Environ Sci Pollut Res (2016) 23:13467–13479
DOI 10.1007/s11356-016-6543-2

RESEARCH ARTICLE

Enhancement of sludge anaerobic biodegradability by combined microwave-H_2O_2 pretreatment in acidic conditions

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Received: 25 September 2015 / Accepted: 22 March 2016 / Published online: 30 March 2016

Abstract The aim of this study was to increase the sludge disintegration and reduce the cost of microwave (MW) pretreatment. Thermodynamic analysis of MW hydrolysis revealed the best fit with a first-order kinetic model at a specific energy of 18,600 kJ/kg total solids (TS). Combining H_2O_2 with MW resulted in a significant increment in solubilization from 30 to 50 % at 18,600 kJ/kg TS. The pH of H_2O_2-assisted MW-pretreated sludge (MW + H_2O_2) was in the alkaline range (pH 9–10), and it made the sludge unfavorable for subsequent anaerobic digestion and inhibits methane production. In order to nullify the alkaline effect caused by the MW + H_2O_2 combination, the addition of acid was considered for pH adjustment. H_2O_2-assisted MW-pretreated sludge in acidic conditions (MW + H_2O_2 + acid) showed a maximum methane production of 323 mL/g volatile solids (VS) than others during anaerobic biodegradability. A cost analysis of this study reveals that MW + H_2O_2 + acid was the most economical method with a net profit of 59.90 €/t of sludge.

Keywords Advanced oxidation processes · Biogas production · Combined pretreatment · Microwave · Anaerobic biodegradability · Sludge disintegration · Cost analysis

Responsible editor: Gerald Thouand

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Introduction

The dairy industry is one of the largest sources of the food processing industries that produce a huge amount of waste-activated sludge with diverse characteristics. There are over 18,550 food processing industries in India, releasing large quantities of surplus sludge, which are identified as a major source of environmental pollution and also create a disposal problem (Zhen et al. 2013). The excess sludge must be processed because of its enormous organic and pathogen content. However, the management of sludge is considered to be a very expensive crisis part in the treatment plant operation (Yu et al. 2013). The sludge management alone costs around 20–60 % of total operational cost (Yi et al. 2013). Anaerobic digestion is considered as a promising method to eradicate this problem through proper treatment of sludge (Jang and Ahn. 2013). The proper handling of sludge causes the conversion of sludge into valuable resources for renewable energy production (Yan et al. 2013). Worldwide, anaerobic digestion is a well-known technique for treating excess waste sludge, stabilizing the organic matter, reducing the biomass, and producing biogas (Shen et al. 2014). The first step of anaerobic digestion, hydrolysis, limits the rate and extent of the digestion process (Kavitha et al. 2015). This limitation can be overcome by different pretreatment methods (Mottet et al. 2010). Previously investigated pretreatment technologies have been shown to enhance biodegradability by promoting hydrolysis process, such as chemo-mechanical and heat pretreatment with NaOH (Kavitha et al. 2014a), ultrasonic pretreatment (Riau et al. 2015; Khanal et al. 2007; Braguglia et al. 2011), alkaline pretreatment, and bacterial pretreatment (Kavitha et al. 2014b).

Several studies on microwave (MW) irradiation of sludge have been reported as one of the promising methods for sludge solubilization because rapid internal heating leads to the evaporation of intracellular water. Consequently, it increases the

internal pressure in the medium, thereby rupturing the cell walls. The attractive feature of MW technology is the synergistic action of thermal and non-thermal effects (Houtmeyers et al. 2014).

Current studies are focused on the combined treatment method, to improve the biological stabilization process. Hence, MW combined with H_2O_2 has been investigated in the present study. Several studies have reported that hydrogen peroxide can act as an oxidant, synergistically improving the disintegration of sludge by developing the hydroxyl radicals (OH), which causes destruction of cell walls and membranes and then breakage of DNA strands (Tyagi and Lo 2013; Eskicioglu et al. 2008). Many studies proved that the rate of decomposition of H_2O_2 depends on temperature (Eskicioglu et al. 2008; Wang et al. 2009). When H_2O_2 was applied in conventional or MW heating, an increase in temperature leads to the synthesis of hydroxyl radicals (*OH), with an oxidation potential of 2.33 V, and the generated hydroxyl radicals (*OH) enhance the oxidation process (Wang et al. 2015).

Some kinetic models, frequently adopted in the literature, have been used to examine their fit with the hydrolysis data, in order to estimate the activation energy and rate of reaction of the system (Luo et al. 2012). This study discusses various possible state-of-the-art sludge treatment processes with respect to practical applications and their potential in the treatment of dairy wastewater. The main advantage of MW pretreatment is effective disintegration of sludge biomass, which further enhances the biogas production efficiently. The main drawback of this pretreatment is high energy consumption that limits the application of MW disintegration. Hence, it was planned to reduce the amount of MW energy by combining it with other methods, such as H_2O_2 and acid. Thus, there was an investigation of the effect of MW pretreatment, using low specific energy to disintegrate the sludge particles by applying radiation as well as oxidizing organic molecules by H_2O_2. Microwave and H_2O_2 pretreatment were combined with the acid to maintain the sludge pH during disintegration in order to make it more amenable for subsequent anaerobic digestion.

This study aims to investigate (1) the synergistic effect of MW, hydrogen peroxide, and acidic pH on the effectiveness of waste-activated sludge (WAS) disintegration. (2) to evaluate the effectiveness of this combined process on hydrolysis and acidification. (3) to examine the proficiency of combined MW pretreatment in further anaerobic degradability studies, and (4) to evaluate the feasibility of this combined disintegration process.

Materials and methods

Waste sludge samples and characterization

Dairy waste-activated sludge was obtained from a dairy wastewater treatment plant in Madurai, India. The collected sludge was tested for the initial characteristics. The waste sludge characteristics are shown in Table 1. The characteristics of treatment plant are summarized as follows: chemical oxygen demand (COD), 190–2700 mg/L; BOD, 1200–1800 mg/L; pH, 7.2–8.8; average temperature, 25–30 °C; total nitrogen, 84 mg/L; total phosphorous, 11.7 mg/L; and chloride, 105 mg/L.

Microwave and H_2O_2 pretreatment

A domestic MW oven (2450 MHz frequency, 900 W) with a polytetrafluoroethylene (PTFE) vessel was used to irradiate the sludge. A PTFE cover was fixed to minimize the sludge loss caused by hot spot formation during the process. The sludge MW experiments were performed in batch tests using 500 mL of dairy WAS. The irradiation time varied from 1 to 20 min at varying power level. The range of temperature was observed as between 30 and 110 °C, which were monitored at varying time and irradiation power. The samples were collected and analyzed periodically at the time interval of 1 min. For pilot scale cost analysis, the capacity of the microwave was calculated to be 7000 L and the power required for pretreatment was 31 kWh. The MW + H_2O_2 experiment was performed with various concentrations of H_2O_2 (0.1 to 1.0 mg/g suspended solids) at optimum specific energy. A sampling device was installed, and the samples were collected through the sample port. For making the sludge amenable for anaerobic digestion at the optimized MW + H_2O_2 condition, experiments were carried out by varying the initial sludge pH from 2 to 7 using H_2SO_4.

Hydrolysis experiments

To measure the implementation effect of combined MW-disintegrated sludge on anaerobic fermentation, a hydrolysis test was performed in four 300-mL serum bottles of A_1 (control sludge), A_2 (sludge pretreated with MW), A_3 (MW combined with H_2O_2-pretreated sludge), and A_4 (MW combined with H_2O_2 and acid-pretreated sludge) with a working volume of 250 mL, respectively, for 3 days. In each bottle, the substrate inoculum was maintained in the ratio 9:1 (*V*/*V*), based on the work of Ebenezer et al. (2015a). The inoculum used for the experiments was anaerobically digested sludge, and their initial characteristics were summarized as follows: pH, 7.4; TCOD, 11,860 mg/L; total solids (TS), 24,110 mg/L; and suspended solids (SS), 20,910 mg/L. These bottles were subjected to heat treatment at 102 °C and on cooling 50 mM of 2-bromoethanesulfonic acid (BESA) was added to inhibit the growth of methanogens. The bottles were purged with nitrogen, and it was sealed airtight and kept in an orbital shaker at 120 rpm for 72 h at 35 °C. The treated sludge was

Table 1 Initial characteristics of dairy raw sludge

Initial characteristics	Parameter values
Total solids (mg/L)	25,000 ± 300
Total COD (mg/L)	24,550 ± 400
Soluble COD (mg/L)	200 ± 10
Suspended solids (mg/L)	19,000 ± 200
Volatile solids (mg/L)	15,200 ± 300
Soluble protein (mg/L)	39.7 ± 0.5
Soluble carbohydrate (mg/L)	5 ± 0.1
pH	7.15

collected at time 0 and after 72 h to analyze the soluble organics (protein and carbohydrate) and volatile fatty acids (VFA).

Anaerobic biodegradability assay

An anaerobic biodegradability assay was carried out as a batch process to measure biomethane or biogas (Montanes et al. 2014) produced by dairy WAS in anaerobic conditions, following the methodology detailed by Gayathri et al.(2015). The anaerobic biodegradability of the control and pretreated sludge samples was assessed at mesophilic temperature. The retention period was 30 days. The inoculum and substrate were taken in the ratio of 3:1. The inoculum used was bovine rumen fluid. The gas pressure in the reactor was allowed to displace the syringe plunger, and the displaced volume was recorded as biogas. The methane content in the biogas was analyzed using a Baroda gas chromatograph. The specific methane production data of batch digestion were evaluated for control sludge using a modified Gompertz model (Budiyono et al. 2013; Yusuf et al. 2011; Kavitha et al. 2014b). The exponential model and logistic model were employed for MW, MW + H_2O_2, and MW + H_2O_2 + acid pH-pretreated samples with phase separated biogas production. The modified Gompertz model, the logistic model, and first-order exponential model were adopted according to the work of Merrylin et al. (2013) and Rincon et al. (2013). The specific methane production was recorded, and the model fit was executed using the Origin 9.0 software.

Analytical parameters

The TS, SS, volatile solids (VS), and COD were determined following procedures outlined in the standard methods (APHA 2005). The concentration of protein was determined by using the Lowry method (Merrylin et al. 2013), and the carbohydrate concentration was determined by the anthrone method (Uma et al. 2012).

Energy and cost assessment

The technical and economic aspects of pretreatment methods have to be considered to employ pretreatment efficiency on a full-scale digestion process. As low energy input is desirable, the calculation of specific energy becomes inevitable for evaluating the cost of the pretreatment. The SE was computed, based on Eq. (1), according to Yang et al. (2013):

$$\text{Specific energy(kJ/kg TS)} = \frac{\text{Power of microwave(kw)} \times \text{irradiation time (s)}}{\text{Sample volume(L)} \times \text{total solids (kg/L)}} \quad (1)$$

To assess the potency of pretreatment methods, theoretical energy balances and cost assessment were performed for pilot scale reactors with the experimental data obtained. For pilot scale analysis, the estimation was performed for 1 t of sludge based on the previous study (Ebenezer et al. 2015b). The theoretical calculation for methane was carried out based on the COD consumed and was executed using the following equation:

$$\text{CH4 production}\left(\text{m}^3\right) = \text{COD consumed(kg)} \times \left(0.35\ \text{m}^3/\text{kg COD}\right) \times \text{biodegradability}(0.28) \quad (2)$$

Biodegradability is the relationship between theoretical methane and experimental methane and is used to assess the level of biodegradability of a substrate (COD consumed).

Output energy (Eo) was calculated based on methane production and was estimated by the following equation (Ferrer et al. 2009; Passos and Ferrer. 2014):

$$\text{Eo} = P_{\text{CH4}} \xi V \eta \quad (3)$$

where Eo is the output energy (KJ/day), P_{CH4} is the methane production rate (m^3 CH_4/m^3 day), ξ is the lower heating energy value of methane (KJ/m^3 methane), V is the useful volume (m^3), and η is the energy conversion efficiency (90 %).

To calculate the energy applied, the energy spent for MW pretreatment (31 kWh) at the pilot scale level was taken for contemplation. The energy spent for sludge pretreatment by MW was arrived at by using COD solubilization as an index based on the following equation:

$$Q_{\text{MW}}(\text{kWh}) = \frac{(P_{\text{MW}} \times T)}{V \times \text{SS}} \quad (4)$$

where Q_{MW} is the energy spent for sludge pretreatment in kilowatt-hour, P_{MW} is the power of microwave (31 kWh), T is the time, and V is the capacity of pilot scale plant (L). Energy spent for pumping and stirring in anaerobic digestion

(Q_P) was calculated as per the calculations detailed in Metcalf and Eddy (2003).

Energy required in upsurging the temperature of the sludge (Q_T) to the digester temperature was calculated by following equation.

$$Q_T = P \times (100/\mathrm{Ps}) \times (T_d - T_s) \times (1/2) \times C_p \quad (5)$$

where P is the fresh dry sludge solids added per day (kg), Ps is the percentage dry solids in the fresh sludge (%), T_d and T_s are the temperature digester and sludge, respectively (°C), and C_p is the specific heat constant (4200 J/kg °C).

The heat required to make up for losses at the top, walls, and bottom (Q_L) was estimated by the following equation:

$$Q_L = CA \times \Delta T \quad (6)$$

where C is the coefficient of heat flow (J/m^2/h/°C), A is the surface area (m^2), and Δ is the difference between tank temperature and outside material (°C).

To perform the energy balance (ΔE) and assay the net energy production, the total input energy was subtracted from the output energy based on the following equation (Passos and Ferrer. 2014):

$$\Delta E = \mathrm{Eo} - (\mathrm{Ei,\ heat} + \mathrm{Ei,\ electricity}) \quad (7)$$

where ΔE is the energy balance, Eo is the output energy, Ei, heat is the input heat energy, and Ei, electricity is the input electricity.

Results and discussion

Impact of MW specific energy on sludge disintegration

The specific energy was an imperative factor and fundamental operating variable for determining the economic feasibility and energy consumption of MW pretreatment. Figure 1 portrays the impact of the MW specific energy input on SCOD, protein, carbohydrate release, and SS removal. It was observed that the trend of soluble organic release (SCOD, protein, and carbohydrate) could be perceptibly distinguished into two phases: a rapid release phase and a slower degradation phase. Phase 1 extends from a specific energy input of 0 to 18,600 kJ/kg TS. Phase 2 extends from a specific energy input of 18,600 to 30,000 kJ/kg TS.

In phase 1, a rapid release trend of soluble organics (SCOD, protein, and carbohydrate) was obviously observed on increasing the specific energy from 0 to 18,600 kJ/kg TS. Several studies have reported that the MW technique tends to collapse the complex floc structure of WAS. As a result of cell wall disintegration, both the extracellular and intracellular cytoplasmic materials start to be released into the soluble phase (Uma et al. 2013). This could be the reason for an increment in the soluble organics in phase 1. At 18,600 kJ/kg TS, the concentrations of SCOD, protein, and carbohydrate were observed to be 7.4, 0.7, and 0.05 g/L, respectively. Further increasing the specific energy input beyond 18,600 kJ/kg TS not only decreases the solubilization percentage but also increases the treatment cost.

In phase 2, a slower degradation of soluble organics was observed, and it could be because of the loss of organics through evaporation (Ebenezer et al. 2015b). Many studies investigated that the use of high specific energy during MW treatment causes lower solubilization (Park et al. 2010; Toreci et al. 2009). In contrast to the pattern of soluble organic release, the SS removal exhibited a stabilizing pattern at phase 2. During phase 1, SS removal was gradual and from the initial value of 19 g/L, it reduced to 15 g/L. Beyond the specific energy of 18,600 kJ/kg TS, the SS reduction was slower and nearly stable. This could be because of the condensation of sludge. At elevated MW energy, the evaporation of water occurs, which results in the condensation of sludge. The increase in energy input also increases the temperature of the medium or sludge, which leads to a loss of organics because of evaporation. These observations were similar to the work of Eskicioglu et al. 2007 and Uma et al. 2013. Many researchers (Eskicioglu et al. 2007; Uma et al. 2013) have employed a cover to avoid evaporation loss. Hence, based on that, in order to minimize the evaporation loss, a PTFE cover was fixed to minimize the sludge loss caused by the hot spot formation during the process. Under these circumstances, removal of SS could conceivably occur because of the volatilization of organic matter but this requires an enormous amount of energy that was not satisfactorily reached in the present study (Eskicioglu et al. 2007). Therefore, only a slight increment in SS reduction was observed beyond the specific energy input of 18,600 kJ/kg TS. On increasing the specific energy input, 0, to 18,600 kJ/Kg TS, only a slight loss in organics (1–2 %) was observed. Further increasing the specific energy input beyond 18,600 kJ/Kg TS, the evaporation loss was observed to be 20–25 % which is relatively higher than that observed in the optimal specific energy input. In addition, increasing the specific energy beyond 18,600 kJ/Kg TS, only a slight increment in SS reduction was observed. The currently achieved SS reduction at the optimal specific energy of 18,600 kJ/kg TS was found to be 21 %. By doubling the specific energy input to 30,000 kJ/kg TS, only a relatively slight increment in SS reduction (22.7 %) was obtained. Therefore, it can be concluded that an increment in specific energy beyond 18,600 kJ/kg TS was not economically feasible. On the basis of aforementioned outcomes, it can be concluded that the specific energy input of 18,600 kJ/kg TS was considered optimum, and this optimal specific energy was employed for further studies.

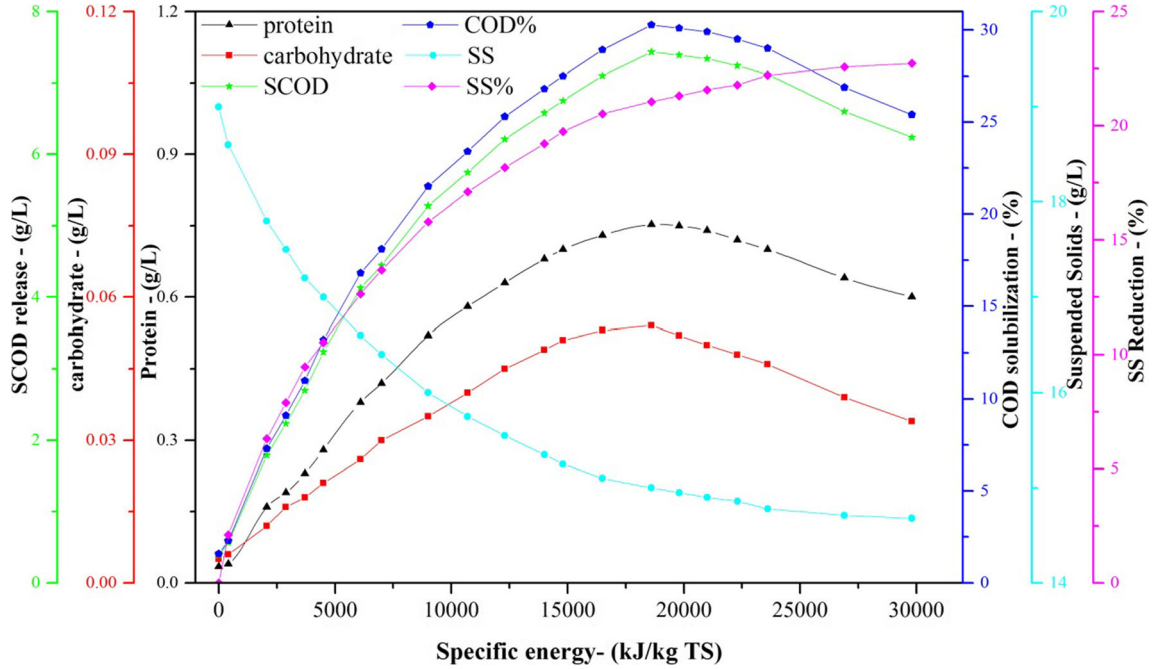

Fig. 1 Effect of microwave specific energy on soluble organic release and SS reduction during microwave pretreatment

Thermodynamic analysis of WAS hydrolysis using MW

Several studies have reported that thermal disintegration of sludge offers more advantages over other methods of sludge pretreatment. There are different thermal disintegrations, such as moist heat, dry heat, and radiation heat, which are available to disintegrate sludge (Wilson and Novak 2009; Gianico et al. 2013). In thermal treatment, the possible solubilization cannot be achieved at a lower treatment time, whereas a prolonged treatment time leads to the formation of refractory organic compounds that limit the rate of degradation (Uma et al. 2012). In MW pretreatment, the treatment time was comparatively lower and the possible solubilization was achieved at a lower treatment time. Considering this fact, the MW pretreatment was considered to be more efficient than thermal treatment, the basis of the reaction activation energy.

This can be done by using first-order kinetic modelling, which contributes to the traditional simplification of substrate biodegradation in terms of the SCOD release. The effect of MW irradiation on dairy sludge hydrolysis was simplified to single first-order kinetics, based on following equations.

$$-dS/dT = kS \tag{8}$$

$$ln\ S = -kt + b \tag{9}$$

where S denotes the SCOD concentration, K is the rate constant, and b is the constant of integration. Table 2 represents the kinetic data relevant to the SCOD release enhanced by MW irradiation pretreatment and thermal pretreatment (control) at different temperatures and specific energies.

By plotting $ln\ S$ versus t, the slope and intercept could be obtained, which corresponded to the values of k and b, respectively. The regression for $ln\ S$ versus t, arrived at different temperatures, is tabulated in Table 2. The mean value of temperature was taken for the thermodynamic analysis. The activation energy was calculated from the following equation.

$$ln\ k = -Ea/RT + ln\ A \tag{10}$$

where A is the pre-exponential factor, Ea (kJ/mol) is the reaction activation energy, T(K) is the absolute temperature, and R is the gas constant (8.31 J K^{-1} mol^{-1}). In this study, the value of pre-exponential factor was found to be 0.498 and the reaction activation energy for SCOD release in the pretreated MW and control (thermally pretreated) was evaluated to be 0.135 and 0.598 kJ/mol, respectively. The currently achieved activation energy, 0.135 kJ/mol, was lower than that achieved in other studies where researchers achieved 20.19 kJ/mol (Luo et al. 2012) in the enzymatic treatment of sludge, which therefore suggests that MW irradiation increased the rate of chemical reaction largely by lowering the activation energy. Thus, in brief, the MW technique was found efficient for effective sludge solubilization.

Effect of H_2O_2

The effect of H_2O_2 on MW pretreatment was studied by fixing MW energy and varying the H_2O_2 dosage in the range of 0.1 to 1.0 mg/g SS. There are varieties of oxidizing agents being used to pretreat the sludge. Among those, H_2O_2 was proved to be efficient and cost-effective (Wang et al. 2015). The *OH could

Table 2 Kinetic data relevant to SCOD release enhanced by microwave irradiation pretreatment at different temperatures

Treatment	Specific energy kJ/kg TS	Temp. (°C)	Dynamic equation	Rate constant (h^{-1})	Coefficient R^2
Microwave	6100	30	$y=-0.0051x+9.129$	0.306	0.9026
	10,300	50	$y=-0.0056x+9.109$	0.336	0.9012
	14,400	90	$y=-0.0058x+9.068$	0.348	0.9232
	16,500	100	$y=-0.0071x+9.064$	0.426	0.9301
	18,600	110	$y=-0.0075x+9.068$	0.450	0.9363
Thermal (control)	9600	30	$y=0.069x+3.610$	−0.069	0.811
	13,800	50	$y=0.088x+3.415$	−0.88	0.883
	18,800	90	$y=0.103x+5.211$	−0.103	0.841
	24,500	100	$y=0.106x+6.125$	−0.106	0.850
	31,100	110	$y=0.107x+6.526$	−0.107	0.856

react rapidly and non-selectively with nearly all organic pollutants. This reduces the treatment time and enhances the solubilization plausibly. The strongest oxidants and most powerful reactive agents are the hydroxyl radicals, which have a reduction potential of 2.8 eV (Kato et al. 2014; Steriti et al. 2014).

The effects of the H_2O_2 concentration on COD solubilization, soluble protein, and carbohydrate were investigated and are shown in Fig. 2. Up to 0.3 mg/g SS of H_2O_2 dosage, the concentration of protein, carbohydrate, and SCOD release were found to be increased and the corresponding values were observed to be 1.52, 0.045, and 12.35 g/L, respectively. A further increase in H_2O_2 concentration decreases the release of soluble organics. For example, an increase in H_2O_2 dosage from 0.3 to 0.4 mg/g SS causes a decrease in COD solubilization from 12.35 to 11.56 g/L. A similar kind of decrease was also observed for the release of soluble organics. This was because of the fact that higher concentrations of H_2O_2 lead to the scavenging of *OH radicals and, as a result, the release of HO_2* will occur, as described by the following equations:

$$H_2O_2 + {}^*OH \rightarrow HO_2{}^* + H_2O \quad (11)$$

$$HO_2{}^* + {}^*OH \rightarrow H_2O + O_2 \quad (12)$$

It is important to note that HO_2* is less reactive than HO* and thus an increasing concentration of hydrogen peroxide resulted in a diminished reaction rate (Herney et al. 2010). Therefore, 0.3 mg/g SS of H_2O_2 was found to be the optimum dosage for sludge solubilization when it was combined with MW.

Effect of pH

The pH of the MW + H_2O_2-pretreated sludge was found to be in the range of 9.5 to 10. The increment in pH after pretreatment was because of the formation of ammonia (produced by the degradation of protein) (Luo et al. 2011). A similar observation was found by Uma et al. (2013). This highly alkaline nature of pretreated sludge makes it unattractive towards subsequent anaerobic digestion. Healthy anaerobic digestion happens in the pH range of 6.8 to 7.5 (Uma et al. 2014; Liu et al. 2014). In addition, the performance of H_2O_2 was observed to

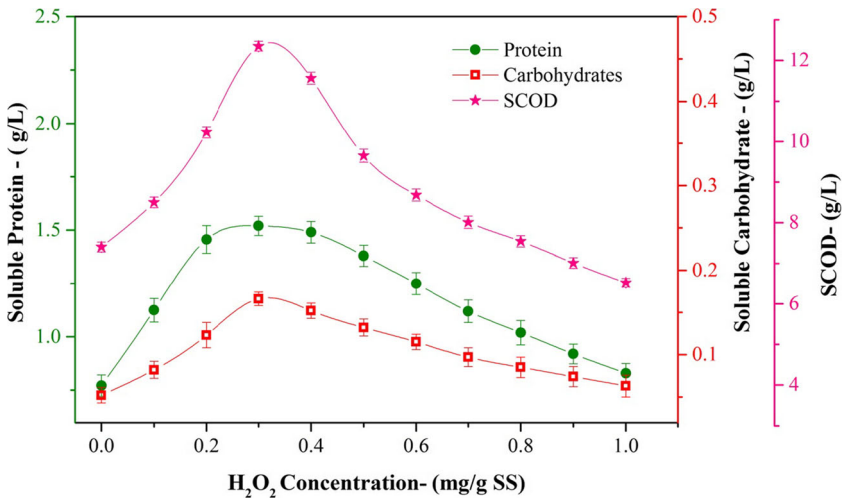

Fig. 2 Optimization curves of H_2O_2 dosage for the release of SCOD, protein, and carbohydrate obtained at the energy of 18,600 kJ/kg TS

be effective at pH 5 and a final pH of 7 was attained after pretreatment, which is evidenced in Fig. 3. In order to make this alkaline sludge amenable for anaerobic digestion, it has to be neutralized with acid. This leads to an idea of combining acidic pH with MW + H_2O_2, with an interest focused towards the sludge final pH.

Hong et al. (2012, 2015) have reported that OH radicals of H_2O_2 perform well under acidic pH, and as a result the efficiency of H_2O_2, has been improved for a further disintegration process. Keeping this in mind, it was planned to maintain an acidic condition in the medium to enhance the disintegration efficiency of MW + H_2O_2 pretreatment. Figure 3 shows the effect of pH on the sludge solubilization. It is evident that the MW + H_2O_2 pretreatment efficiency was increased by decreasing the pH of the sludge. The soluble organics and soluble COD release were found to be higher at pH 2 and 3. However, the final pH of the pretreated sludge at this condition was found to be 3.12 and 4.18. This makes the process less attractive as it demands neutralization of the sludge for subsequent aerobic or anaerobic biodegradation. This has been suggested by many researchers, in which Uma et al. 2014 reported that the efficient degradation of organic matter was possible at the optimum pH of 6.3–7.8, whereas at a lower and higher pH condition, the methanogenic activity in anaerobic digestion will be slow and decrease the biogas production.

The effect of combined MW-H_2O_2 pretreatment on sludge disintegration

Figure 4 represents the influence of combined pretreatment on the concentration of suspended solids, SCOD, protein, and carbohydrate, SS percentage, and COD solubilization. From the figure, it was observed that at optimal specific energy input (18,600 kJ/kg TS), the SCOD concentration, protein, and carbohydrate in the medium were found to increase with all types of MW pretreatment. The SCOD release and protein and carbohydrate release at this energy level were found to be 7.4, 12.3, and 13.8 g/L, 0.7, 1.5, and 1.7 g/L, and 0.05, 0.15, and 0.16 g/L, respectively.

The increase in the soluble organics was mainly due to synergistic effects brought about by the combined action of MW, H_2O_2, and acid. Among different treatments, combined pretreatment was proven to be effective when compared to MW alone (Eskicioglu et al. 2008). At the MW energy of 18,600 kJ/kg TS, COD solubilizations for MW, MW + H_2O_2, and MW + H_2O_2 + acid were recorded to be 30.2, 50.3, and 56.1 %, respectively. The highest solubilization (56.1 %) was noted with the MW + H_2O_2 + acid combination. This could be because of the fact that at a lower pH, the hydroxyl radical formation was higher, which increased the efficiency of H_2O_2. The currently achieved COD solubilization (56 %) at an energy input of 18,600 kJ/kg TS was relatively greater than that achieved in other studies, where authors used greater energy input to obtain the similar solubilization, which was summarized in Table 3.

Similarly, the SS concentration in the medium was found to decrease in all types of MW disintegration of sludge. At the MW specific energy of 18,600 kJ/kg TS, the SS concentrations for MW, MW + H_2O_2, and MW + H_2O_2 + acid were recorded to be 15, 13.3, and 12.7 g/L, respectively. The corresponding SS reductions at this energy level were calculated to be 20.9, 29.5, and 33.1 %, respectively. The addition of H_2O_2 dosage resulted in a significant increase in MW-assisted SS reduction from 20.9 to 29.5 % (Fig. 4). This could be because of rapid formation of the MW-mediated hydroxyl radicals from H_2O_2. The acidification of sludge (pH 5) further increases the SS reduction from 29.5 to 33.1 %.

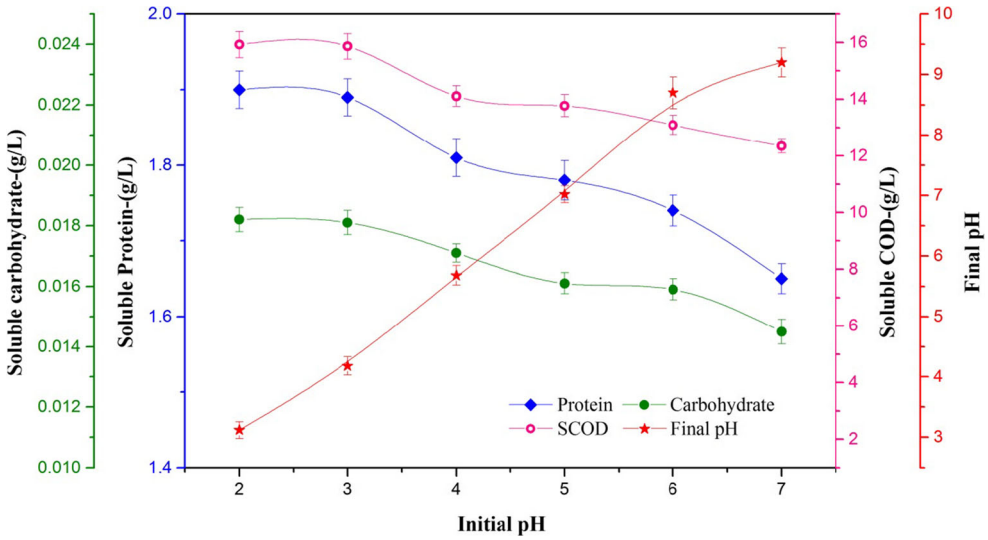

Fig. 3 Effect of pH for the release of SCOD, protein, and carbohydrate in optimum condition of MW + H_2O_2. *Initial pH* before pretreatment. *Final pH* after pretreatment

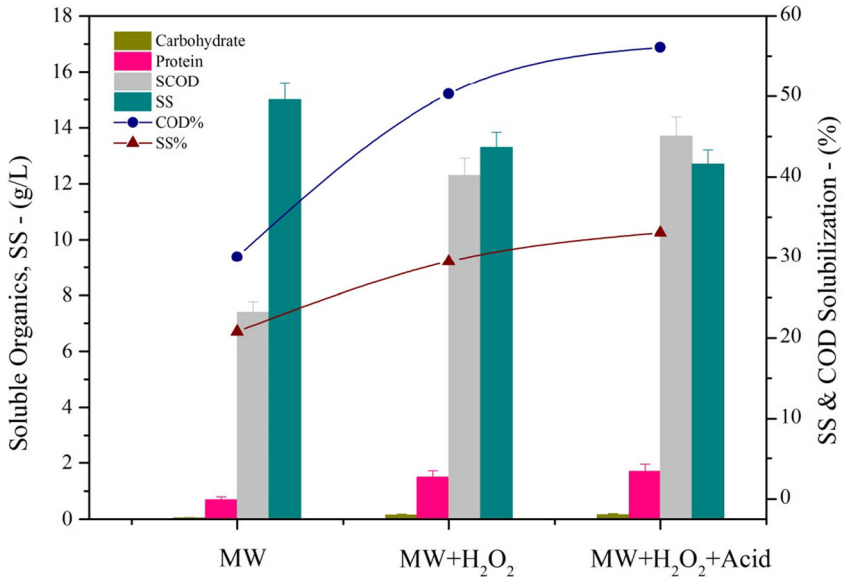

Fig. 4 Effect of combinative pretreatment on soluble organics and SS reduction at optimized specific energy input of 18,600 kJ/kg TS

The effect of combined MW irradiation on sludge fermentation

The rate of soluble organic formation and its subsequent conversion into volatile fatty acids determine the efficiency of the anaerobic digestion process. In this study, differently hydrolyzed substrates were subjected to anaerobic fermentation. The VFA are a product of hydrolysis and acidification and a precursor for methane production (Poornima Devi et al. 2014). Figure 5 shows the profile of the soluble protein, carbohydrate, and VFA concentration of the control and MW-treated sludge. From Fig. 5, it was evident that the profile of protein and carbohydrate in the control improved from 42 to 70 mg/L and from 10 to 18 mg/L, respectively, after 72 h. This kind of increase was uncharacteristic for anaerobic fermentation, and it indicates the predominance of hydrolysis because of heating applied during anaerobic fermentation.

In contrast, a precipitous decrement in soluble protein and carbohydrate concentration (from 848, 1700, and 1850 mg/L to 660, 1200, and 1250 mg/L, respectively) was noticed after 72 h in MW and its combined pretreatments. This indicates the effective utilization of hydrolytic by-products by fermentative bacteria. As a result of which, an accumulation of VFA occurred. The accumulation of VFA was higher (2050 mg/L) for MW + H_2O_2 + acid-treated sludge than MW + H_2O_2 (1950 mg/L) and MW (730 mg/L)-pretreated sludge. The formation of VFA in control sludge was meager (35 mg/L), thereby indicating poor fermentation. From this data, it can be concluded that the present method of combined sludge pretreatment (MW + H_2O_2 + acid) hydrolyze the sludge more efficiently than those of other studies where the researchers (Ebenezer et al. 2015a; Kavitha et al. 2015) achieved comparatively very low VFA concentration (840 and 640 mg/L), respectively. This clearly specifies the proficiency of the combined MW + H_2O_2 + acid pretreatment.

Anaerobic biodegradability assay

The anaerobic biodegradability assay was performed with MW, MW + H_2O_2, and MW + H_2O_2 + acid-treated and the control sludge and was carried out for 30 days. Figure 6

Table 3 Comparison of irradiation energy with various pretreatment methods

Process	COD solubilization, %	Specific energy, kJ/kg TS	References
Microwave	41	717,680	Saha et al. (2011)
Ultrasonic	42	117,719	Saha et al. (2011)
Microwave	18.60	82,400	Uma et al. (2013)
MW + alkaline	66.62	38,400	Yang et al. (2013)
Microwave	31	14,000	Ebenezer et al. (2015b)
MW + H_2O_2 + acid	56.12	18,600	This study

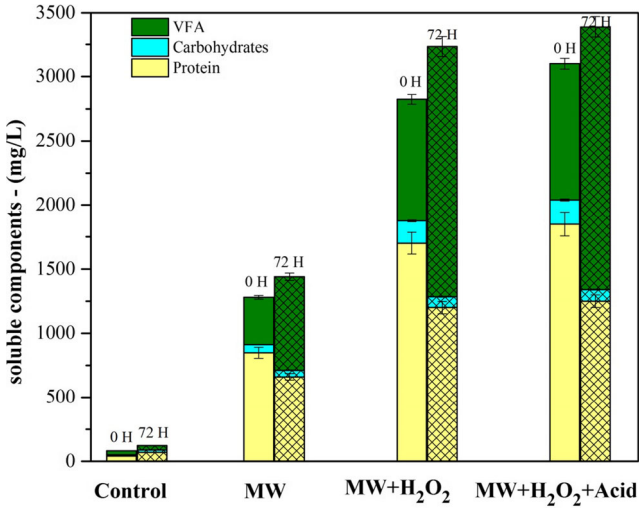

Fig. 5 Effect of pretreatment on soluble organics during anaerobic fermentation (*VFA* volatile fatty acids)

presents the methane production trend of the differently pretreated samples. Among them, the MW + H_2O_2 + acid-pretreated sample produced the highest methane yield of 323 mL/g VS at the end of 30 days. The MW + H_2O_2-pretreated sample had a maximum methane production of 288 mL/g VS, and for MW-pretreated sample, the methane production was 175 mL/g VS. The methane production of the control sludge was low, which was 33 mL/g VS. This could be because of the occurrence of a lesser or inconsequential amount of freely accessible substrate.

The methane production for the control sludge had a lag period of 8 days, and this prolonged lag phase may be because of the deliberate hydrolysis of the substrate. Two separate exponential methane production phases were observed for the MW, MW + H_2O_2, and MW + H_2O_2 + acid-pretreated sludges. The first exponential phase persisted for 6–10, 5–7, and 4–6 days of operation in the MW, MW + H_2O_2, and MW + H_2O_2 + acid-pretreated sludge, respectively. The initial exponential increase in the biogas production is because of the presence of the readily available soluble organic compounds that under anaerobic digestion are converted into biogas. Among the various samples, the MW + H_2O_2 + acid-pretreated sludge exhibited an early start of the first exponential phase, thereby indicating a better hydrolysis of the

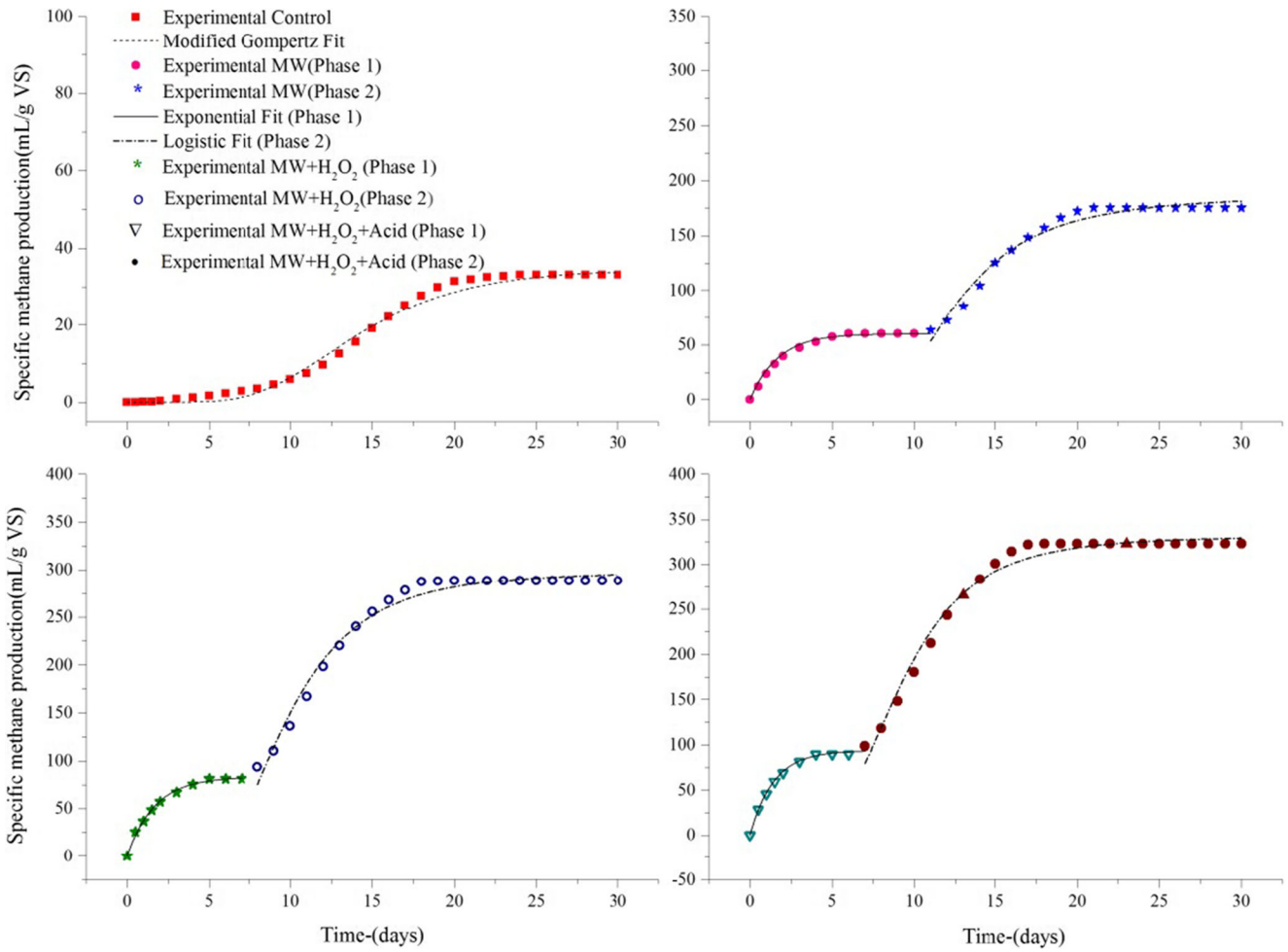

Fig. 6 Plot showing the experimental data of specific methane production fit with the modified Gompertz equation

Table 4 Kinetic parameter calculated using modified Gompertz equation for various sludge samples

Reactor/model	Model parameter					
	Bc mL/g VS	P mL/g VS	Rm mL/g VS day	Kh Day^{-1}	λ Days	R^2
Control						
Modified Gompertz	–	34.5	12.3	0.22	8.3	0.9858
MW						
Exponential	–	59.77	–	0.6	–	0.9870
Logistic	63.5	265.2	11.3	–	4.3	0.976
MW + H_2O_2						
Exponential	–	83.10	–	0.6	–	0.996
Logistic	93.6	352.3	14.1	–	2.9	0.983
MW + H_2O_2 + acid						
Exponential	–	93.6	–	0.7	–	0.994
Logistic	98.3	345.1	15.2	–	2.3	0.985

Bc methane production potential at the startup of second stage, *P* ultimate methane production, *Rm* maximum methane production rate, *Kh* specific rate constant, λ lag time, R^2 coefficient of determination

substrate. The first exponential phase was followed by a transitional lag period. The second exponential increase was associated with the degradation of the non-soluble particulate organic matter. The second exponential phase extends from 7 to 16, 8 to 17, and 11 to 20 days for the MW+ H_2O_2 + acid, MW+ H_2O_2, and MW-pretreated sludges, respectively.

To simulate the two observed exponential phases, two different models were used for MW, the MW + H_2O_2, and MW+ H_2O_2 + acid-pretreated samples. The first one was the exponential model and was applied to model the first exponential increase in methane production (ranging from 0 to 5 days of digestion). The experimental data was found to be in

Table 5 Energy balance and cost analysis

	MW	MW + H_2O_2	MW + H_2O_2 + acid	Unit
Energy balance (per ton SS of sludge)				
Average increase in methane production	38.3	38.3	38.3	m^3
Output energy as methane	381	381	381	kWh
Energy spend for pretreatment	612	408	204	kWh
Energy required to raise the temperature of the sludge to the digester temperature	25	25	25	kWh
Energy spend for pumping and stirring in anaerobic digestion	96	96	96	kWh
Energy required to make up losses through top, walls, and bottom of digester	0.674	0.674	0.674	kWh
Energy required for sludge thickening (gravity thickener)	13.6	13.6	13.6	kWh
Energy required for biogas purification	1.4	1.4	1.4	kWh
Energy required for biogas compression	1.1	1.1	1.1	kWh
Total input energy	749.8	545.7	341.7	kWh
Net energy (output–input)	−368	−164.7	39.3	kWh
Cost calculation (per ton SS of sludge)				
Energy cost (at 0.187 €/kWh)	−68.8	−30.8	7.4	€
Decrease in SS to be disposed	301	301	301	kg
Reduced sludge disposal cost (at 0.3 €/kg SS)	90	90	90	€
Chemical cost (H_2O_2, 10,705 €/t)				
(H_2SO_4, 4754 €/t)	0	−2.5	−2.5	€
		−26.2	−34.9	
Net profit	21.2	30.5	59.9	€

agreement with the goodness of fit prominent for the combined MW-pretreated samples (Fig. 6). The higher values of R^2, shown in Table 4, reveal the goodness of fit for all the experimental data with the proposed models and thereby indicating a positive correlation between the model and experiment. A second model is the logistic model, and it was used to model the second exponential increase in the biogas production (10–30 days). The model fit for the control sludge was made with a modified Gompertz equation, as no phase separation was evident in the control. The kinetic parameters for all the models were evaluated using nonlinear regression and are summarized in Table 4. It was observed that the rate constant K for the MW+ H_2O_2 + acid-pretreated sample was higher (0.77 day^{-1}) than the control (0.2054 day^{-1}) and MW (0.426 day^{-1}). The ultimate methane yield (P) for the control was found to be very low (150.3 mL/g VS) because of the lack of easier accessibility of the substrate to the methanogens. The high rate constant for MW+ H_2O_2 + acid was attributed to more SCOD release. Similarly, the maximum rate of methane production (Rm) and methane production potential (Bc) were found to be higher. In contrast, the lag time for the MW+ H_2O_2 + acid was less (2.3 days) than the other treatment methods and the control (8.3 days) because of the readily available substrate for degradation.

Cost analysis

The economic feasibility of any newly established method can be governed by its operating cost. Hence, an absolute cost analysis was conducted at the pilot scale level. To analyze the competence of different pretreated sludges in terms of net energy production and cost, an energy balance study was performed, and the outcomes were summarized in Table 5. Among the methods, the MW + H_2O_2 + acid pretreatment demands low MW specific energy (204 kWh) to achieve 30 % COD solubilization when compared with others. Thus, there was a considerable amount of energy saving resulting from this method. One of the benefits associated with the anaerobic digestion of pretreated sludge was the production of fuel gas in the form of methane. Based on biodegradability (0.28), 38.3 m^3 of methane was obtained per liter of methane. The COD solubilization of all pretreated sludge was the same; hence, the methane production also remains the same (381 kWh). The energy cost of methane was calculated as 0.187 € per kWh of energy, and it remains the same for all types of pretreatment. Similar to methane, the cost savings can be obtained by reducing the SS to be disposed. This could occur because anaerobic biodegradability remains the same for the substrate with a similar amount of COD solubilization (Saha et al. 2011). All the heat requirements were expressed as kilowatt-hour of heat power. The energy consumed for sludge pumping and mixing in the anaerobic digester was calculated to be 96 kWh for all treatment processes. Energy required to raise the temperature of the sludge to the digester temperature and energy required to make up losses through top, walls, and bottom of digester was calculated to be 25 and 0.674 kWh, respectively. Gravity thickener was used for thickening of sludge. Energy consumed for this process was assessed to be 13.6 kWh. The energy spent for biogas purification and compression was 1.4 and 1.1 kWh, respectively. Therefore, the total input energy was estimated to be 749.8, 545.7, and 341.7 kWh for MW, MW + H_2O_2, and MW + H_2O_2 + acid pretreatment. The energy consumed for sludge pumping and mixing in the anaerobic digester was calculated to be 95.4 kWh for all treatment processes. The cost of H_2O_2 and H_2SO_4 used for the combined disintegration was also considered. In an economic analysis, the capital investment for sludge pretreatment was not considered. The results suggested that the MW + H_2O_2 + acid was the most economically feasible method with a net profit of 59.90 €/t of sludge. Pilot scale experiments with these optimized conditions and more realistic energy consideration are strongly recommended in the future.

Conclusion

In the MW pretreatment, the optimum specific energy used was 18,600 kJ/kg TS. Further increasing the specific energy did not lead to significant increase in the COD solubilization. The combined pretreatment of MW with H_2O_2 (0.3 mg/g SS) enhances the performance of sludge disintegration, owing to the generation of hydroxyl radicals. From this study, the pH was noticed as a key factor in determining the efficiency of H_2O_2 utilized and makes the sludge amenable for anaerobic digestion. Thus, the combined treatment of MW with hydrogen peroxide at acid pH 5 enhances the sludge solubilization up to 56.1 % and also influences the biogas production. The outcome of cost analysis reveals that the MW + H_2O_2 + acid disintegration of sludge was considered to be a feasible process both energetically and economically with a net profit of 59.90 €/t of sludge.

Acknowledgments The authors are thankful to DST, India for giving economic support for this assignment (SR/FTP/ETA-0021/2010) under their Young Scientist Scheme.

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