mixture, at different concentrations, on the co-digestion of food waste and domestic wastewater are currently under study.

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