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Improvement of Anaerobic Digestion of Sewage Sludge, Using Combined Hydrogen Peroxide and Thermal Pre-Treatment

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ABSTRACT: The present study investigates the influence of individual and combined hydrogen peroxide and thermal pre-treatment of waste activated sludge on anaerobic digestion. For so doing, it employs anaerobic batch reactors in the mesophilic conditions. For comparison, soluble fractions of organic matter, biogas production, biochemical methane potential, removal of chemical oxygen demand (COD), and volatile solids (VS) have been measured during the anaerobic digestion process in systems with and without pre-treatment. Hydrogen peroxide pre-treatment has been tested in two concentrations of 30 g H_2O_2/kg VS and 60 g H_2O_2/kg VS and thermal pre-treatment has been performed at two temperatures of 75℃ and 90℃. According to the results, the solubalisation of organic matter considerably improves, when combined hydrogen peroxide and thermal pre-treatment is employed. As a result, in comparison to the control reactor, higher amounts of biogas (71%) and methane (81%) have been produced in the bioreactor, pre-treated with combined hydrogen peroxide (30 g H_2O_2/kg VS) and heat (90 ℃). In addition, the removal efficiency of COD and VS from the digested sludge has been enhanced in the pre-treated reactors (up to 39% and 92%, respectively) in comparison to the control reactor. The improved methane yield, COD, and VS are of paramount importance, not only because higher amounts of renewable energy are obtained from the anaerobic digestion process, but because sludge transport costs are reduced and the digested sludge obtains a higher potential application to agricultural lands.

Keywords: Anaerobic digestion, waste activated sludge, hydrogen peroxide, thermal pre-treatment, methane production.

INTRODUCTION

Today, wastewater treatment plants are crucial for protection of water streams from contamination. Thanks to its ease of operation and high efficiency, activated sludge process is a promising method to be used in wastewater treatment plants, wherein an important issue will be generation of large amount of waste-activated sludge (Nazari et al., 2017; Neyens et al., 2004), as sludge treatment units in the downstream process are the most cost-intensive sections in the plants, accounting for about 60% of total operation costs (Appels et al., 2010; Neyens et al., 2004). In addition, digestion of waste-activated sludge is often restricted by poor biodegradability and slow rate of fermentation processes (Appels et al., 2010; Sanscartier et al., 2012). Therefore, several researches have focused on finding proper solutions for this problem in recent years.

Anaerobic digestion of sewage sludge is an environmentally-friendly and economically-attractive method to stabilize

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sewage sludge. The advantages of this method include bio-methane production as renewable energy and lower need for aeration facilities that reduce capital and operation costs in wastewater treatment plants. Furthermore, anaerobic digestion of sewage sludge can capture methane, a major greenhouse gas, from sludge treatment units, where half of the total greenhouse gases of the wastewater treatment plants are produced (Pilli et al., 2016). Nevertheless, there are some major drawbacks attributed to anaerobic digestion of waste activated sludge, like poor biochemical methane potential and slow rate of hydrolysis process (Appels et al., 2008; Sanscartier et al., 2012; Tiehm et al., 2001; Zahedi et al., 2017). Several strategies have been suggested to address these issues, e.g., chemical, mechanical, and enzymatic pretreatment of sewage sludge prior to anaerobic digestion (Ennouri et al., 2016; Farhat et al., 2018; Ruolin Guan et al., 2018; Li et al., 2018; Pilli et al., 2015a; Sólyom et al., 2011; Zahedi et al., 2017; Zhang et al., 2011). The intermediary treatment as well as post-treatment of sewage sludge also currently-used strategies (Campo et al., 2017; Svensson et al., 2018). These treatments disrupt cell walls and extra cellular polymeric substances (EPS) that account for 70% and 80% of proteins and carbohydrates in waste activated sludge, respectively (Carrère et al., 2010; Foladori et al., 2010; Ma et al., 2015; Neyens et al., 2004). In spite of several advantages of these strategies, they are not promising from an environmental and economic point of view (Carballa et al., 2011; Ma et al., 2015).

Hydrogen peroxide (H_2O_2) has recently been used to disintegrate anaerobic biomass (Jiang and Yuan, 2013), which is due to the production of free radicals, such as $NO^{\bullet}_2$ and $HO^{\bullet}$ that accelerate hydrolysis of cell walls, proteins, membrane phospholipids, and EPS (Guan et al. 2018; Liu et al. 2018; Lobachev & Rudakov 2006; Neyens et al. 2004; Wang et al. 2018). It has also been revealed that H_2O_2 could be obtained in a bio-electrochemical process from wastewater treatment plants (Rozendal et al., 2009). Zhang et al. (2015) revealed that H_2O_2 pre-treatment of waste activated sludge with 50 g of H_2O_2/kg TS and for 24 hours of exposure time enhanced methane production by 23% in anaerobic digestion of sewage sludge.

Another interesting strategy is thermal pre-treatment of waste activated sludge, which improves the anaerobic digestion process by accelerating hydrolysis of organic matter and enhanced production of methane as a renewable energy in wastewater treatment plants (Choi et al. 2018; Farhat et al. 2018; Nazari et al. 2017; Neumann et al. 2017; Svensson et al. 2018). In addition, thermal pre-treatment of waste activated sludge may stimulate the growth of hydrogen-using methanogens, providing a good balance and syntrophic association among various microbial communities (Ennouri et al., 2016). Thermal energy is readily available in anaerobic digestion process due to methane production, which can be used as a renewable energy resource for thermal pre-treatment. Wang et al. (2014) reported that thermal pre-treatment of waste activated sludge at 70℃ increased the hydrolysis rate and methane production by 21%, compared to the control reactor.

This research aims at studying how combined H_2O_2 and thermal pre-treatment can improve anaerobic digestion of waste activated sludge, in comparison to the application of these pre-treatment methods individually. For this purpose, it investigates the influences of individual and combined H_2O_2 as well as thermal pre-treatment on solubalisation of organic matter, biogas production, methane production, and removal of COD and VS in anaerobic digestion of sewage sludge, making it the first study to investigate the effect of combined H_2O_2 and thermal pre-treatment on anaerobic digestion of sewage sludge.

MATERIALS AND METHODS

Total Solid (TS), Volatile Solid (VS), Total Suspended Solid (TSS), Volatile Suspended Solid (VSS), Chemical Oxygen Demand (COD), and Soluble Chemical Oxygen Demand (SCOD) got measured in accordance with standard methods (APHA, 2012). Biopolymers (i.e., proteins and polysaccharides) got measured in the soluble phase both before and after the pretreatment. To separate solids from liquid, the sludge was centrifuged for 30 minutes at 10000 rpm and the supernatant passed through a glass fiber filter, the pore size of which was 0.45 µm. Proteins were measured with the Folin Phenol Reagent based on Lowry et al. (1951) and Peterson (1977) method. Phenol and sulfuric acid were also used for polysaccharide measurement (Dubois et al., 1956). They have been widely used to find out the concentration of proteins and polysaccharides, even in sludge pre-treatment studies so that the effect of pre-treatments on sludge properties could be determined (Li et al., 2016; Ma et al., 2015; Yang et al., 2015; Zahedi et al., 2017, 2016).

The volume of produced biogas was measured via liquid displacement method (Walker et al., 2009). The liquid barrier, used in this method, was 100% saturated with NaCl and acidified with H_2SO_4 (pH = 2) in order to reduce dissolution of the biogas (specifically CO_2 and CH_4) in the liquid barrier and eliminate the measurement errors (Walker et al., 2009). Both Gas Chromatography (GC) with a thermal conductivity detector (TCD) at 100 ℃ and helium as a carrier gas were used to analyze the main biogas composition (CH_4 and CO_2). The biogas produced in the bioreactors was collected in Tedlar gas bags before GC measurements.

In order to assess the application of combined pre-treatment technology in real units, primary sludge and waste activated sludge were mixed prior to anaerobic digestion as it is the case in the majority of wastewater treatment plants. The pre-treatments were not applied on primary sludge due to the presence of considerable soluble organic fractions in primary sludge. This could be evidenced by considerably higher SCOD/COD in primary sludge, compared to waste activated sludge.

One-way factor analysis of variance ANOVA with significance levels of $p < 0.05$ was used to determine the significance of differences in the obtained results, with data analysis and graph processing, carried out with Microsoft Excel (2010).

The substrate (waste activated sludge along with primary sludge) and the inoculum, used in this study, were collected from the south wastewater treatment plant of Tehran, Iran, the biggest wastewater treatment plant in the Middle East with six mesophilic anaerobic digesters. Primary sludge gets thickened in this plant with gravitational sedimentation, while waste activated sludge gets thickened with belt thickener. Table 1 demonstrates the characterizations of the sludge, used in this study, with error obtained from triplicate tests.

Hydrogen peroxide and thermal pre-treatment experiments were carried out in reactors, each with a volume of one liter. Same specified amount of waste activated sludge was added to different reactors for pre-treatment. Afterwards, certain

Table 1. Characterizations of the sludge

Characteristics	Waste activated sludge (g/L)	Primary sludge (g/L)	Inoculum (g/L)
Total Solids	73.4 ± 0.55	28.8 ± 0.21	29 ± 0.10
Volatile Solids	58.4 ± 0.21	20.12 ± 0.15	17.4 ± 0.25
Total Suspended Solids	66.06 ± 0.52	24.22 ± 0.58	22.14 ± 0.12
Volatile Suspended Solids	51.12 ± 0.41	17.76 ± 0.12	14.58 ± 0.20
Chemical Oxygen Demand	83.50 ± 0.72	35.90 ± 0.41	37.00 ± 0.18
Soluble Chemical Oxygen	6.52 ± 0.04	5.25 ± 0.03	4.23 ± 0.04

Demand

concentrations of H_2O_2 (30 and 60 g/kg VS) were added to the reactors, under the conditions, mentioned in Table 2. For thermal pre-treatment, the reactors were heated by automatic heaters at 75 °C and 90 °C. Both set of pre-treatment experiments had an exposure time of 24 hours. For combined pre-treatment, initially H_2O_2 pre-treatment was conducted with designated concentrations for 24 hours, followed by a thermal pre-treatment for a same amount of time (at 75℃ and 90℃, respectively). A control reactor without chemical additives at room temperature (≈25 ℃) was also tested. All of the reactors were mixed with magnetic stirrers during the experiment at 150 rpm. During the pre-treatments, pH was monitored, remaining around 6.5 in the reactors.

For the biochemical methane potential tests, as much as 1000 mL batch reactors with a working volume of 600 mL were tested in mesophilic condition (Fig. 1). The inoculum to substrate ratio (I/S) was set to 2, based on dry VS for better inoculum performance (Boulanger et al., 2012). Prior to mixing the substrate with the inoculum, its pH was set to 7 and it got heated up to 36 ± 1 ℃, to prevent temperature and pH shock to anaerobic microorganisms. Afterwards, the reactors got sealed and flushed with N_2, to retain strict anaerobic environment. For mesophilic condition, the reactors settled in warm water bath, maintained at 36 ± 1 ℃ by automatic heaters (Fig. 1). The digestion process continued for 20 days, as long as the amount of biogas production in the bioreactors was negligible. In order to retain homogenous temperature and food distribution, the bioreactors were continuously stirred at 100 rpm with magnetic stirrers during the digestion process.

Table 2. Conditions of pre-treatment experiments

Pre-treatment	H_2O_2 (g/kg VS)	Temperature (℃)
	Individual pre-treatment	
Hydrogen peroxide 1	30 g/kg VS	≈ 25
Hydrogen peroxide 2	60g/kg VS	≈25
Heat 1	0	75
Heat 2	0	90
	Combined pre-treatment	
Hydrogen peroxide 1 + Heat 2	30 g/kg VS	90
Hydrogen peroxide 2 + Heat 1	60g/kg VS	75

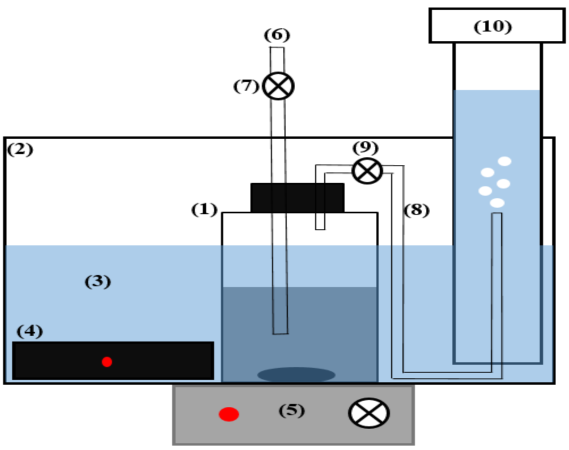


Fig. 1. Schematic depiction of the experimental system: 1) biochemical methane potential reactor, 2) aquarium, 3) saturated and acidified water, 4) automatic heater, 5) magnetic stirrer, 6) sampling pipe, 7) sampling control valve, 8) biogas collecting pipe, 9) biogas control valve, and 10) graduated cylinder

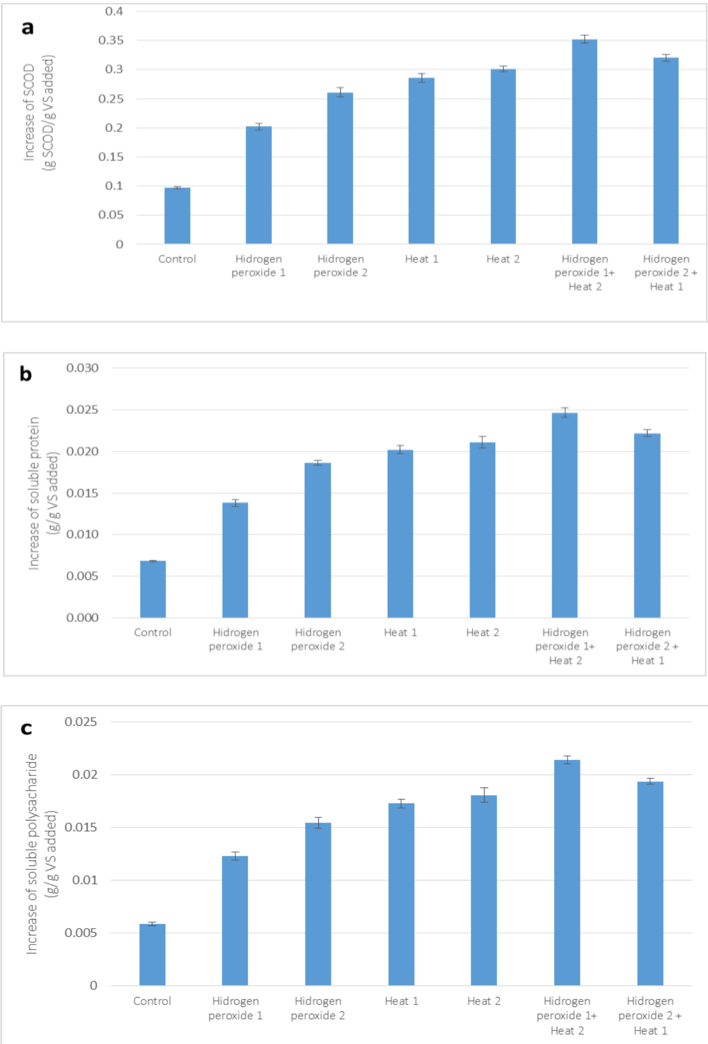
RESULTS AND DISCUSSION

The amount of soluble fractions of organic matter in the waste activate sludge were measured before and after treatments. Fig. 2 demonstrates the effect of pre-treatments on solubalisation of organic matter. As can be observed, the amounts of organic matter in all reactors increased considerably through pre-treatments, which can be due to the disruption of microbial cell walls and breakage of organic compounds like proteins and carbohydrates that make up around 60% of the organisms composition (Appels et al., 2010; Dhar et al., 2012; Pilli et al., 2015b). Soluble fractions of organic matter in the control reactor experienced a slight increase, suggesting some solubalisation even without pre-treatment. This agrees with previous studies, wherein a slight increase was observed in the control reactor without chemical additives (Wang et al., 2014; Zahedi et al., 2017).

Fig. 2-a shows the amount of SCOD increase after treatments. As can be seen, the amount of SCOD mounted in all pre-treated reactors significantly, mainly due to the cell wall disruption and release of organic matter into liquid phase as a consequence of formation of free radicals from hydrogen peroxide ($NO^{\bullet}_2$ and $HO^{\bullet}$) and high temperature during pre-treatment. The reactor, pre-treated with combined hydrogen peroxide (30 g H_2O_2/kg VS), along with the heat (90 ℃) achieved the highest rise of SCOD with 0.35 g SCOD/g VS. However, the amount of SCOD in these pre-treatments alone ascended by 0.2 and 0.3 g SCOD/g VS, respectively. A similar trend was achieved by Kim et al. (2015), although in that study far greater temperature (210 ℃) as well as relatively high pressure (3.5 MPa) was applied to waste activated sludge prior to biochemical methane potential tests. Wang et al. (2014) showed that via thermal pre-treatment of waste activated sludge at 70℃ for an exposure time of 24 hours could increase SCOD by 0.25 g SCOD/g VS. Slightly higher SCOD was achieved in this study, which further corroborated the effectiveness of thermal pre-treatment in solubalisation of organic matter.

Since not all types of organic matter are biodegradable for anaerobic organisms, soluble fractions of protein and polysaccharide, the two important constituents of SCOD, were measured before and after the treatments. Fig. 2-b and 2-c show the impact of pre-treatments on soluble fractions of protein and polysaccharide. According to the data in these figures, the highest increase in soluble fractions of protein (0.024 g/g VS) and polysaccharide (0.021 g/g VS) belonged to the combination of pre-treatment of hydrogen peroxide (30 g H_2O_2/kg VS) and heat (90℃). Afterwards, the other combined pre-treatment (60 g H_2O_2/kg VS and 90 ℃) caused the highest solubalisation of these constituents. Enhancement of soluble fractions of protein and polysaccharide after treatments, affirmed the availability of more readily biodegradable organic matter for anaerobic organisms as a result of cell walls' disruption and EPS in the substrate. The effect of pre-treatments on solubalisation of protein was higher than polysaccharide. This can be attributed to biocidal effect of the pre-treatments that affect the proteins more than the polysaccharide, since the main composition of organisms' cell is around 50% protein (Pilli et al., 2015b). The improvement of organic solubalisation was consistent with the results, achieved in previous studies, where soluble fraction of organic matter rose considerably after H_2O_2 and thermal pre-treatments (Liu et al., 2018; Neumann et al., 2017; Wang et al., 2014).

Fig 2-d shows the percentage of the reduction of VSS after the treatments. The amount of VSS in all pre-treated reactors declined considerably. Decrease of VSS confirmed that volatile solids were converted from suspended phase to liquid one, which further corroborated the enhanced SCOD, soluble protein, and polysaccharide after the pre-treatments. The highest decrease in the amount of VSS (23%) belonged to the combination of hydrogen peroxide (30 H_2O_2/kg VS) and thermal treatment (at 90°C). Among the non-combined pre-treatments, heat 2 (at 90°C) led to the most significant decrease in the VSS (19%), while hydrogen peroxide 2 (60 gH_2O_2/kg VS) did not reduce the amount of VSS more than 15%, which was 10% lower than the VSS reduction, achieved in the study by Pilli et al. (2016) wherein Fenton reagent (H_2O_2 + Fe^{+}) was used as an advanced oxidation process for sewage sludge pre-treatment.



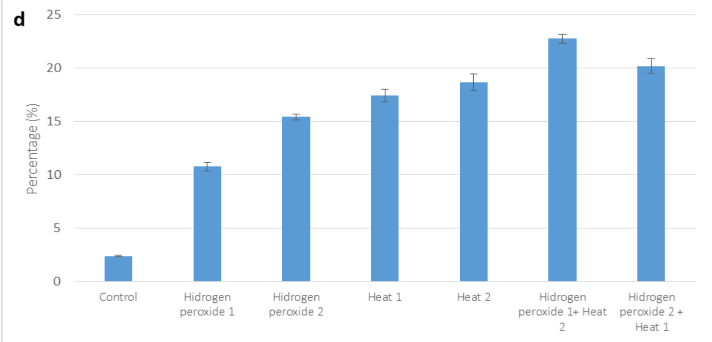
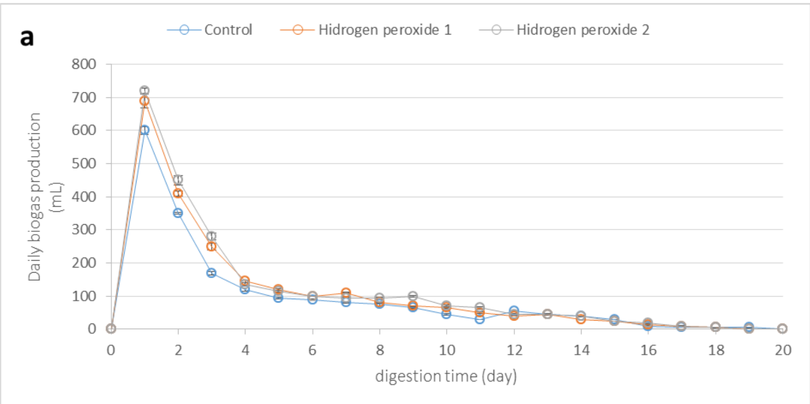


Fig. 2. Biomass specific production of (a) SCOD, (b) soluble proteins, (c) soluble polysaccharides, and (d) VSS after pre-treatments. The error bars represent standard errors, resulting from triplicate tests.

The amount of biogas production was measured daily. According to Fig 3, biogas production was improved by the pre-treatments, particularly during the first days of the digestion process. This was due to higher amounts of readily biodegradable organic matter, available to anaerobic organisms in the pre-treated reactors as well as stimulated growth of hydrogen-using methanogens that provided good balance and syntrophic association among various microbial communities (Ennouri et al., 2016). The maximum daily biogas production (890 mL) belonged to the bioreactor treated with hydrogen peroxide 1 along with heat 2, being 49% higher than the maximum daily biogas produced from the control reactor. However, hydrogen peroxide 1 and heat 2 pre-treatments alone increased the maximum daily biogas production only by 36% and 17%, respectively. The surface area below each chart represents the cumulative biogas production from the bioreactors, which was significantly higher in pre-treated reactors than the control at the end of the digestion. It is also demonstrated that the amount of biogas production was significantly enhanced in the combined pre-treatments, compared with the individual pre-treatments ($p < 0.05$), affirming synergistic influence of the combined hydrogen peroxide and thermal pre-treatment on biogas production. After 5 days, the difference between the amounts of daily biogas production from the bioreactors declined considerably, which can be attributed to the reduction of biodegradable organic matter in the bioreactors and high I/S employed in this study for better performance of inoculum. Kim et al. (2015) revealed that cumulative biogas production increased by 62% when hydrothermal pre-treatment was employed at 210°C, 3.5 MPa, and for 30 minutes of exposure time. This was 11% higher than the cumulative biogas production in the current study at 90°C.

The methane production was measured regularly during the anaerobic digestion. Fig. 4 shows the amount of cumulative methane production from the pre-treated and control bioreactors. According to the reported data, the amount of cumulative methane production experienced a significant increase in all pre-treated bioreactors, with the amount of cumulative methane production rising from 271 mL CH_4/g VS $_{added}$ in the control reactor to 490 mL CH_4/g VS $_{added}$ in the bioreactor, pre-treated with combined hydrogen peroxide1 and heat 2. This was significantly higher than methane production obtained from hydrogen peroxide 1 (328 mL CH_4/g VS $_{added}$) and heat 2 (438 mL CH_4/g VS $_{added}$) alone ($p < 0.05$), corroborating synergistic effect of the combined hydrogen peroxide and thermal pre-treatment on methane production. The enhanced methane production was the result of biodegradable organic matter release in the pre-treated bioreactors (Fig. 2). Higher concentrations of pre-treatment constituents as well as higher temperature resulted in enhanced organic solubalisation and methane production. The methane/biogas yield was slightly improved by the pre-treatments, indicating that the increased methane production was mainly due to the improved biodegradability of organic matter, not the methane content. In addition, the CO_2/biogas ratio fell slightly during the anaerobic digestion process. From an economic and environmental perspective, the enhanced methane production was of great significance because not only could higher renewable energy be generated in wastewater treatment plants, but methane emission into the atmosphere, as a major greenhouse gas, could decline considerably from sludge treatment units, responsible for the production of 50% of total greenhouse gas emission of wastewater treatment plants (Pilli et al., 2016). The amount of methane produced in the system by means of single hydroxide or thermal pre-treatment was consistent but slightly higher than the methane production, obtained in previous studies, further confirming the effectiveness of hydrogen peroxide and thermal pre-treatment when enhancing anaerobic digestion of sewage sludge (Wang et al., 2014; S. Zhang et al., 2015; T. Zhang et al., 2015). Zhang et al. (2015) revealed that pre-treatment of waste activated sludge with 50 mg H_2O_2/g TS for 24 hours can enhance methane production by 23%, while in this study an enhancement of 32% was observed that can be attributed to the nature of sludge and operational conditions. Wang et al. (2014) reported that thermal pre-treatment of waste activated sludge at 70℃ improved methane production around 21%, while in the current study, a higher amount of methane was achieved in thermal pre-treated bioreactors.



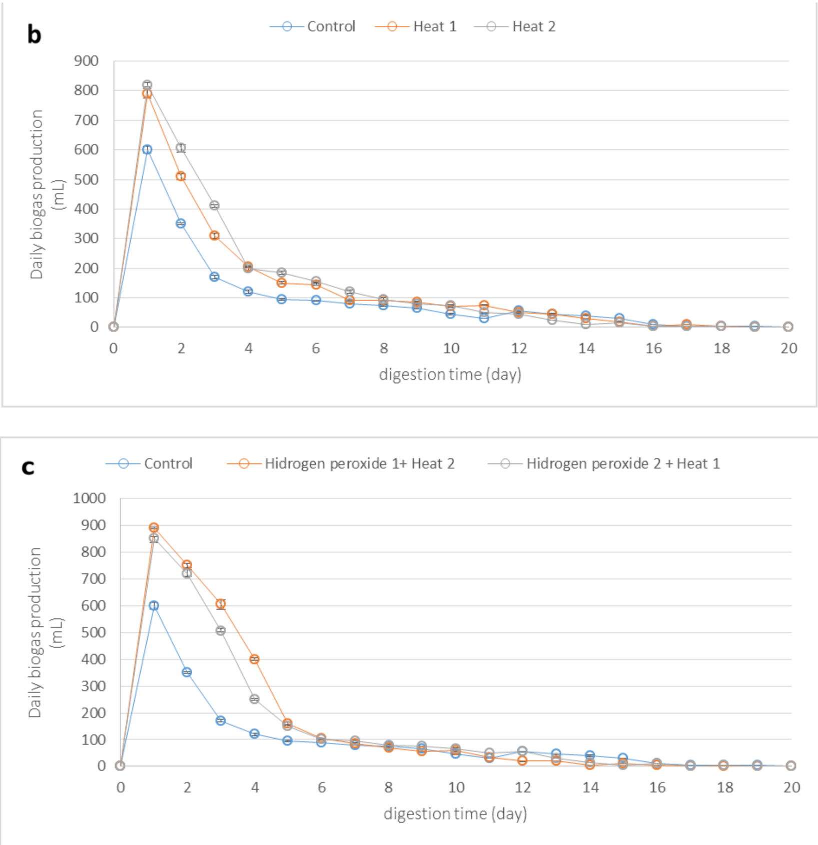
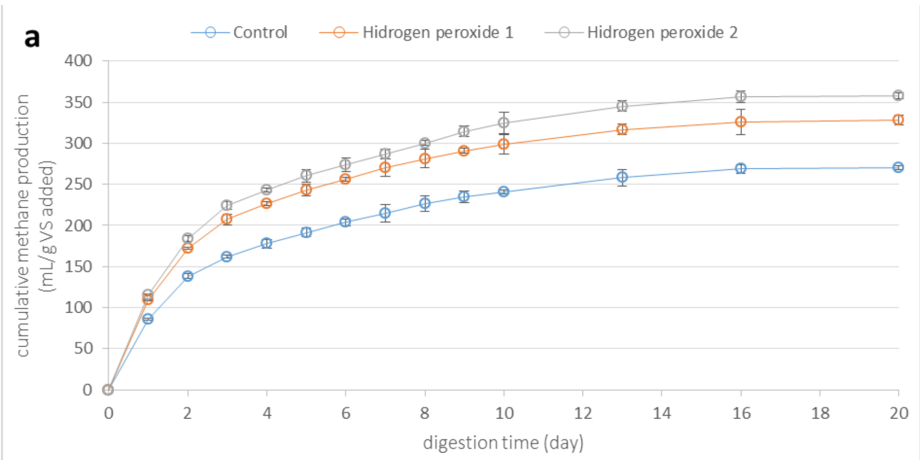
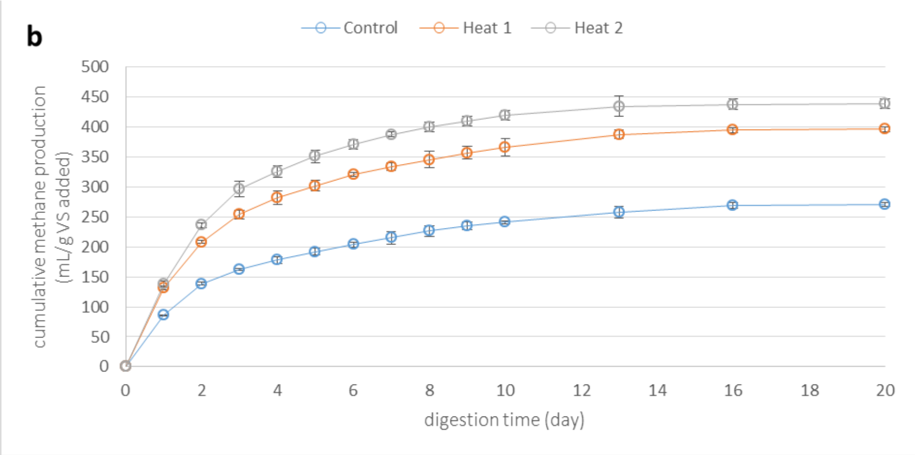


Fig. 3. Daily biogas production in a) pre-treated reactors with hydrogen peroxide, b) pre-treated reactors with heat, and c) pre-treated reactors with combined hydrogen peroxide and heat. Error bars represent standard errors, obtained from triplicate tests.





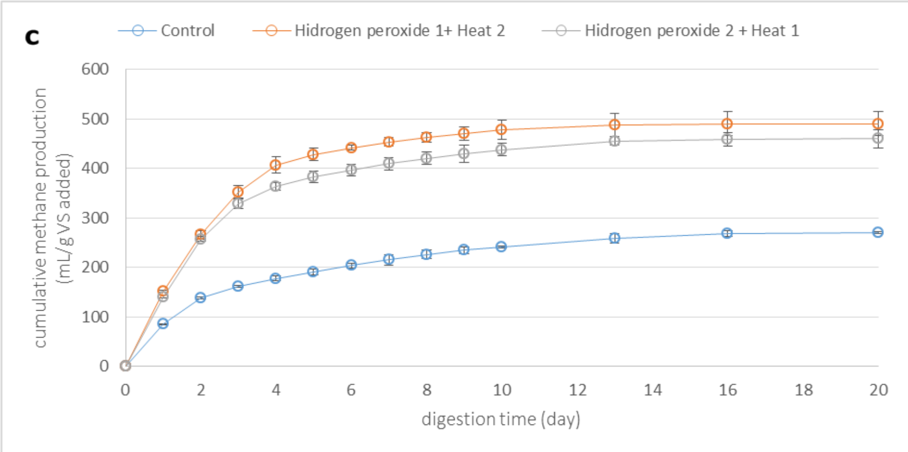


Fig. 4. Cumulative methane generation in a) pre-treated reactors with hydrogen peroxide, b) pre-treated reactors with heat, and c) pre-treated reactors with combined hydrogen peroxide and heat. Error bars represent standard errors, obtained from triplicate tests.

The COD and VS of digested sludge are crucial characteristics for application of sludge to agricultural lands and forests. The amount of COD and VS removal was improved in all bioreactors, treated with hydrogen peroxide and/or heat (Fig. 5). The highest COD and VS removal were obtained from the bioreactor pre-treated with hydrogen peroxide 1 and Heat 2, where COD and VS removal was enhanced by 39% and 92%, respectively, in comparison to the control bioreactor. This was 25% and 53% higher than the COD and VS removal, obtained from thermal per-treatment (at 90°C) alone, the highest removal efficiency obtained among the non-combined pre-treatments. The improved COD and VS are linked to higher biogas and methane production from the biochemical methane potential reactors because production of higher methane (in relatively constant methane/biogas yield) implies consumption of higher amounts of organic matter by anaerobic organisms, resulting in lower COD and VS at the end of the digestion process. The enhanced COD and VS removal in this study were of paramount importance, because it lowered the amount of sludge, reducing the associated costs of transport. It also paved the way to shape an integrated, sustainable system for treatment of sewage sludge through application of digested sludge to agricultural lands and forests.

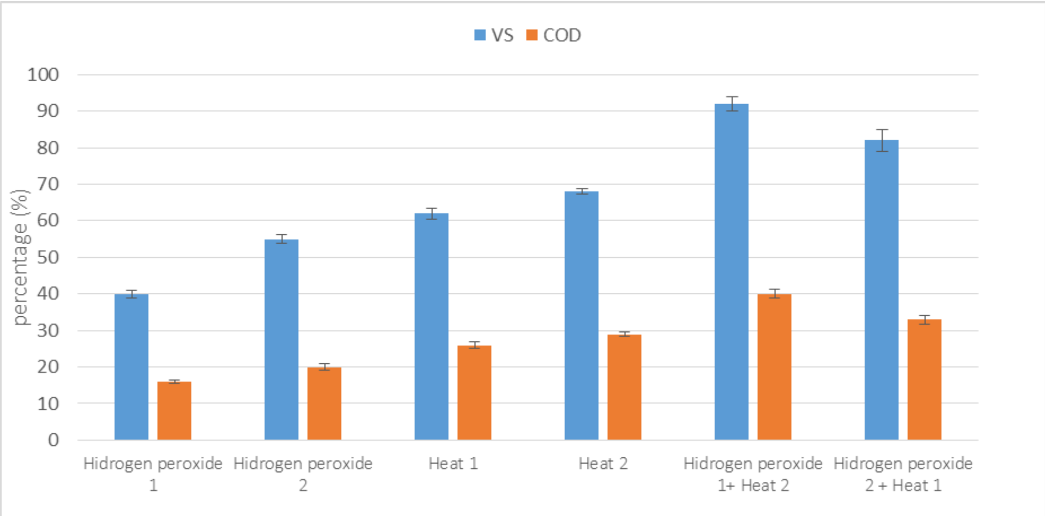


Fig. 5. Increase of the removed chemical oxygen demand and volatile solids at the end of the digestion. Error bars represent standard error, obtained from triplicate tests.

Despite the significant results, represented in this research, applying new systems to anaerobic digestion of sewage sludge entails a great deal of money and time. Therefore, in future studies, a precise economic assessment for full-scale application of combined hydrogen peroxide and thermal pre-treatments seems indispensable. In addition, the influence of pre-treatments on microbial community should go under the spotlight to delve deeply into these pre-treatments' mechanism as well as probable long-term side-effects on microbial behavior.

CONCLUSION

The current study investigated the effects of combined pre-treatment of heat and hydrogen peroxide on solubalisation of organic matter, biogas production, methane yield, COD removal, and VS. According to the analyses, soluble fractions of organic matter got enhanced in the combination of hydrogen peroxide and thermal pre-treatment significantly more than these pre-treatments by themselves. The daily biogas and cumulative methane production analogously experienced a considerable increase in the combined pre-treatment, facilitating generation of higher energy in wastewater treatment plants. In addition, the enhanced COD and VS removal in this study was important as it lowered the amount of sludge and reduced the associated costs of transport. Combined hydrogen peroxide and thermal pre-treatment is potentially an economically-attractive and environmentally-friendly technology, particularly when considering that both are obtainable as by-products from anaerobic digestion of sewage sludge.

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