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Effects of copper and zinc on the anaerobic co-digestion process of waste activated sludge and septic tank sludge

Duy-Cam Bui[a], Quang-Minh Nguyen[a,b], Xuan-Quang Chu[c], JiHoon Kim[d], Kitae Park[d], Van-Huong Doan[a], Quang-Trung Do[a,*]

[a]*VNU University of Science, Vietnam National University (VNU), Hanoi, Vietnam, Tel. +84-912120780; email: doquangtrung@hus.edu.vn (Q.-T. Do)*
[b]*Hai Phong University, Hai Phong, Vietnam*
[c]*Center for Advanced Materials Technology, National Center for Technological Progress (NACENTECH), Hanoi, Vietnam*
[d]*Graduate School of Water Resources, Sungkyunkwan University (SKKU), Suwon, Korea*

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ABSTRACT

The effects of copper and zinc on the anaerobic co-digestion process of waste activated sludge and septic tank sludge in Hanoi were investigated. The anaerobic fermentation tests were carried out in 32 batch fermenters with 20 d of hydraulic retention time at mesophilic temperature conditions. The different metal ion concentrations (19, 40, 60, and 80 ppm) were utilized for the anaerobic experiments, respectively. Cumulative biogas and change of total solids (TS) concentrations, volatile solid (VS), chemical oxygen demand (COD) were tested during the experiments. The results revealed that the TS, VS and COD removal efficiency at 80 ppm Cu(II) were 3.95%, 9.01%, and 6.51%, respectively. Similar, this figure at 80 ppm Zn(II) was 8.44%, 13.03%, and 11.42%, respectively. The biogas yield decreased by 35.2% with 80 ppm Cu(II), decreasing 32.13% with 80 ppm Zn(II) compared with the original sample. The results showed at higher metal concentration, the digestion process was inhibited, led to the removal of organic substances and produced biogas were reduced.

Keywords: Anaerobic; Co-digest; Copper; Zinc; Inhibiter

1. Introduction

The average population of Hanoi capital in 2017 is 7,657,374 people, accounting for 8% of the population of Vietnam. The current daily production of urban sludge ranges from 60 to 90 g of dry solids per population equivalent in European Union [1]. The amount of waste activated sludge (WAS) generated in Hanoi an average is 1,421.1 $m^3 d^{-1}$; septic tank sludge (STS) is about 517 $m^3 d^{-1}$. Municipal sludge is collected and gathered to the city's landfill in Yen-So and Kieu-Ky villages (Hanoi). The treatment and disposal of urban sludge have become great challenges in environmental management across the globe, which is especially true for developing countries. In the context of increasingly exhausting energy sources, anaerobic methods are selected for the treatment of organic-rich wastewater by generating methane (CH_4) and the sludge after anaerobic digestion contains abundant nutrients and organic substances that can make fertilizer for plants.

Anaerobic digestion is affected by many factors such as temperature, pH, organic loading and retention time [2], including the influence of heavy metals. Metals in organic and inorganic wastewater are generated by various causes such as the use of metallic chemicals in production, pipeline corrosion, the process of washing machine equipment, bleaching, neutralization [13]. Heavy metals are often

* Corresponding author.

present in industrial and municipal wastewaters and urban sludges in significant concentrations [4], the most frequently found are copper (Cu), zinc (Zn), lead (Pb), mercury (Hg), chromium (Cr), cadmium (Cd), iron (Fe), nickel (Ni), cobalt (Co) and molybdenum (Mo) [5]. The primary source of heavy metals in urban wastewater is industry, which represents up to 50% of the total heavy metal content in urban sludge. Domestic sources are mainly associated with the leaching from plumbing materials (Cu and Pb), gutters and roofs (Cu and Zn), and galvanized materials, the use of detergents and washing powders containing Cd, Cu and Zn, and the use of body care products containing Zn [1]. Many essential metals (e.g. Cu, Zn, Se) are required for the activation or functioning of many enzymes and coenzymes in anaerobic fermentation [6].

However, excessive amounts of heavy metals can lead to the inhibition of anaerobic [6]. Other studies revealed that the inhibition effect of toxic metals was quite different with the pattern of Zn > Cr > Cu > Cd > Ni > Pb [3] or Zn > Cr > Ni ≈ Cd [5]. A previous study reported that certain heavy metal ions can inactivate enzymes, thus inhibiting the growth of bacteria such as Cu, Pb, Cr(VI) and Zn consequently inhibiting the anaerobic digester [7]. Therefore, the presence of unwanted heavy metals can jeopardize the digester [8]. Another research on the effect of zinc and copper on anaerobic stabilization of sewage sludge, that sludge samples were taken from the anaerobic sewage sludge stabilization tank located at the wastewater treatment plant, shown that zinc and copper causes the significant inhibition of biogas production [9].

The above studies show that the effects of metals on the anaerobic digestion of each kind of sludge were different. To date, no such studies have been performed to assess the effect of copper and zinc on anaerobic processes of WAS and STS. This study, the effect of essential metals such as copper and zinc on the co-anaerobic stabilization of WAS – STS and the eventually specify the inhibitory effect of these metals on the anaerobic stabilization of urban sludge. It is a key process to recover energy from organic waste.

2. Materials and methods

2.1. Sludge sampling

WAS collected from Kim Liên wastewater treatment plant located on Dong-Tac street (Hanoi). This wastewater treatment plant has a treatment capacity of 3,700 $m^3\ d^{-1}$ of wastewater, which treats all wastewater from a residential area of 4,6 km^2 before discharging to the Lu river. The sources of waste in the sewers include dormitories, hotels, hospitals, metalwork, markets, etc.

STS took at the STS treatment plant (Urenco 7, Cau Dien, Hanoi) that mainly collected from public toilets, households, and agencies in Hanoi with a quantity of 50–60 $m^3\ d^{-1}$.

2.2. Chemicals and the biogas reactor

Chemicals: $Cu(NO_3)_2$, $Zn(NO_3)_2$ were obtained from Merck Chemicals (Darmstadt, Germany).

The biogas reactor: Thirty-two anaerobic batch tests of 1.0 L volume were installed at the Centre for analytical sciences development and application (Fig. 1). The reactors were manufactured and were made from a transparent glass bottle. The volume of each reactor is 1.0 L and it would be filled up to 0.7 L, and the rest volume was for the produced biogas. The batch reactor was connecting to a gas-measuring column and close the top tidily. The pipe connection for gas sampling was controlled by a screw valve.

2.3. Experimental design

All the experiments were conducted in self-designed batch digesters fabricated from 1 L glass bottles. Each anaerobic digestion reactor contained 120 mL WAS and 480 mL STS and was tightly closed with a rubber septum and screw cap. The WAS/STS ratios of 20:80 (% of total feedstock measured as wet weight (w/w)) (sludge sample blank (SSB)) [10,11] was tested under mesophilic (35°C ± 1°C) condition for 20 d with the initial total solids (TS) concentration of 7.35%. The initial sludge sample had a concentration of Cu (0.0233 ppm);

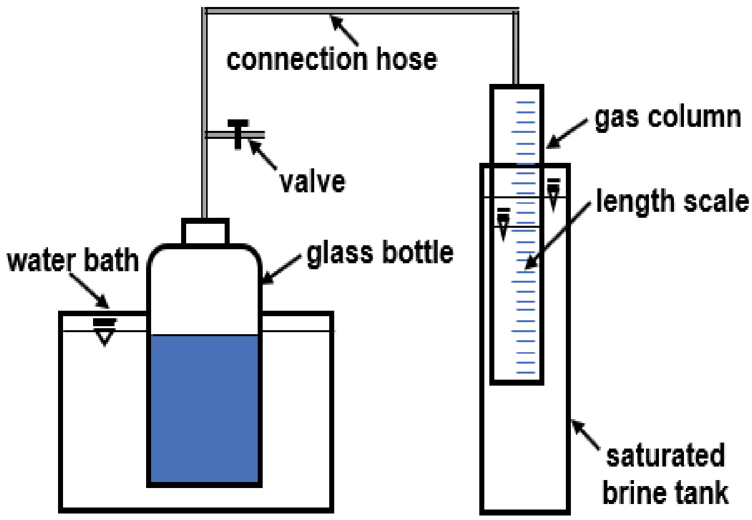

Fig. 1. Anaerobic batch tests digestion.

Zn (0.0677 ppm). The Cu(II) or Zn(II) salt was dissolved in distilled water, then added to the reactors at concentrations of 19, 40, 60, or 80 ppm (corresponding samples ECS1, ECS2, ECS3, ECS4 and EZS1, EZS2, EZS3, EZS4). The compaction capacity of the reactors reached 0.62 L. Each sample was mixed for 3–5 min before anaerobic digestion to obtain a homogeneous mixture. All reactors were shaken manually for 1 min each day during the anaerobic digestion process.

2.4. Determination of TS, volatile solids and chemical oxygen demand

The TS, volatile solids (VS) and chemical oxygen demand (COD) were determined in accordance with APHA Standard Methods [12]. The TS was determined by drying at 105°C with a universal oven (Model UN55, Memmert, Germany) for 24 h under the SMEWW 2540. B: 2000; The VS was determined by calcining dry samples in ceramic cups at 550°C with a furnace (Model B180, Nabertherm, Germany) for 8 h according to the SMEWW 2540. E: 2000. The COD was determined by dichromat and photometric measurements at 605 nm with a spectrophotometer (Model UH-5300, Hitachi, Tokyo, Japan) according to SMEWW 5220.C: 2012; The volume of the biogas produced was measured by using the water displacement method each day throughout the anaerobic digestion process.

3. Results and discussion

3.1. Physicochemical characterization of SSB

The carbon sources used for anaerobic metabolism (glucose, volatile fatty acids etc.), measured evaluation parameter (methane or hydrogen production, COD removal etc.), used reactors (batch or continuous), characteristics of anaerobic sludge, binding strength of a heavy metal ion to the anaerobic sludge (sorption, precipitation) [16]. The potential toxicity of heavy metals is significantly controlled by the physical and chemical environment in which they are present, and this is correlated to different ion-specific physicochemical parameters, e.g. standard redox potential, electronegativity, the solubility product of the corresponding metal-sulfide complex, the Pearson softness index, electron density and the covalent index [6]. Moreover, the operating solids level significantly impacts the heavy metal toxicity in anaerobic digesters by providing protection from metal inhibitory effect [4].

For the above reasons, it is necessary to specify the characteristics of tested urban sludge, which are shown in Table 1. For the purpose of assessing the influence of copper and zinc on the anaerobic co-digestion process of WAS and STS in Hanoi

Table 1
Physicochemical characterization of a sludge sample blank

	pH (–)	TS (%)	VS (%)
SSB	7.52	7.35	83.14
	COD (mgO_2 L^{-1})	Content of Zn (mg L^{-1})	Content of Cu (mg L^{-1})
	6,863.6	0.0677	0.0233

3.2. Effects of copper and zinc for TS and VS

Anaerobic digestion can only partially decompose the organic fraction due to the limitation of digestion time. VS reduction is frequently used as an indication of sludge stability and reduction, characterizing the performance of sludge anaerobic digestion [13].

According to data reported in Fig. 2 and Tables 2 and 3 were calculated shows effects of copper and zinc on the anaerobic digestion of WAS and STS through the change of TS and VS. TS and VS were only partially removed through biogas formation while the remaining fraction was removed in the digestate and also transformed into soluble organic compounds [14]. The removal efficiency of TS, VS for the experiment increased gradually over the course of the experiment.

The effect of Cu(II) is shown in Fig. 2 and Table 2. The TS and VS of sludge samples were decreased with the increasing anaerobic digestion time. The TS and VS of the SSB sample significantly decreased from 7.35% to 5.22% and 83.14% to 62.23%, respectively. The TS, VS or TS removal efficiency of the ECS1, ECS2, ECS3, ECS4 samples decreased with the increasing of Cu(II) concentration. The ECS4 sample (Cu(II) concentration = 80 ppm) showed a low digestion efficiency compared to other samples. The TS and VS of ECS4 sample were 7.06% (removal efficiency = 3.95%) and 75.65% (removal efficiency = 9.01%), respectively. The surface of the microorganism was adhered to and hindered the metabolism of microorganisms to the process during the anaerobic digestion with the presence of Cu(II) [15].

At the higher concentration of Cu(II), the growth of microorganisms was inhibited by the anaerobic digestion, resulting in the reduction of TS and VS. Similar to previous results, Fig. 2 and Table 3 show the results of TS, VS and the removal efficiency. The TS and VS were decreased with the increasing anaerobic digestion time. Zn(II) supplemented samples showed a lower TS removal efficiency than the original sample (SSB).

The results indicated that TS, VS of the EZS3 sample (Zn(II) concentration = 40 ppm) were significantly decreased compared to the other Zn samples. The removal efficiency of TS and VS was 27.07% and 20.04%, respectively. The TS, VS removal efficiency of EZS1, EZS2, EZS4 samples were reduced with the increasing of Zn(II) concentration. The removal efficiency of TS and VS was 27.07% and 20.04% respectively. The TS, VS or TS removal efficiency of EZS1, EZS2, and EZS4 sludge samples were decreased with the increasing of Zn(II) concentration. The EZS4 sample (Zn(II) concentration of 80 ppm) showed the lowest digestion efficiency compared to other samples at low Zn(II) concentration. The TS, VS of EZS4 sample were 6.63% (removal efficiency was 8.44%) and 61.63% (removal efficiency was 13.03%), respectively. Zn(II) can make a complex with sludge particles because of a positive charge, leading to precipitate at the bottom of the tank. Therefore, the anaerobic digestion of the microorganism will be reduced.

Through the results of the study showed that metal supplementation reduced the ability to remove TS, VS or the ability to decompose organic volatile matter. Cu(II) supplementation showed a lower TS, VS removal efficiency compared with Zn(II), the higher the metal concentration, the greater the

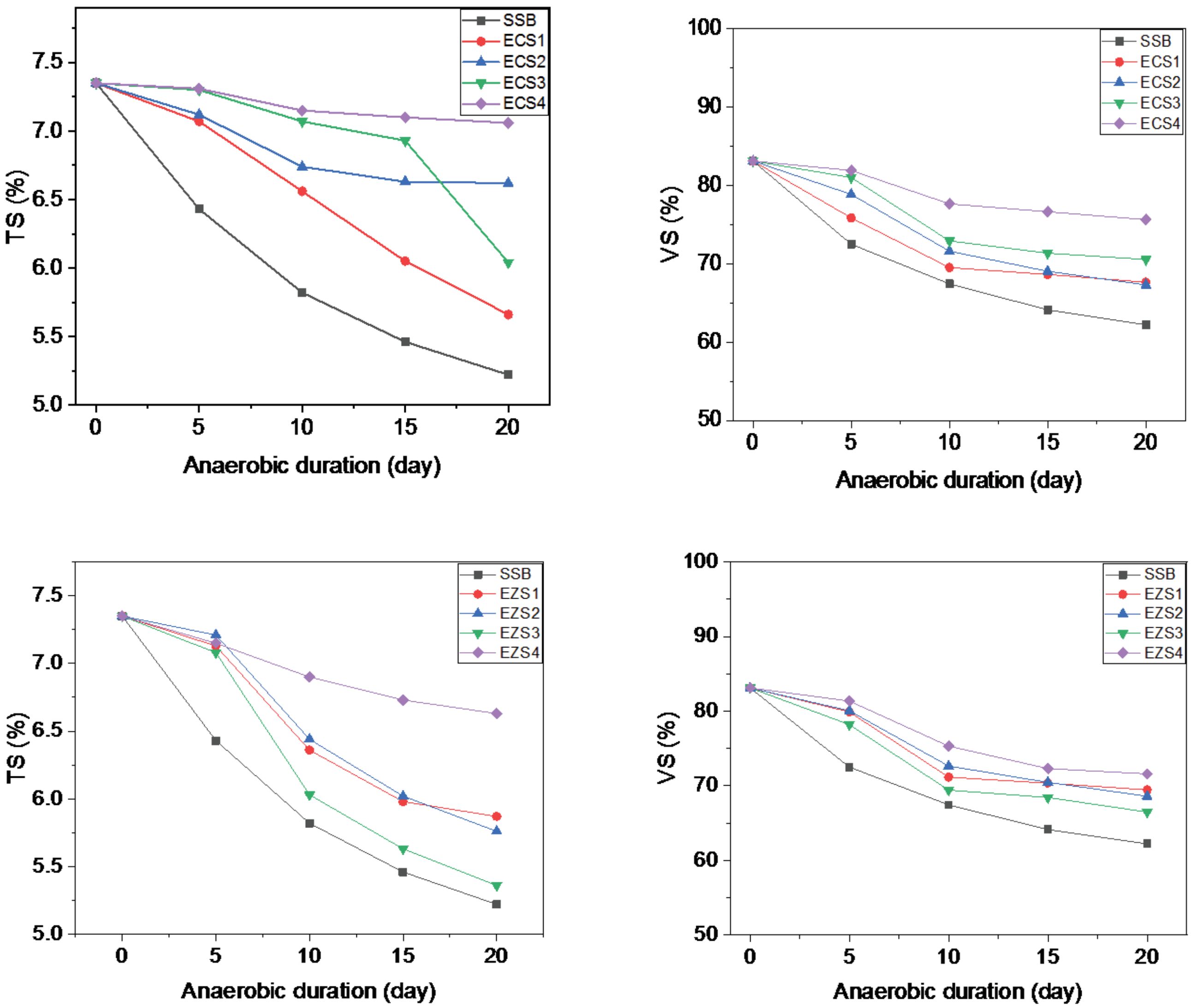

Fig. 2. Effects of copper and zinc on total solids and volatile solid removal.

Table 2
TS, VS removal performance during digestion (%)

Sample (d)	SSB		ECS1		ECS2		ECS3		ECS4	
	TS	VS	TS	VS	TS	VS	TS	VS	TS	VS
5	12.52	12.79	3.81	8.73	3.13	5.12	0.68	2.54	0.54	1.46
10	20.82	18.87	10.75	16.38	8.30	13.86	3.81	12.28	2.72	6.59
15	25.71	22.85	17.69	17.43	9.80	16.94	5.71	14.17	3.40	7.79
20	28.98	25.15	22.99	18.62	9.93	19.03	17.82	15.13	3.95	9.01

effect on the process. According to previous research [17], the addition of copper in a up-flow anaerobic sludge blanket (UASB) reactor influent at low concentrations affected adversely its performance; though, it did not cause complete inhibition to anaerobic microorganisms. Metal speciation results in the inoculum and the UASB reactor evidenced that the fraction which had the major affinity with copper was the organically/sulfide bound fraction, however, further studies are needed to establish which is the weight of organic matter and sulfide in copper binding. Therefore, at higher metal concentration, the inhibition of the growth of microorganisms during anaerobic digestion would be increased. The effects

Table 3
TS, VS removal performance during digestion (%)

Sample (d)	SSB		EZS1		EZS2		EZS3		EZS4	
	TS	VS	TS	VS	TS	VS	TS	VS	TS	VS
5	12.52	12.79	2.99	3.89	1.90	3.69	3.67	5.93	2.72	2.13
10	20.82	18.87	13.47	14.41	12.38	12.62	17.96	16.49	6.12	9.41
15	25.71	22.85	18.64	15.37	18.10	15.25	23.40	17.69	8.44	13.03
20	28.98	25.15	20.14	16.45	21.63	17.48	27.07	20.04	9.80	13.87

of metals during anaerobic digestion were mainly in phase I (hydrolysis) and II (acidification), and there was no significant difference in phase III and methanogens.

3.3. Effects of copper and zinc for COD

The COD removal speed and ability were closely related to the ability of the gas production from the anaerobic digestion process. Through these measurements, it is possible to assess microbial activity and thereby can evaluate the overall effects of Cu(II) and Zn(II) in the digestion mixture. The COD values that were monitored and analyzed with a sampling frequency of 5 d are shown in Fig. 3.

Fig. 3 shows that the COD of the samples decreased with decay time. During the first 5 d of digestion, the COD of the SSB sample reduced 21.51%. Whereas, the COD removal of all ECS1, ECS2, ECS3, ECS4, EZS1, EZS2, EZS3, EZS4 samples were significantly reduced. It is most inhibited for the case of ECS4 and EZS4 samples with a reduction of only 3.9% and 1.2%, respectively. The results recognized with the next 5 d of digestion showed that the COD of all samples was slightly reduced. The COD removal efficiency for SSB was 28.89%; whereas those for ECS1, ECS2, ECS3, and ECS4 samples were respectively 17.29%, 11.18%, 10.70%, 6.51%; and for EZS1, EZS2, EZS3, EZS4 samples were respectively 17.25%, 15.19%, 9.96%, and 11.42%. Then, the decrease in COD removal ability indicated the low organic content in the sludge. Also, the composition of difficult biodegradable organic substances reduced the microbial activity of the organism. Inefficient microbial activity leads to the inefficient stabilization of persistent organic compounds that need to be removed when scaling up the anaerobic waste treatment [18].

The toxicity of Cu(II), Zn(II) is due to the disruption of enzyme function and structure by binding metal ions to thiol and other groups on protein molecules or by substituting natural metals in fake enzyme groups. Enzymes of the microorganism make them more likely to grow and the biomass weakens, resulting in a weakened COD. In a previous study [19], it was found that heavy metals inhibit the activity of CH_4 microorganisms of starch granules during anaerobic digestion.

After 20 d of digestion, the initial sample had the highest COD removal efficiency (down from 6,863 to 4,456 mgO$_2$ L^{-1} with removal efficiency equal to 35.07%). The COD removal ability would be lower for all samples containing Cu(II) or Zn(II). It means that these metal ions affected the digestion mixture, lead to the reduction in the COD removal capacity of the mixture, and prevented the breakdown of organic compounds or inhibited microbial growth.

3.4. Effects of copper and zinc for biogas produced during digestion

Normally, approximately 0.2–1.11 m^3 of biogas could be collected when decomposing 1 kg of dry organic matter [20]. However, the amount of biogas produced is influenced by

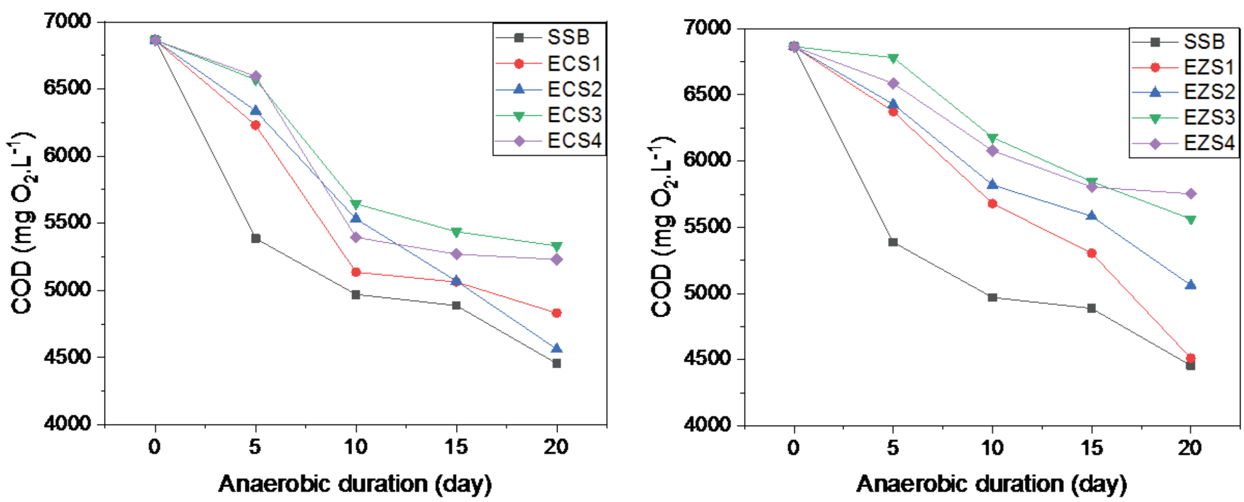

Fig. 3. COD removal during anaerobic digestion without and with the presence of copper and zinc.

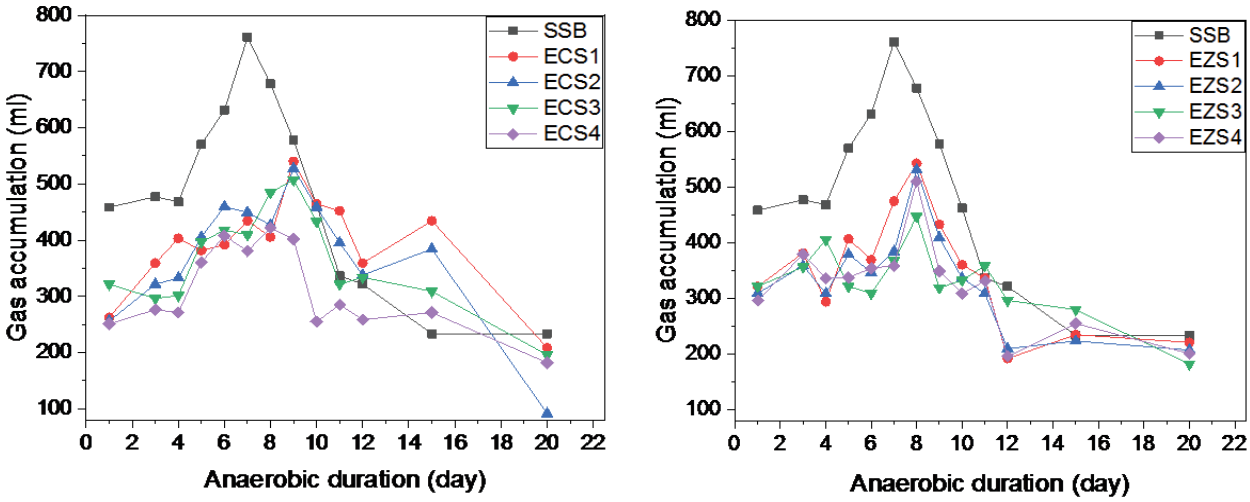

Fig. 4. Biogas generated during digestion in the presence of copper and zinc.

many factors of anaerobic fermentation. Fig. 4 depicts biogas production in experiments with initial mixed sludge samples and supplemented metal samples. The results from experiments show that there are always two vertices of maximum gas. This phenomenon demonstrates that biogas production is related to the digestion of organic compounds contained in the input materials. The first strong gas-phase corresponds to the digestion of the decomposing organic compounds and the second weaker phase shows the digestion of the persistent organic compounds when it takes sufficient time to systematically. Microorganisms adapt and dissolve [21].

Maximum gas volume was generated after 8 d digestion in the case of the SSB, but it was only observed after 10 d digestion in the case of the sample containing Cu(II). It was recognized the maximum produced-gas volume from the SSB is 6210.92 ml, while the volumes from the ECS1, ECS2, ECS3, ECS4 samples were respectively 5,098.10; 4,848.16; 4,730.10; and 4,024.22 ml. Thus the higher Cu(II) concentration existed led to the less volume of gas produced. It can be explained due to the precipitation of Cu(II) with sulfide, carbonate and hydroxide groups [17]. Similarly, Fig. 4 shows the results of biogas volume generated during digestion in the presence of zinc. Gas was produced very slow within the first 5 d. The maximum volume was recognized at the day 8th in the case of SSB and the day 10th in the case of a sample containing Zn(II). This result indicates that Zn(II) also inhibits gas production. After 20 d, the average amount of gas produced was respectively 4,569.33; 4,314.36; 4,299.29; and 4,215.14 ml for sample EZS1, EZS2, EZS3, and EZS4. Comparing the maximum generated-gas volume, it was found the lowest volume in the case of the EZS4 sample. Therefore, it could be concluded that the biogas yield decreased by 35.2% with Cu(II) at 80 ppm, and 32.13% with Zn(II) at 80 ppm compared to the sample without metal (SSB). Biogas yield is suitable for the removal of COD, TS, and VS in the above cases.

4. Conclusion

Biogas production and effects of copper and zinc were studied in the anaerobic co-digestion process of WAS and STS. The concentrations of Cu(II) and Zn(II) from 20 to 80 ppm were both inhibitory to the anaerobic co-digestion process of WAS and STS in Hanoi. When the concentration of Cu(II) and Zn(II) increases, the anaerobic digestion capacity of the sludge mixture decreases. The effect of Cu(II) inhibits the anaerobic digestion of the sludge mixture more strongly than that of Zn(II). Therefore, it is recommended that the presence of such toxic heavy metals such as Cu, Zn in municipal sludge should be avoided or controlled in the anaerobic digester for biogas production, as well as the safe land application of this biomass.

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