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ADVANCES & PROSPECTS IN THE FIELD OF WASTE MANAGEMENT

Effects of microwave, H_2O_2/MW and H_2O_2/heat pre-treatments on the methane production from wastewater sludges: experimental and modeling approach

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Abstract

The wastewater sludge stabilization by anaerobic digestion is sufficient to reduce the organic content of the sludge, so that it can be safely disposed of without causing odor problems and pathogen contamination, while producing energy in form of biogas. Efficiency of anaerobic digestion in terms of biogas/methane production and organic removal can be enhanced by pretreating the sludge prior to anaerobic digestion. This study compares the effects of microwave (MW), combined hydrogen peroxide/microwave (H_2O_2/MW), and combined hydrogen peroxide/heat (H_2O_2/heat) pre-treatments on the digestion efficiency and methane production potential of wastewater sludges. The methane productions were also estimated by using modified Gompertz equation through the calculation of the kinetic parameters. The pre-treatments applied to sludge samples speeded up the hydrolysis step and improved the biodegradability of the organics by increasing their solubility. Application of MW, combined H_2O_2/MW, and combined H_2O_2/heat pre-treatments increased the methane yields by 64%, 38%, and 19%. The modified Gompertz model fitted well to the experimental results (R^2 of 0.999, 0.983, 0.997, and 0.998 for control, MW, H_2O_2/MW, and H_2O_2/heat, respectively).

Keywords Anaerobic digestion · Hydrogen peroxide pre-treatment · Microwave irradiation · Methane production · Modified Gompertz model

Introduction

The increasing amount of sewage sludge production in wastewater treatment plants (WWTPs) has become a serious problem. To overcome the rising problem, the wastewater sludge disposal amount should be diminished by the application of varied sludge treatment and pre-treatment methods. The sludge stabilization must be applied to wastewater sludges for the safe disposal.

The wastewater sludge production is increasing worldwide with gradual growth of population and industrialization. The energy need is also increasing with the developing world and there is a necessity of alternative energy source. The anaerobic digestion (AD) is a promising technology for generating energy from waste sludge by producing biogas. Biogas, which comprises of biomethane and carbon dioxide, is a renewable source of energy obtained from biodegradable organic wastes like biomass, agricultural and animal wastes, and industrial waste (W. Li et al. 2018; Kuglarz et al. 2013; Abudi et al. 2016).

AD is the most widely used beneficial approach for wastewater sludge stabilization reducing odors and pathogens in sludge, while providing recovery of renewable energy through the biogas production (Ahn et al. 2009; Priadi et al. 2014; Weiland 2010). Anaerobic digestion is a complicated conversion process of biodegradable organic material in microorganisms converting into biogas in the absence of oxygen, and it comprises mainly methane (CH_4) and inorganic end-products like carbon dioxide (CO_2). Anaerobic digestion of organic material occurs in four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Climent et al. 2007; Lastella et al. 2002; Wu-Haan 2008).

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The performance of anaerobic digestion of sludges can be enhanced with the application of various physical (thermal, mechanical, ultrasonic, microwave), chemical (alkaline, hydrogen peroxide, ozone oxidation), and biological (enzymatic) pre-treatment methods or their combinations. These pre-treatments disintegrate the sludge solids and improve the biodegradability of sludge solids, biogas/methane production, and removal of the micropollutants (Angelidaki et al. 2009; Ariunbaatar et al. 2014; Climent et al. 2007; Weiland 2010; Tyagi and Lo 2011).

Advanced oxidation pre-treatment techniques have gained importance in recent years. Many disinfectant oxidants like ozone, hydrogen peroxide, chlorine, and chlorine dioxide have been used in the disintegration of the sludge. Hydrogen peroxide (H_2O_2) and ozone (O_3) applications in sludge have been investigated by many researchers. Although ozone is a very strong oxidant, ozonation is an expensive process that limits large-scale application. For this reason, applications of other chemicals such as hydrogen peroxide (H_2O_2) and Fenton (hydrogen peroxide/iron catalyst) have come to the forefront. Hydrogen peroxide is the simplest peroxide and acts as a strong oxidant, enhancing the sludge disintegration. H_2O_2 pre-treatment can be improved by the heat application, direct heat or microwave irradiation, to the sludge samples as a combined pre-treatment method (Bougrier et al. 2006; Eswari et al. 2016; Feki et al. 2015; Hannmann et al. 2012; Liu et al. 2016; Neyens and Baeyens 2003; Shahriari et al. 2012; SONG et al. 2013).

Microwave irradiation is an alternative thermal sludge pre-treatment method. It is more advantageous than the conventional thermal processes due to several reasons like rapid heating, high reaction rate, easy control, compactness, and creation of greater damage on microbial cells at similar applied temperatures compared with conventional heating (Alagöz et al. 2015; 2017; Eskicioglu et al. 2007; Mudhoo et al. 2011). Microwave irradiation disintegrates the sludge flocs and disrupts the sludge cells by the effect of rapid heating. It causes the release of extracellular and intracellular substances leading to an increase in the organic components such as soluble COD, soluble proteins, and soluble carbohydrates in the liquid phase of the wastewater sludges (Eskicioglu et al. 2007; Tyagi and Lo 2013).

Combined pre-treatment methods give more effective results than the single pre-treatment methods. Therefore, it is expected to reach higher biogas production efficiencies with the application of combined pre-treatment methods to sludge samples prior to anaerobic digestion. However, there are some contradicting studies in literature reporting that the H_2O_2/MW and H_2O_2/heat pre-treatments resulted with lower biogas yields compared with MW pre-treatment (Shahriari et al. 2012; Valo et al. 2004; Eskicioglu et al. 2008b; Liu et al. 2017).

This study investigates the effects of microwave (MW), combined hydrogen peroxide/microwave (H_2O_2/MW), and combined hydrogen peroxide/heat (H_2O_2/heat) pre-treatments on the anaerobic digestion efficiency of wastewater sludges in terms of methane production and organic removal. Biochemical methane potential (BMP) test was used to determine the anaerobic digestibility of sludge samples by measuring biogas productions. The kinetic parameters of methane production were also modeled by using modified Gompertz equation.

Materials and methods

Sludge samples

The wastewater sludge samples were obtained from recirculation unit of a biological wastewater treatment plant located in Istanbul. The inoculum sludge was supplied from the anaerobic digester of the same plant.

The inoculum and sludge samples were characterized by analyzing their total solids (TS), volatile solids (VS), chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), total suspended solids (TSS), volatile suspended solids (VSS), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), phosphorus (P), volatile fatty acids (VFA), alkalinity concentrations, and the pH values. All of the characterization analyses were conducted in triplicates as described in the Standard Methods of the Examination of Water and Wastewaters (APHA 2012). The characteristics of wastewater sludge and inoculum are given in the Table 1.

Table 2 summarizes the analytical methods and instruments used in this study.

Table 1 Characteristics of the sludge samples

Parameter	Unit	Wastewater sludge	Inoculum
TS	g/L	13.5	44
VS	g/L	8.3	20.2
TSS	g/L	13	41
VSS	g/L	8.2	18.4
pH	–	6.6	7.6
COD	mg/L	19576	41805
sCOD	mg/L	255	1106
TOC	mg/L	230	235
TKN	mg/L	880	1935
NH_3-N	mg/L	165	1330
P	mg/L	310	720
VFA (as acetic acid)	mg/L	3.9	18.8
Alkalinity	mg CaCO3/L	1220	8365

Table 2 The analytical methods and instruments used in the study

Parameter	Methods and special instruments
TS (g/L)	2540 B (APHA 2012)
VS (g/L)	2540 B and E (APHA 2012)
TSS (g/L)	2540 G (APHA 2012)
VSS (g/L)	2540 D and E (APHA 2012)
COD (mg/L)	5220 D dichromate closed reflux method (APHA 2012) (HACH COD digester, HACH DR/2010 spectrophotometer)
sCOD (mg/L)	Centrifugation and 5220 D dichromate closed reflux method (APHA 2012) (Hettich Universal 16A Centrifuge, HACH COD Digester HACH DR/2010 spectrophotometer)
TKN (mg/L)	4500-N B digestion method (APHA 2012) (Gerhardt Vapodest digester apparatus)
P (mg/L)	4500-P E method ascorbic acid (APHA) (HACH DR/3 spectrophotometer)
TOC (mg/L)	Solid sample combustion method (Shimadzu TOC Analyser-V CSH)
VFA (mg/L)	Chromatography (Perkin Elmer Clarus 600)
Alkalinity (mg/L)	2320 B method titration (APHA 2012)
pH	4500-H B method electrometric (APHA 2012) (WTW Inolab pH meter)
Gas production	Manometry (LUTRON electronic manometer, PM-9107)
Gas composition	Chromatography (Agilent HP 6850 gas chromatograph)

Application of sludge pre-treatments

The wastewater sludge samples were pre-treated with MW, combined H_2O_2/MW, and H_2O_2/heat pre-treatment methods to show their effects on methane production comparatively.

Microwave pre-treatment

The microwave pre-treatment was applied to sludge samples by irradiating them for 15 min at 160 °C and 2000 kPa in a microwave (MW) digestion (Berghoff MWS+3) by using a 5-staged temperature program. In the 1st and 2nd stages, the temperature is risen to 120 ° C in 2 min and then 140 °C in the following minute. In the 3rd stage, the temperature reached to 160 °C and remained constant for 10 min. In the next 2 min, the temperature drops to 140 °C and then 100 °C in the 4th and 5th stages, respectively. The application conditions of MW pre-treatment were selected based on the results of a preliminary MW optimization study (TUBITAK-KAMAG 2013).

Combined hydrogen peroxide and MW pre-treatments (H_2O_2/MW)

Combined H_2O_2/MW treatment consisted of a preheating step, H_2O_2 (30% *w*/*w*) addition, and microwave irradiation. First, the sludge samples were heated at 120 °C for 15 min in the MW system to destruct the biological enzymes in the sludge to avoid the excessive consumption of hydrogen peroxide (Wang et al. 2009). After the preheating step, 1 g H_2O_2/g TS was added into the sludge samples, and the samples were irradiated in a microwave digester at 160 °C for 15 min. The applied peroxide concentration of 1 g H_2O_2/g TS was selected based on the results of the studies in literature using the wastewater sludges as substrate (Bilgin Oncu and Akmehmet Balcioglu 2013; Jung et al. 2014; Kim et al. 2009; Wong et al. 2006; Yin et al. 2007). Especially, the optimization study by Bilgin Oncu and Akmehmet Balcioglu (2013) used a wastewater sludge having quite similar characteristics to the sludge used in this study.

Combined hydrogen peroxide and heat pre-treatments (H_2O_2/heat)

In combined H_2O_2/heat pre-treatment, the sludge samples placed in polytetrafluoroethylene (PTFE) beakers were preheated to 75 °C for 2 min prior to the addition of 1 g H_2O_2/g TS (30% *w*/*w*) in order to initiate the chemical reaction. Then, the sludge samples were subjected to heat treatment at 75 °C for 90 min in a temperature-controlled water bath (Julabo, SW22). The heat pre-treatment conditions were selected based on a previous study conducted in the Institute of Environmental Sciences, Boğaziçi University (Mercan 2015).

Biochemical methane production potential experiments

The biochemical methane potential (BMP) test was used to investigate the effects of MW, combined H_2O_2/MW, and combined H_2O_2/heat pre-treatments on the anaerobic digestion efficiency of wastewater sludges in terms of methane production. Biochemical methane potential test helps to determine the anaerobic digestibility of sludge samples by measuring biogas productions. The BMP assay process was first established by Owen et al. (1979) as a simple and inexpensive procedure to monitor relative anaerobic biodegradability of substrates.

In this study, the BMP tests were performed in six parallel sets of four different reactor groups (total of 24 reactors) according to the procedure described by Owen et al. (1979). The four main reactor groups were control reactors, MW reactors, H_2O_2/MW reactors, and H_2O_2/heat reactors. Table 3 shows the contents of the reactor groups.

The pre-treatments were applied to the wastewater sludge (substrate) samples only. The pretreated wastewater sludge samples were mixed with the inoculum in reactors having 80 mL active volume. In the reactors, the inoculum-to-substrate ratio (ISR) was adjusted to 1:1 (*w/w* on VS basis) by feeding the reactors with 23 mL of inoculum and 57 mL of wastewater sludge. The control reactors included inoculum and un-pretreated sludge.

The initial pH of the reactor contents was adjusted to 7–7.2 to be in the favorable range for anaerobic digestion (Appels et al. 2008; Feki et al. 2015). In the same way, the initial alkalinity concentrations in the reactors were adjusted to be in the range of 3000–4500 mg/L as $CaCO_3$ to keep the alkalinity in the safe range for anaerobic digestion (Raposo et al. 2012; Turovskiy and Mathai 2006). The reactors were sealed and flushed with nitrogen gas for 2 min to create an anaerobic environment. The reactors were anaerobically digested at 37 °C for 40 days under mixing conditions in the temperature-controlled shaking water baths.

The effects of applied pre-treatments on the removal of organic matters were investigated by measuring TS, VS, COD, and sCOD concentrations of the reactor contents weekly by opening one of the parallels for each reactor groups.

Total biogas productions in reactors was measured daily with the pressure method by using a manometer (Lutron PM-9107). The biogas compositions were analyzed weekly by using a gas chromatograph (GC) (Agilent HP 6850). The gas samples were taken from each reactor with a GC autosampler syringe and injected into the GC to analyze the gas compositions in the reactors.

Table 3 Contents of the reactor groups

Reactor names	Explanations of the reactor contents
Control reactors	Inoculum + un-pretreated sludge
MW reactors	Inoculum + MW pretreated sludge
H_2O_2/MW reactors	Inoculum + H_2O_2/MW pretreated sludge
H_2O_2/heat reactors	Inoculum + H_2O_2/heat pretreated sludge

Kinetic modeling of methane production

In this study, kinetic modeling of methane production was performed by using modified Gompertz equation. Gompertz equation was found to be the most suitable model for the biogas/methane productions (Zwietering et al. 1990). The modified Gompertz equation was originally developed for the prediction of bacterial growth. Later, the Gompertz equation was implemented for the modeling of specific growth rate of methanogenic bacteria. The kinetics of methane yields directly link with the specific growth rate of methanogenic bacteria.

In many studies, the nonlinear regression of Gompertz equation was used for modeling of biogas and methane production potentials of several systems (L. Li et al. 2015; Y. Li et al. 2013; Syaichurrozi and Sumardiono 2013; Tsapekos et al. 2017; Yusuf et al. 2011; Budiyono et al. 2014).

The modified Gompertz equation is as follows:

$$M(t) = P.\exp\left(-\exp\left(\frac{R_m.e}{P}(\lambda - t) + 1\right)\right)$$

where M is the cumulative methane production (mL CH_4/g VS) at time t (day), λ is the lag time (day), P is the methane production potential (mL CH_4/g VS), R_m is the maximum methane production rate (mL CH_4/g VS/day), and e is the mathematical constant (2.7182) (Córdoba et al. 2018).

Kinetic constant of P, λ, and Rm was evaluated by using nonlinear regression approach with the help of solver function of the MS Excel (Matheri et al. 2016; Yusuf et al. 2011; Ghatak and Mahanta 2017; Ghatak and Mahanta 2014).

Results and discussions

Effects of pre-treatments on sludge solubility and organic removal

The pre-treatments considerably improved the solubility of organics in sludge samples. The microwave pre-treatment disrupts the sludge flocs and cells, breaks the hydrogen bonds, and releases the soluble organic components into the liquid phase of the sludge. In the H_2O_2 pre-treatment, the hydroxyl radicals (OH•) and hydroperoxyl radicals (HO_2•), generated from the decomposition of hydrogen peroxide, attack on sludge particles and cause the destruction of cell walls of the microorganisms and solubilize the particulate component of sludge into the soluble form.

TS and VS reductions

The application of pre-treatments to the sludge samples increased the total solid (TS) and volatile solid (VS) removal rates in the anaerobic digestion process. The control reactor, containing un-pretreated sludge and inoculum, has an initial TS concentration of 25 g/L and a VS concentration of 13 g/L. The TS and VS concentrations in the reactors were measured weekly by opening one of the parallel reactors. At the end of the digestion period, the overall TS and VS removal rates in the control reactor were 15% and 24%, respectively. In the combined H_2O_2/MW, H_2O_2/heat, and MW pretreated sludge–containing reactors, the TS removal efficiencies were determined to be 53%, 29%, and 28%, respectively. The VS removal efficiencies in these reactors were about 59%, 40%, and 42% in the same order. Figure 1 shows the VS concentration changes in the reactors during anaerobic digestion period.

COD and sCOD removals

The initial COD concentrations in the reactors were measured to be in the range of 20000 to 22200 mg/L. At the end of the anaerobic digestion period, the COD removal rate in the control reactor was 18%. The applied sludge pre-treatments increased the COD removal efficiencies in the reactors two- to threefolds by increasing the solubility of the sludge organics. The COD removal efficiencies were found to be 58%, 55%, and 43% in the MW, H_2O_2/MW, and H_2O_2/heat pretreated sludge–containing reactors, respectively.

Accordingly, Wang et al. (2015) applied a lower H_2O_2 dose of 0.2 g H_2O_2/g TSS to a wastewater sludge sample at 100 °C and reported that H_2O_2/MW pre-treatment resulted to a COD removal of 19.35% for 15 min. to a wastewater sludge, having similar characteristics with the sludge used in this study, and achieved a COD removal of 23% and 41%, respectively (Bilgin Oncu and Akmehmet Balcioglu 2013).

The pre-treatments considerably improved the solubility of sludge samples by disintegrating the sludge structure and releasing organic matter into the soluble phase. The initial sCOD of inoculum and un-pretreated sludge mixture in the control reactor was measured to be 470 mg/L. After the application of pre-treatments, the initial sCOD concentrations in the reactors were increased by 751%, 517%, and 158% for H_2O_2/heat, H_2O_2/MW, and MW pre-treatments, respectively.

This increase in the solubility of the sludge solids led to an improvement in the sCOD removal rates. The sCOD removal rates increased from 14% (in control reactor) to 74%, 68%, and 59% in the MW, H_2O_2/MW, and H_2O_2/heat pretreated sludge–containing reactors, respectively. In the MW pre-treatment–applied reactor, the conversion of sCOD to biogas started immediately after sealing the reactor in day 0. The change in sCOD concentrations during anaerobic digestion is shown in Fig. 2.

In accordance with this study, Wong et al. (2006) investigated the effect of combined H_2O_2 and MW pre-treatment at different temperatures on sewage sludge treatment and achieved COD solubilization of 72% and 77% with 1 mL H_2O_2 addition and MW application at 120 °C and 100 °C, respectively. When they increased the H_2O_2 dose to 2 mL H_2O_2, the COD solubilizations increased to 97% and 104% at 120 °C and 100 °C, respectively. Their study showed that the increased temperature of MW in combined H_2O_2 and MW pre-treatment may lead to lower COD solubilization (Wong et al. 2006). Similarly, combined MW and hydrogen peroxide pre-treatment (110 °C and 0.3 H_2O_2 mg/g SS) of waste activated sludge obtained COD solubilization of up to 50.3% (Eswari et al. 2016).

Effects of pre-treatments on methane production

The biochemical methane potential (BMP) test was used to investigate the effects of MW, combined H_2O_2/MW, and combined H_2O_2/heat pre-treatments on the methane production potential of the wastewater sludges. The VFA and ammonia concentrations in the reactors were measured weekly to

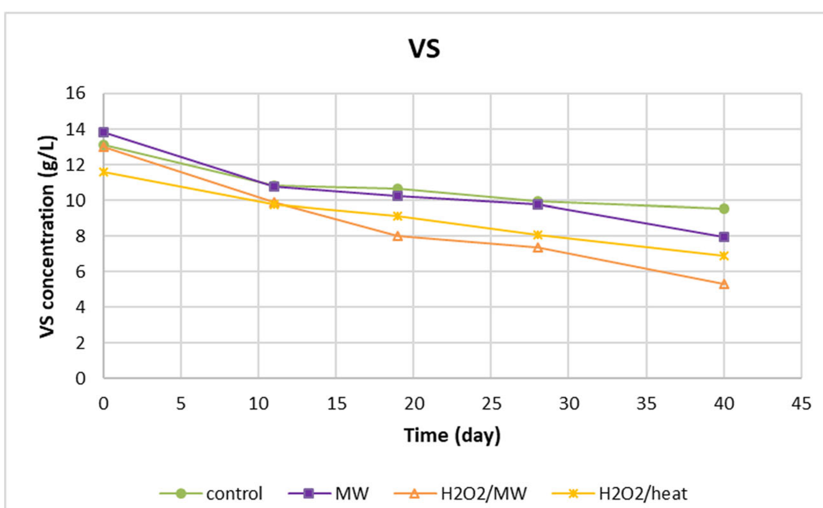

Fig. 1 VS concentrations in the reactors during anaerobic digestion

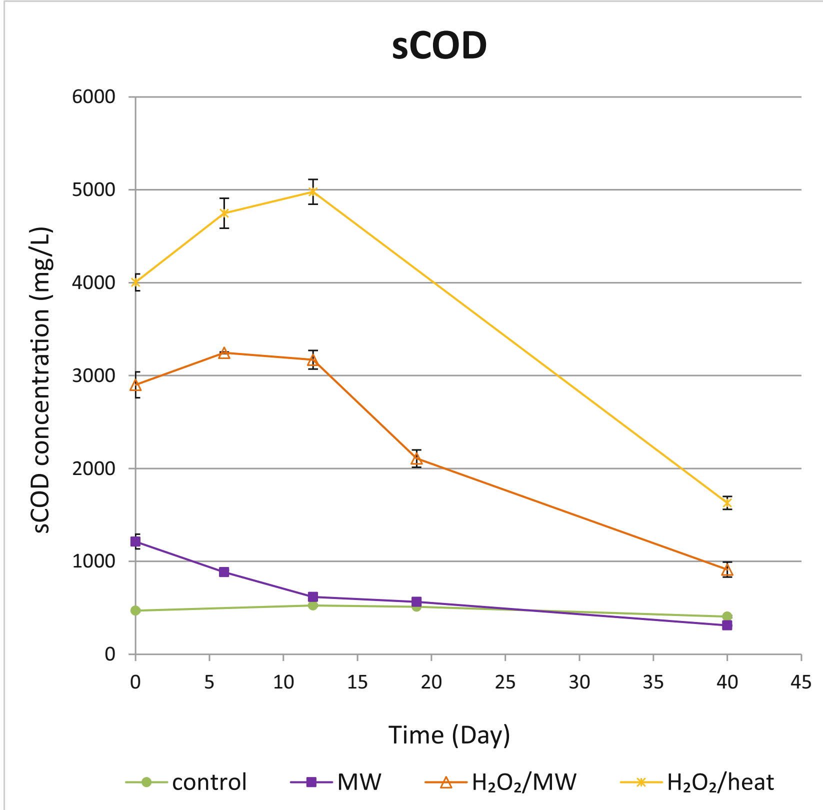

Fig. 2 Change in sCOD concentrations during anaerobic digestion

control the formation of ammonia and/or VFA inhibition during the anaerobic digestion period. The ammonia concentrations in the reactors were ranged between 275 and 930 mg/L throughout the digestion process, being much lower than the critical inhibition concentration of 1700 mg/L for anaerobic digestion (Franke-Whittle et al. 2014; Koster and Lettinga 1984). The highest VFA concentration measured in the reactors was 1340 mg/L. Based on the literature, this concentration was in safe limits for a successful anaerobic digestion. There are many studies reporting that the VFA concentrations should be under 4000 mg/L to control any possible inhibition in an anaerobic digestion process (Lee et al. 2015; Chen et al. 2008; Fricke et al. 2007). Siegert and Banks (2005) stated that total VFA concentrations higher than 4000 mg/L cause to a slight inhibition and concentrations higher than 8000 mg/L to a serious inhibition in the anaerobic digestion process.

The pre-treatments applied to sludge samples improved the methane productions. The cumulative methane productions were increased by 64%, 38%, and 19% in the reactors containing sludges pretreated with MW, H_2O_2/MW, and H_2O_2/heat, respectively. The cumulative methane productions in the reactors are given in Fig. 3. In the MW pre-treatment–applied reactor, the biogas/methane production started right after the start of anaerobic digestion process.

The methane contents of the biogas produced in the reactors stayed in the range of 55–65%, indicating successful methane production. The contribution of the inoculum sludge was subtracted from the total gas productions in each reactor when calculating the yields. The highest methane yield of 618 mL CH_4/g VS was obtained from MW pretreated sludge. Application of MW, combined H_2O_2/MW, and combined H_2O_2/heat pre-treatments to the sludge samples improved the methane yields by 64%, 38%, and 19%, respectively. The methane yields were in accordance with the sCOD removal rates in the reactors.

Supportively, Kuglarz et al. (2013) achieved 41% and 52% improvement in the methane productions from wastewater sludge samples by the application of microwave pre-treatment at temperatures of 60 °C and 70 °C, respectively. In the same way, Alagöz et al. (2015) reported that microwave pre-treatment applied to the sludge samples at 175 °C improved the methane yield by 52%. Eskicioglu et al. (2008a) obtained 10.8%, 10.9%, 16%, and 31% increase in the overall biogas production from the application of microwave pre-treatment to the sludge samples prior to mesophilic digestion at 65 °C, 75 °C, 85 °C, and 175 °C, respectively.

The combined H_2O_2/MW pre-treatment (1.0 g H_2O_2/g TS) resulted with lower biogas/methane production than the MW pre-treatment alone. Based on the literature, this can be explained with the negative effect of H_2O_2 residual or byproducts on the methanogens. In the anaerobic digestion process, methanogenesis is generally the rate limiting step due to the sensitivity of methanogens to the environmental conditions. In accordance with the results of this study, there are several

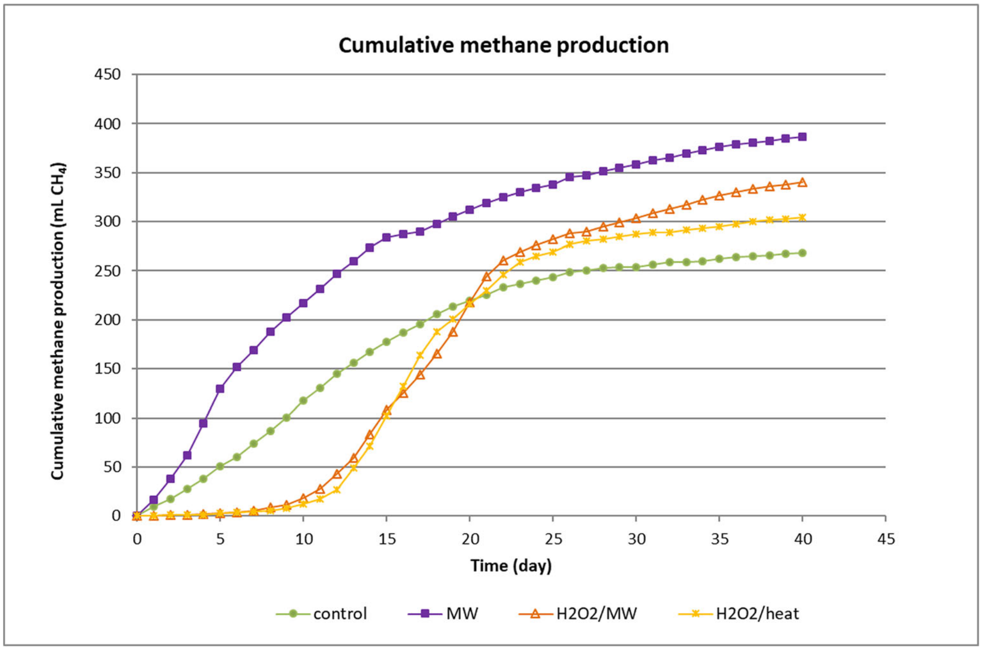

Fig. 3 The cumulative methane production

studies in literature stating that the residual H_2O_2 or byproducts sourced from the application of H_2O_2 to the sludge samples may cause to a limiting effect on the activity of methanogens, and decrease the biogas production. Liu et al. (2015) investigated inhibitory effect of the residual H_2O_2 after the application of H_2O_2/MW pre-treatment to the waste activated sludge samples at three different concentrations (0.2 g H_2O_2/g TS, 0.6 g H_2O_2/g TS, and 1.0 g H_2O_2/g TS). They reported that application of combined H_2O_2/MW pre-treatment to the sludge samples with high H_2O_2 concentrations (0.6 and 1.0 g H_2O_2/g TS) created an inhibitory impact on the metabolic activity of methanogens and decreased the methane yield due to the generation of H_2O_2 refractory compounds and rise in a long lag phase in the initial days of methane productions throughout the anaerobic digestion process. They stated that the low H_2O_2 concentration in pre-treatment increased the sludge biodegradability and anaerobic digestion performance (Liu et al. 2015). In the same way, Valo et al. (2004) obtained higher methane production with the application of MW pre-treatment than combined H_2O_2/MW and combined H_2O_2/$FeSO_4$ MW pre-treatments in their study. They reported that the addition of chemicals (H_2O_2 and H_2O_2/$FeSO_4$) limits the positive effect of high-temperature thermal pre-treatments applied to the waste activated sludge samples. Similarly, Eskicioglu et al. (2008b) applied MW and H_2O_2/MW (1.0 g H_2O_2/g TS) pre-treatments to the thickened waste activated sludge samples at temperatures of 60 °C, 80 °C, 100 °C, and 120 °C and obtained 20–54% higher methane yields with MW pre-treatment than combined H_2O_2/MW pre-treatment at all temperatures. They stated that soluble organics generated by the application of combined H_2O_2/MW pre-treatment were slower to biodegrade or more refractory than those generated by the application of MW pre-treatment (Eskicioglu et al. 2008b). Additionally, Shahriari et al. (2012) applied the combined H_2O_2/MW pre-treatment (0.66 g H_2O_2/g TS at 85 °C) to a different substrate of organic fraction of municipal solid waste. They also obtained lower methane production by combined H_2O_2/MW pre-treatment than the MW pre-treatment and reported that the residual H_2O_2 or refractory compounds from advanced oxidation can inhibit methanogenesis and decrease biogas production (Shahriari et al. 2012).

Kinetic modeling of methane production by using modified Gompertz equation

The results obtained from the modified Gompertz equation model by using nonlinear regression showed good fit to the experimental data for cumulative methane yield. Figure 4 shows the comparison of cumulative methane yields obtained from experimental data and modified Gompertz model. The kinetic parameters estimated with the model are presented in Table 4. The pre-treatments considerably improved the methane yields and the methane production rates as compared with the control. The model resulted slightly lower methane production potential values (P) than the experimental methane yields (EMY) for all of the pre-treatments. The difference between experimental and predicted methane yields is under 4.4% for all of the pre-treatments. The lag phase time (λ) shows the start-up time of anaerobic digestion process. In the MW pre-treatment–applied reactor, the conversion of sCOD to biogas started immediately after sealing the reactor in day 0. Then, no lag phase was observed in this reactor during the anaerobic digestion period. The solver function of the MS Excel created the best fit by trials and resulted a lag phase time of − 1.367 for MW pre-treatment. It should be

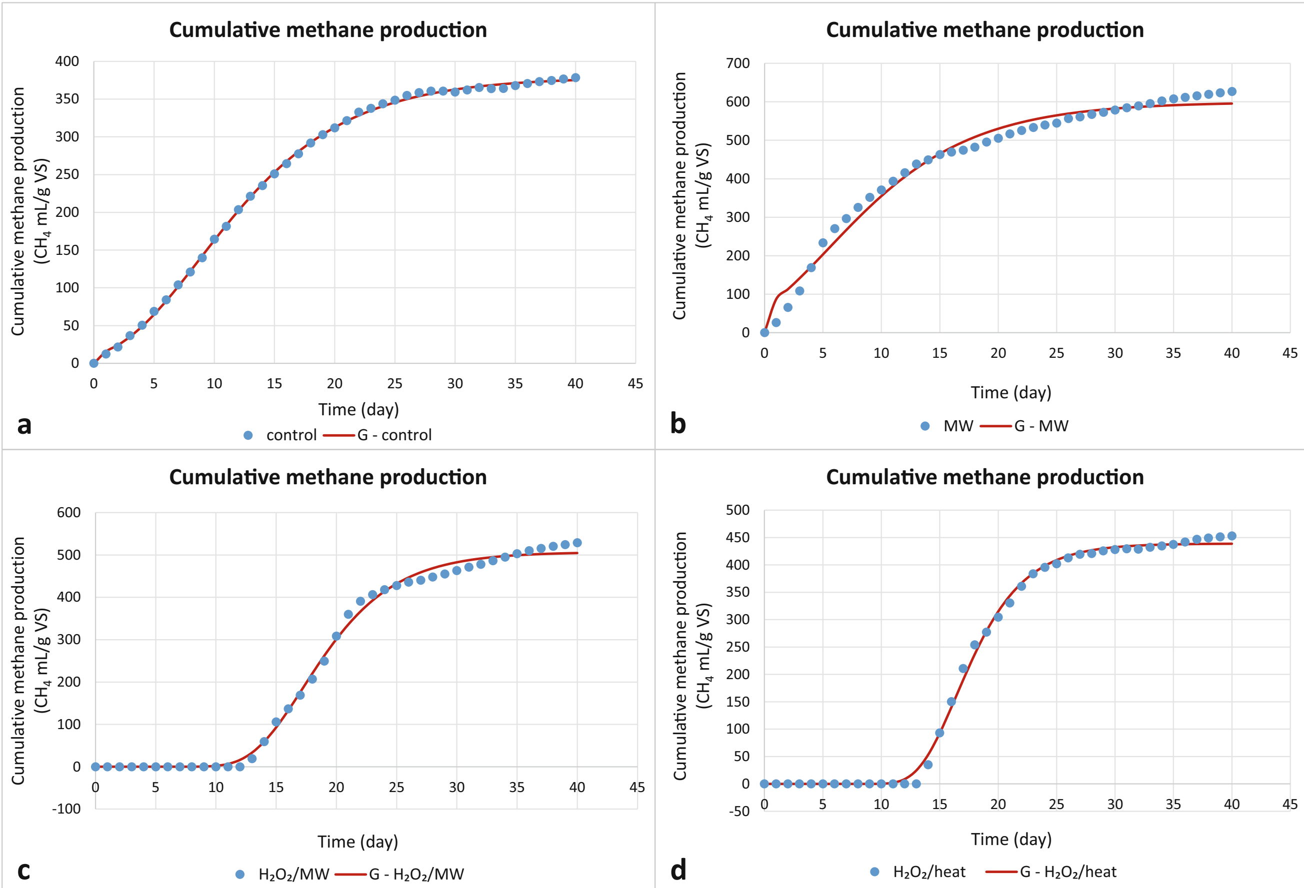

Fig. 4 Comparison of experimental data and modified Gompertz model for cumulative methane yield. **a** Control. **b** MW pre-treatment. **c** H_2O_2/MW pre-treatment. **d** H_2O_2/heat pre-treatment

noticed that the methane production data fitted with the popular Gompertz model can render a negative lag time, which has no physical meaning. This is one of the results of the Gompertz model's mathematical structure, which implies that methane production potential in day 0 is not equal to initial methane production potential ($P(0) \neq P_0$) but has little influence on its fit (Normand and Peleg 2014). In literature, there are many studies which used Gompertz model and resulted with a negative lag time (H. Zhang et al. 2018; L. Li et al. 2015; Budiyono et al. 2014).

The combined H_2O_2/MW and H_2O_2/heat pre-treatments had long lag phase time of about 12 days related to the limiting effects of residual H_2O_2 or byproducts on the activity of methanogens, leading to deceleration of the start-up time. The correlation coefficients (R^2) ranged from 0.983 to 0.999 that showed the results of modified Gompertz equation were well fitted to the cumulative methane yield in this study. The kinetic study proved that the pre-treatments significantly increased the anaerobic digestion performance.

Table 4 The kinetic parameters of methane yield from the modified Gompertz model

Parameters	Control	MW	H_2O_2/MW	H_2O_2/heat
P (mL CH_4/g VS_{added})	379	599.433	506.849	438.815
R_m (mL CH_4/g VS_{added}/d)	20.522	20.134	32.886	42.865
λ (d)	2.073	−1.367	13.013	13.185
R^2	0.999	0.983	0.997	0.998
EMY (mL CH_4/g VS_{added})	378.24	626.65	528.92	453.12
Difference between experimental (EMY) and predicted (P) methane yield (%)	0.2	4.34	4.17	3.16

Conclusion

This study investigated the effects of microwave (MW), combined hydrogen peroxide/microwave (H_2O_2/MW), and combined hydrogen peroxide/heat (H_2O_2/heat) pre-treatments on the digestion efficiency and methane production potential of wastewater sludges. Pre-treatments improved the methane yields considerably by increasing the solubility and the biodegradability of the organics in sludges. Application of MW, combined H_2O_2/MW, and combined H_2O_2/heat pre-treatments increased the methane yields by 64%, 38%, and 19%, respectively. The predicted results by nonlinear modified Gompertz equation model were compatible with the experimental methane yields, and kinetic parameters showed a good fit to the experimental data.

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