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Effects of biochar and activated carbon on biogas generation: A thermogravimetric and chemical analysis approach

M. Rasapoor[a,b], B. Young[a], A. Asadov[a], R. Brar[b], Ajit K. Sarmah[c], W.-Q. Zhuang[c], S. Baroutian[a,*]

[a] Department of Chemical & Materials Engineering, Faculty of Engineering, The University of Auckland, Auckland, New Zealand
[b] EnviroWaste Services Limited, Auckland, New Zealand
[c] Department of Civil & Environmental Engineering, Faculty of Engineering, The University of Auckland, Auckland, New Zealand

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ABSTRACT

Applying carbon-based additives can be an ideal strategy to maximise biogas yield, due to low operating costs and high adaptability to large scale implementation. Although several studies have revealed the positive impact of carbon-based additives on biogas generation, the mechanisms and reasons behind this have not yet been comprehensively studied for anaerobic digestion of organic waste. The mechanism of direct interspecies electron transfer (DIET) has been widely used to describe the effect of carbon-based additives on anaerobic processes. However, there are other mechanisms which are associated with this process. In this study, activated carbon and biochar were used as additives in anaerobic digestion (AD) of the organic fraction of municipal solid waste. Thermogravimetric, physical and chemical analyses were conducted to investigate the effect of these additives on the degradation process. The results showed a direct relationship between the thermogravimetric characteristics and the reaction rate. Using 20 g/L biochar significantly increased the rate of AD for all types of biochar, as confirmed by the thermogravimetric results. The physical properties of the additives, including electrical conductivity and surface area, were found to influence only the rate of AD process and not the biogas production yield. Biochar showed more promising results in terms of biogas generation compared to activated carbon due to its ability to adsorb ammonia nitrogen. Although activated carbon efficiently increased the organic degradation rate, concentrations higher than 10 g/L dramatically increased the ammonia nitrogen concentration, which resulted in hindering the methanogenic bacteria activity due to its inhibitory effect. As a result, biogas generation yield did not increase using a high concentration of activated carbon.

1. Introduction

Organic waste such as the organic fraction of municipal solid waste (OFMSW), wastewater treatment sludge, and rural and forest residues comprise a large proportion of the total waste generated around the world [1]. Recent years have witnessed increasing attention to the use of anaerobic digestion (AD) for the treatment of different sources of organic waste. The AD process produces biogas, which can be converted into heat and power, and the remaining residues can be safely spread onto fields as soil amendment [2]. Several studies have focused on improving the AD performance and energy efficiency of biogas generation technologies in accordance with world-wide demands for a reliable and clean source of energy. For instance, Europe is attempting to reach a target of one-fifth renewable energy by 2020 just by increasing the energy efficiency of the current technologies [3]. Considering the nature of organic waste, different approaches have been identified to improve the digestibility of these waste materials including co-digestion, pre-treatments and the use of carbonaceous additives to stimulate microbial activities and decrease the inhibitory concentration of some by-products [4]. Amongst the aforementioned methods, carbonaceous additives can be practically applied on a commercial scale, especially in landfills, due to the ease of application without any need of infrastructure modification [4,5]. Carbonaceous additives proved to be effective due to their positive impact on biogas generation, their widespread accessibility, and the low cost of implementation [6]. For example, low-cost Activated carbon (AC) can be produced via steam activation from char, a by-product from woody biomass gasification [7]. Nowadays, using AC as an additive has been implemented successfully in AD to enhance process efficiency in wastewater treatment plants [8,9]. For bioreactor landfills, carbonaceous additive can be easily used via leachate circulation program during the operation or even after landfill closure. AC has been commercially used as an

* Corresponding author.
E-mail address: s.baroutian@auckland.ac.nz (S. Baroutian).

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Table 1
Characteristics of OFMSW and inoculum.

Material	TS content (wt. % wet basis)	VS content (wt. % wet basis)	Initial pH	Soluble COD (mg/L)	Total COD (mg/L)
Inoculum	10.7 ± 0.8	38.6 ± 3.2	6.7 ± 0.2	180 ± 20	370 ± 50
OFMSW	21.4 ± 1.6	77.3 ± 1.23	5.8 ± 0.3	55735 ± 1145	80860 ± 1125

adsorbent to upgrade landfill gas, mainly to adsorb siloxane and H_2S from biogas before sending to the gas engine [10]. Amongst all the technologies which are being used to upgrade biogas, AC is recognised as one of the most economically viable methods [11].

From a biological point of view, different groups of microorganisms participate in hydrolysis, acidogenesis, acetogenesis, and methanogenesis to fulfil the AD process. Interspecies electron transfer between syntrophic and methanogens bacteria play a key role in boosting AD performance [12]. Methane generation was subjected to mediated interspecies electron transfer (MIET) via hydrogen and formate. However, recent studies have shown that direct interspecies electron transfer (DIET) via conductive materials, nanowires, and shuttle molecules is much more efficient in terms of energy efficiency due to the independence from multiple enzymatic steps to produce hydrogen and formate as an electron carrier [13]. Both AC and biochar (biomass-derived carbonaceous material) have been suggested to promote DIET in the AD of different types of materials such as food waste, activated sludge, ethanol, and dairy manure [14,15]. However, much remains to be discovered to prove the role of DIET in the AD process of complex organic waste [16]. Previous studies have shown that using biochar and AC could increase the biogas generation from 17% up to 400% [17,18]. However, it is not absolutely clear either the DIET or other processes involved. For example, both AC and biochar have an acceptable adsorption capacity, which may be positive in terms of reducing the toxic effects of inhibitory compounds in the AD system.

Thermogravimetric analysis (TGA) has received attention as a reliable method for investigating the degradation mechanisms operating in different processes [19]. Determination of mass losses of a sample subjected to a range of temperatures can reveal the different stages of degradation related to the AD process [20]. Protein, hemicellulose, and cellulose decomposition stages can be distinguished using TGA [21], making it possible to examine the impact of the different additives on the process acceleration.

The current study has investigated the effects of different AC and biochar additives on biogas generation yield during AD of complex organic waste rather than mono-substrate waste, as reported in most of the previous studies. Few studies have employed thermogravimetric approach to determine the relationship between the TGA results and the kinetics of the reactions for biological and non-biological processes [22–24]. However, in this study, a detailed relationship between thermogravimetric characteristics and AD reaction rates was obtained for first time. This new information can lead to a more in-depth understanding of the mechanism of carbonaceous additives in AD and their effects on the different steps of the digestion. The potential of carbonaceous additives to adsorb ammonia nitrogen, which has an inhibitory effect on methanogens bacteria, has been hitherto overlooked in many of the past studies. Therefore, additionally, in this study, the adsorption potential of AC and biochar and its impact on biogas generation have also been considered.

2. Materials and methods

2.1. Substrates and inoculum

The OFMSW used for this study was collected from the Hampton Downs landfill site located in the Waikato District of New Zealand. Materials were chosen based on a solid waste analysis report prepared by EnviroWaste services Ltd. All the segregated OFMSW was transferred to the University of Auckland and kept in a refrigerator at 4 °C for further analysis prior to the AD process as suggested previously [25]. To create the same condition for all treated samples, the OFMSW was shredded with a blender to reach a size below 3 mm before digestion. As a 6% total solids (TS) content was selected for this study, OFMSW was diluted with pure water just before starting the AD process. This TS content was selected because a previous study showed that amongst medium-level total solid concentrations, 6% returned the best results [26].

The inoculum used in AD was collected from Rosedale Wastewater Treatment Plant, Auckland. The characteristics of the OFMSW and inoculum are outlined in Table 1. A ratio of 0.9 (volatile solid basis) was selected for adjusting the substrate to inoculum ratio in order to achieve a balance between the digestion time and the impacts of the inoculum on the AD process.

2.2. Carbonaceous additives

Three types of commercial activated-carbon and biochar samples were used as additives in this study. Activated-carbon samples were supplied by ECP Ltd. (New Zealand), Haycarb PLC (Sri Lanka), and Norit Cabot (USA). Biochar samples used in this study were derived from pine sawdust (PS), manuka wood chips (MC), and poultry waste (PW). All the biochar samples were prepared using fast pyrolysis process at a temperature between 500 and 550 °C. The selected range of pyrolysis temperature can not only maintain biochar's functional groups but also improve the absorption potential of the biochar samples [27,28].

2.3. Anaerobic digestion

The digester setup, which had been successfully tested previously [26], consisted of a 100 mL digestion bottle, a 1000 mL water displacement bottle and a water collection bottle (See Fig. 1).

The containers were connected by means of plastic tubing and the displacement of water was used for calculating gas production volume. To make sure that the digester was completely sealed, a silicon plastic sheet was placed between the cap and the gas outlet port to make it completely sealed against ingress. Prior to the experiment, the digester was flushed with pure nitrogen for 2 min to expel the oxygen and make the process anaerobic. The biogas generation yield was calculated by monitoring the displaced water and the chemical oxygen demand (COD) removal daily.

The additives were mixed with the OFMSW at the pre-defined concentrations of 10, 20 and 30 g/L to evaluate the effect of the additives on AD performance and biogas generation yield. All the treatments were conducted at 35 °C for 10 days. Batch AD experiments were conducted in triplicate and the results were analysed by two-way analysis of variance (ANOVA). The single and interactive effects on biogas yield were determined to explore the significance of difference at $p < 0.01$.

A first-order model was used to evaluate the rate of biogas production.

$$B = P \times (1 - \exp(-k \times t)) \quad (1)$$

where B is the produced biogas (mL/g COD), t is the time (day), P is the maximum biogas production (mL/g COD) and k is the first-order reaction rate constant (day^{-1}).

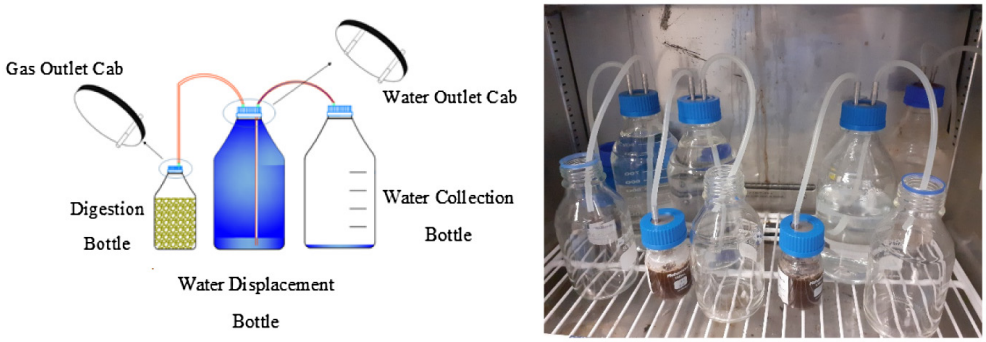

Fig. 1. Experimental setup of anaerobic digestion.

2.4. Analysis

Chemical oxygen demand (COD) was measured for all the treated samples as an index for biogas generation in the AD process. A dichromate digestion method was used for the measurement of COD using HACH test kits and a spectrophotometer (HACH, DR 3900). Ammonia nitrogen (NH_4^+-N) was determined according to the Standard Methods for the Examination of Water and Wastewater [29]. The pH was read using a pH meter (METTLER FE 28)

Thermogravimetric analysis was performed using an STA 449 F5 *Jupiter®* analyser. Around 8 mg of sample was used in each experiment. Analyses were carried out under an air flow of 100 mL/min at a heating rate of 10 °C/min from room temperature to 600 °C.

The surface area of the activated-carbon and biochar samples was determined based on the Brunauer-Emmett-Teller (BET) multipoint method, via liquid nitrogen adsorption measurements using a 3flex analyser (Micromeritics, USA). All the samples were pre-treated under vacuum at 200 °C before use in the device.

Electrical conductivity of the activated-carbon and biochar samples was measured under compression to minimise contact resistance between particles [30]. Briefly, 2 g of each sample was placed between two conductive plates. Then, by applying different loads, the thickness between the two plates and the corresponding resistance were measured until the electrical resistance remained constant. All the experiments were repeated three times and the mean value was reported. Resistivity was calculated using Eq. (2) and with the values of the resistance, final thickness and surface area between the two plates (See Fig. 2).

$$R = \rho\frac{L}{A} \tag{2}$$

where, R (Ω) represents resistance, L (m) and A (m^2) indicate the thickness and the surface area between two conductive plates, and ρ (Ω.m) represents electrical resistivity. The electrical conductivity (S/m) of the additives, which is the reciprocal of electrical resistivity, was then calculated.

Table 2
Surface area and electrical conductivity of activated-carbon and biochar additives.

Additives	EC (mS/cm)	Specific surface area (m^2/g)
Manuka biochar (MC)	0.95 ± 0.07	0.87 ± 0.02
Pine sawdust biochar (PS)	0.14 ± 0.02	1.97 ± 0.01
Poultry waste biochar (PW)	3.5 ± 0.12	7.11 ± 0.03
Norit activated carbon	600 ± 5.18	728.02 ± 1.47
Haycarb activated carbon	350 ± 4.45	1015.22 ± 2.21
ECP activated carbon	220 ± 4.03	1228 ± 2.37

3. Results and discussion

3.1. Surface area and electrical conductivity

The measured ECs and surface areas of the AC and biochar additives summarised in Table 2 show that there was a significant difference between the physical properties of ACs and biochars. The reason for the low surface area of the biochar samples is that biochar samples were produced at a moderate temperature (500–550 °C) without using any kind of pre-treatment to improve their surface area.

An increase in the specific surface area would be expected by increasing the pyrolysis temperature to effect the removal of -OH, aliphatic C–O, and ester C=O groups from the outer surface [31]. Similar to the surface area, EC would increase by exposing the raw materials to higher temperatures. In this case, PW had the highest EC amongst the other additives due to high elemental concentrations in PW as a result of incomplete nutrient assimilation by poultry [32]. Amongst activated-carbon samples, the highest surface area belonged to ECP, but, more interestingly, the surface area had an inversely proportional relationship to the electrical conductivity. This property of AC makes it more attractive in terms of its effect on digestion.

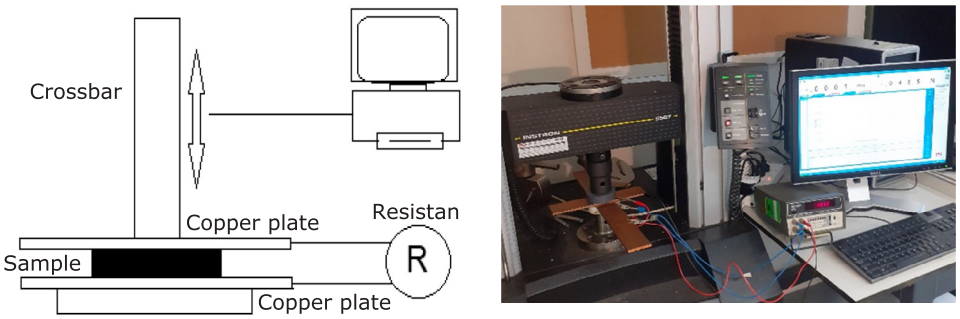

Fig. 2. Designed Set-up to measure EC of additives.

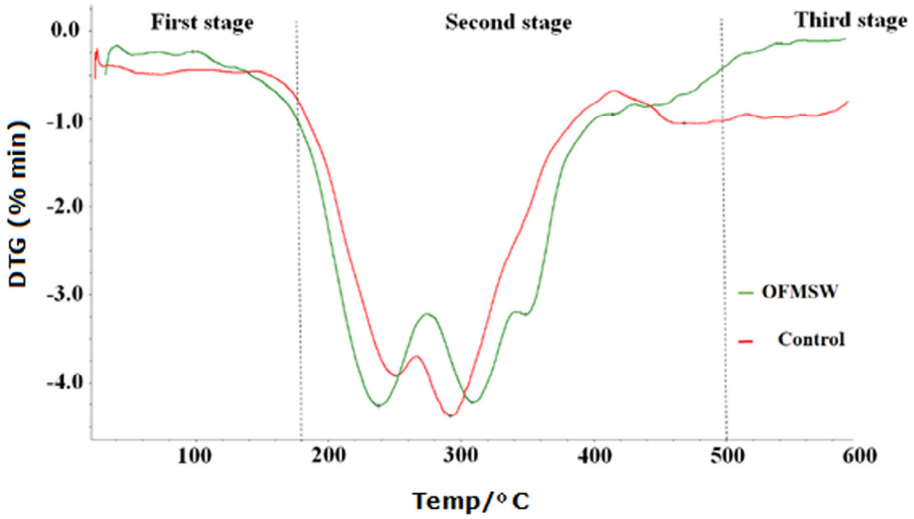

Fig. 3. DTG curves for OFMSW and control digested sample (without additive).

3.2. Thermal degradation behaviours

The mass loss (TG) and derivative curve (DTG) are the two most important outputs of thermogravimetric analysis. Weight-loss trends are obtained via TGA curves. However, the main devolatilisation stages are identified by DTG analysis [33]. Derivative curve (DTG) curves of the raw OFMSW and a control digested sample are shown in Fig. 3, while Fig. 4 presents the DTG curves of samples digested with biochar and AC additives.

During the analysis, the samples were heated from 50 to 600 °C as the organic fraction, mainly volatile, compounds are degraded in this temperature range. Weight-loss sequences and their related quantities were determined by dividing the DTG curves into three stages in order to understand the degradation behaviour of samples. For all biochar additive, control and raw OFMSW samples, the first weight loss (WL) occurred between 50 and 180 °C. The first weight loss for these samples were below 7% and the raw OFMSW showed the highest mass loss of approximately 7%. The high weight loss in this stage was attributed to the moisture dehydration and the presence of low-molecular-weight hydrocarbons in the OFMSW sample [33].

The major weight loss occurred in the second stage in the temperature range of 180 to 500 °C. The highest weight loss was for the raw OFMSW (72.25%), while the lowest weight loss belonged to the samples digested with 30 g/mL of PW and MC biochars (44.89% and 45.09%, respectively). Zhou et al. (2015) suggested that the weight loss in this temperature range was due to the decomposition of organic matter such as proteins, hemicelluloses and celluloses [21]. A small weight loss (1.22% to 2.68%) occurred in the third stage at temperatures above 500 °C as a result of decomposition of mainly inorganic materials such as calcium carbonate [34].

Weight loss of undigested OFMSW was higher compared to those of digested samples indicating a higher organic content in the undigested sample. This result was in agreement with previous findings that showed that the weight loss tends to decrease after the AD process [35,36]. The results also indicated that biochar additives in the range between 10 g/mL and 30 g/mL can decrease the weight loss, possibly by improving the degradation during the AD process.

The main results of the TG and DTG analysis are presented in Table 3. The first-order kinetic constants (k) were calculated for the AD to better explain the results. Furthermore, the mean reactivity (R_M), which implies the thermal characteristics of the samples, is presented. Mean reactivity, first introduced by Ghetto et al. (1996), relies on the fact that DTG peak height (R) is directly proportional to the reactivity, as opposed to corresponding temperature (T_p) which is inversely proportional to the reactivity itself. The sum of (R/T_p) of every individual peak except the moisture peaks is defined as the mean reactivity index (R_M). A higher R_M indicates the better reactivity. This term has been used in many studies where thermogravimetric analysis was used to compare the properties of raw and digested materials [19,35,37].

The results reported in the present work suggest that the reactivity index is not always reliable for comparing different digested samples' weight-loss pattern. It was found that between the digested samples there is no clear relationship between mass loss, R_M, and accumulated gas production. However, the temperature corresponding to each peak is more in line with the AD process, especially with the rate of digestion. As can be observed from Table 3, there is a significant difference between the R_M of the raw and digested samples.

The first-order reaction rate constant (k) was used to explain the reaction process more clearly. For example, according to Fig. 4 and the related results in Table 3, the trend of the curves between T_3 and T_4 (temperatures corresponding to peaks) shows the same reaction process in spite of the changing position of the peaks. Aggarwal et al. [29] assigned this thermal pattern to decomposable cellulose and lignocellulosic substances, which are major components of OFMSW.

The temperature range related to the first and second peaks in the second stage (T_3 and T_4) is more important compared to other temperature ranges due to the higher values of the peaks. However, results presented in Table 3 show that T_3 is the most important temperature, which can explain the effects of digestion. Firstly, T_3 revealed higher DTG changes between raw and digested samples compared to T_4, which shows the effectiveness of the AD process on organic factions in this range of temperatures.

Secondly, reaction rate changes under the effect of different additives contribute to the T_3 value. This means that the reaction rate for those kinds of additives, in which the DTG3 peak occurred at lower temperatures than 238.8 °C (raw sample), was higher, compared to the control sample. Li et al. (2017) found that the first set of temperatures related to the first peak of the second stage or the active stage can show the difference between raw and digested samples. The authors reported that readily degradable organic fractions could turn to the products in these ranges of temperature [35]. More interestingly, for samples which did not reach the peak corresponding to the T_3 ranges, the first-order decay rate was over one. This indicates a swift AD reaction. When two peaks appear in the DTG instead of one, for example as occurs at T_3 and T_4 for most of the curves, the two peaks can correspond to two parallel reactions, two sequential reactions, or two competitive reactions [38]. In this case, for all samples using 20 g/L additives, two reactions were

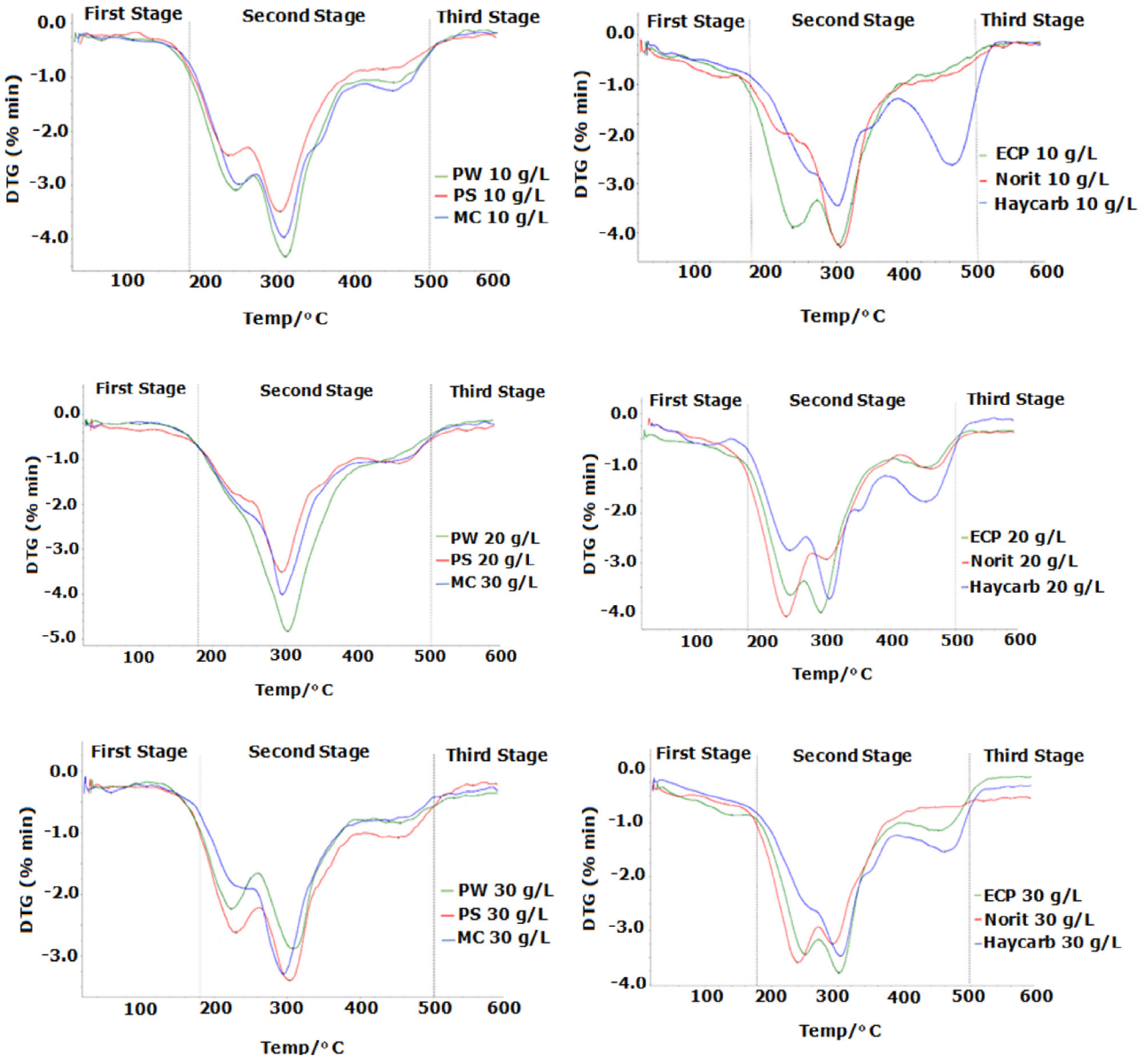

Fig. 4. DTG curves of digested OFMSW samples with different concentrations of additives.

not monitored. It is highly probable that using additives in this dosage could change one reaction pattern in favour of biogas production.

Thermal degradation behaviour for the digested samples with AC followed the same degradation pattern but with some changes in the second stage. Overall, it can be observed from Table 3 that using AC creates more mass loss, probably due to a higher degradation of organic matter. A higher dosage of biochar could create more degradation, while a lower dosage of AC reached the maximum organic degradation. Generally, the R_M for AC samples was higher than that of biochar additives. This is another plausible explanation for biochar being more effective in promoting the anaerobic reaction. However, as compared to biochar samples, there was no direct relationship between R_M and mass loss for all AC samples. Reaction rate values for AC added samples entirely depend on the T_3 value. For those kinds of samples, in which T_3 is equal or near to the T_3 for the control sample, the reaction rate did not change significantly. Similar to biochar-added samples, for all activated-carbon-treated samples the highest reaction rates corresponded to curves in Fig. 4 for which the T_3 value did not detect.

3.3. Biogas generation

Cumulative biogas yield was measured for 10 days to evaluate the effectiveness of the additives with different concentrations on biogas generation. Fig. 5 shows the accumulated biogas volume generation per mass of COD removal for all digested samples with additives and without additive (control) for 10 days of treatment time. Using biochar as an additive resulted in a significant increase in the biogas generation ($p < 0.01$). However, this impact could be attributed to the different sources of biochar. The selected range of optimum additive concentration for biochar application in this study was between 10 g/L and 30 g/L, based on previous studies [15,18]. For most of the samples, the rate of biogas generation was higher than the control sample (without additive), especially at the beginning of the process, indicating better degradation of organic fractions in the treated samples. It is conceivable that the high alkalinity of biochar which is proved in other studies [39,40] could save the media with high organic-acid generation by hydrolytic acidification. Ordinarily, a high concentration of organic acids, especially during hydrolysis, can inhibit the methane generation [41]. In addition, biochar can improve the organic-acid utilisation

Table 3
Summary of DTG curves of raw and digested OFMSW samples.

Sample type			First stage			Second stage								Third stage			RM × 10^3 (% min^{-1} $°C^{-1}$)	k (d^{-1})
			T1	DTG_1	T_2	DTG_2	WL_1	T_3	DTG_3	T_4	DTG_4	T_5	DTG_5	WL_2	T_6	DTG_6	WL_3		
OFMSW			ND	ND	85	0.28	6.76	238	4.26	308	4.28	348.3	3.23	72.25	ND	ND	1.22	40	–
Digested OFMSW without additive			ND	ND	ND	ND	4.63	251	3.92	292	4.38	468.2	1.05	68.39	ND	ND	1.43	32	0.48
Digested OFMSW with biochar additive	PW	10 g/L	64	0.32	105	0.30	6.42	242	3.09	308	4.33	452	1.10	64.05	559	0.16	1.72	16.3	0.35
		20 g/L	ND	ND	99	0.22	4.78	ND	ND	303	4.83	ND	ND	63.58	533	0.23	1.57	22	1.05
		30 g/L	77	0.27	ND	ND	5.01	223	2.24	308	2.88	454	0.84	44.89	527	0.44	2.68	24	0.62
	PS	10 g/L	132	0.29	ND	ND	5.61	233	2.45	301	3.48	438	0.85	52.56	ND	ND	2.12	15	0.54
		20 g/L	ND	ND	99	0.37	5.83	ND	ND	295	3.51	456	1.09	48.95	548	0.37	2.39	25.4	1.26
		30 g/L	55	0.28	ND	ND	5.44	230	2.62	303	3.4	452	1.08	54.29	554	0.24	1.98	28.5	0.80
	MC	10 g/L	ND	ND	ND	ND	4.82	246	2.98	303	3.96	450	1.25	62.11	522	0.32	1.97	16.4	0.43
		20 g/L	ND	ND	ND	ND	4.66	ND	ND	296	4.02	437	1.07	53.70	560	0.37	1.81	21.7	1.18
		30 g/L	59	0.35	108.5	0.25	4.23	242	1.91	294	3.29	438	0.81	45.09	508	0.42	2.23	14.5	0.43
Digested OFMSW with activated-carbon additive	Norit	10 g/L	ND	ND	136	0.5	5.12	ND	ND	305	4.29	ND	ND	55.20	536	0.25	2.21	29	1.63
		20 g/L	ND	ND	ND	ND	4.63	239	4.09	301	2.93	461	1.11	60.1	ND	ND	1.90	27	0.48
		30 g/L	59	0.52	ND	ND	4.97	238	3.59	293	3.25	ND	ND	54.75	519	0.6	1.45	17	0.54
	Haycarb	10 g/L	ND	ND	ND	ND	5.46	ND	ND	301	3.45	463	2.62	64.47	ND	ND	2.56	27	1.9
		20 g/L	ND	ND	113	0.62	5.39	245	2.75	306	3.73	454	1.77	61.46	ND	ND	2.21	14	0.39
		30 g/L	ND	ND	ND	ND	6.12	ND	ND	304	3.47	460	1.54	57.63	ND	ND	1.89	30	2.9
	ECP	10 g/L	ND	ND	ND	ND	5.7	238	3.89	302	4.24	ND	ND	64.12	518	0.22	1.65	30	0.43
		20 g/L	ND	ND	ND	ND	5.55	254	3.65	292	4.00	454	1.08	59.90	ND	ND	2.22	28	0.46
		30 g/L	ND	ND	140	0.86	6.01	251	3.44	301	3.79	451	1.14	59.17	ND	ND	2.09	28	0.45

efficiency of microorganisms [42].

Promoting DIET is another effect of the biochar that can increase the methane generation by improving the electron transfer efficiency [43]. An examination of data revealed that first order decay rate (k) for most of the biochar samples was higher than the control sample (see Table 3). This is in accordance with the higher degradation of easily degradable compounds such as carbohydrate and proteins by stimulating the dehydrogenase activities in a biochar-added media and improving the viability of anaerobic bacteria [44].

Amongst all the biochar samples, biochar derived from PS showed higher k values for all concentrations. However, the highest surface area and EC belonged to biochar derived from PW. Zhang et al. (2018) suggested that biochar can improve cell growth, activity, and accelerate their co-metabolism during AD [45]. The best concentration for obtaining the highest value of k was 20 g/L for PS biochar sample; by increasing the concentration, the k value dropped. Similarly, the highest k values for other types of biochar were achieved using an additive concentration of 20 g/L. These values were 1.18 and 1.05 for MC- and PW-derived biochar, respectively.

The cumulative biogas generation was not significant for some of the treated samples. The highest cumulative biogas yield was achieved using 30 g/L PW biochar (41%) followed by 10 g/L PS biochar (38%). The third highest cumulative biogas was obtained using 30 g/L MC biochar (23%). However, for other digested samples the cumulative biogas amounts were less than 20%. According to the results of this study, a higher amount of cumulative biogas can be obtained using a higher concentration of biochar for PW and MC biochars. However, for PS, the lowest concentration ended up with the highest cumulative biogas yield. It is interesting to note that both EC and surface area could not suggest any relationship between k values and even cumulative biogas yield for biochar additive samples. Although some of the previous studies suggested that surface area and EC directly affect biogas generation, Viggi et al. (2017) reached a similar conclusion to our study that surface area and EC do not have a major impact on biogas generation [18]. Elsewhere, Sadasivam et al. (2015) found that the capacity of biochar to adsorb methane gas could hinder biogas production [46].

As results confirmed the k values raised as biochar concentration increased up to 20 g/L for all biochar samples and decreased as soon as the concentration reached to 30 g/L. in addition, impeding the cumulative biogas generation after a specific period can highlight the importance of the concentration biochar additives. Redox potential is another contributing factor for the impact of biochar additives on biogas generation [18]; although, in our case, this aspect was not investigated, it could become a focus of future research. In addition, the results of thermogravimetric analysis can be used to show the impact of biochar on the reaction pattern of compounds in an AD process.

Unlike the biochar additives, AC additives showed both significant positive and negative effects on biogas generation ($p < 0.01$). As can be seen in Table 2, the EC and surface area of ACs are considerably higher than those of biochar. but the results confirmed that the better physical properties of AC do not necessarily result in an improved digestion.

The results of this study therefore suggest that only the lowest concentration of AC is effective in cumulative biogas generation from the OFMSW. Applying a low concentration of AC as an additive could dramatically increase the k value in the AD process. A significant increase in the k value was observed for 10 g/L and 30 g/L Haycarb AC, and 10 g/L Norit AC. The results are in agreement with those of Liu et al. [37] who found that introducing AC to an AD system can positively decrease the lag phase. An increase in k values can be explained by the EC of the AC. The lowest EC, which belonged to the ECP sample, was not effective in improving the k value, but others, even with different concentrations, increased the k values. More importantly, the pattern of DTG curves was different for digested samples with higher k values, indicating a change in the reaction under the effect of AC. This effect is more pronounced at the beginning of the AD process where a significant increase in decay rates was observed.

Regarding cumulative biogas generation, using 10 g/L of Haycarb and Norit ACs could significantly ($p < 0.01$) increase the biogas generation (42% and 36%, respectively). The increase in the amount of cumulative biogas in this study is in agreement with the results of Zhang et al. They found that introducing 15 g/L biochar with a surface area of 350 m^2/g can improve the biogas generation by up to 41%. This support to the idea that the surface area of AC does not have a significant role in promoting the AD process. The ECP activated carbon with a surface area greater than 1200 m^2/g did not show a significant effect on biogas generation and the results for Norit (728 m^2/g) and Haycarb (1015 m^2/g) AC activated carbons were the same.

Unlike surface area, EC seems to be an important property of the AC, influencing biogas generation. The AC additives with higher EC result in higher biogas generation as they can promote electron transfer in the AD media. Liu et al. (2012) reported that introducing AC as an additive

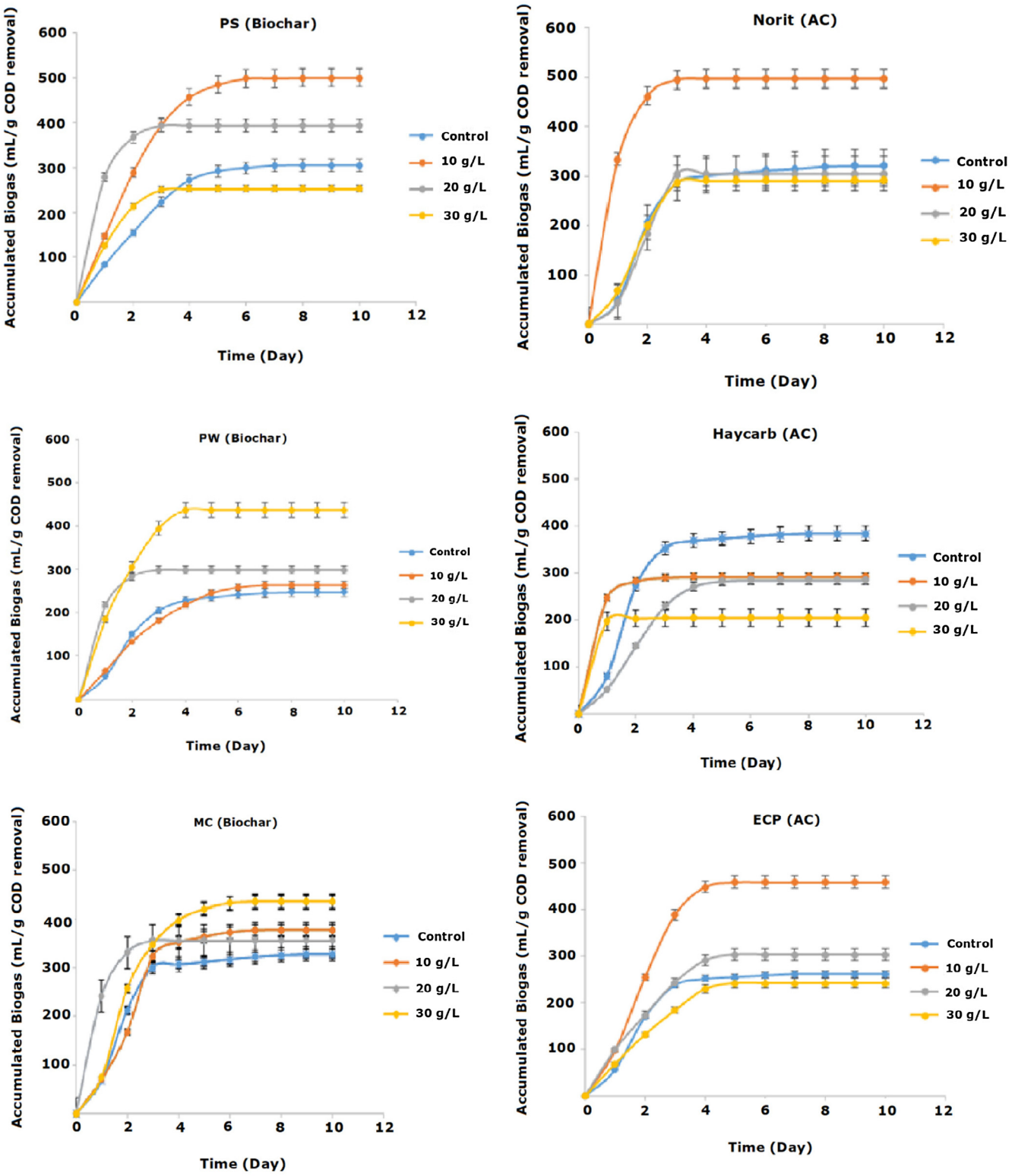

Fig. 5. Cumulative biogas yield using AC and biochar additives.

would increase methane generation due to promoting DIET between syntrophic microbial communities of bacteria and methanogenic archaea in a medium[47]. Xu et al. (2018) showed that applying additives which promote DIET can increase the microbial population of methanogenic bacteria and syntrophic metabolic bacteria [48].

In spite of the positive effect of AC with 10 mg/L, increasing the dosage of AC additive decreased the cumulative biogas generation significantly ($p < 0.01$). A likely explanation is that the high concentration of ammonia nitrogen in the AD during the process may have also played a role. As explained in the following section, the concentration of AC is directly proportional to ammonia nitrogen. Increasing the AC concentrations raised the corresponding ammonia nitrogen, which can inhibit the methane generation.

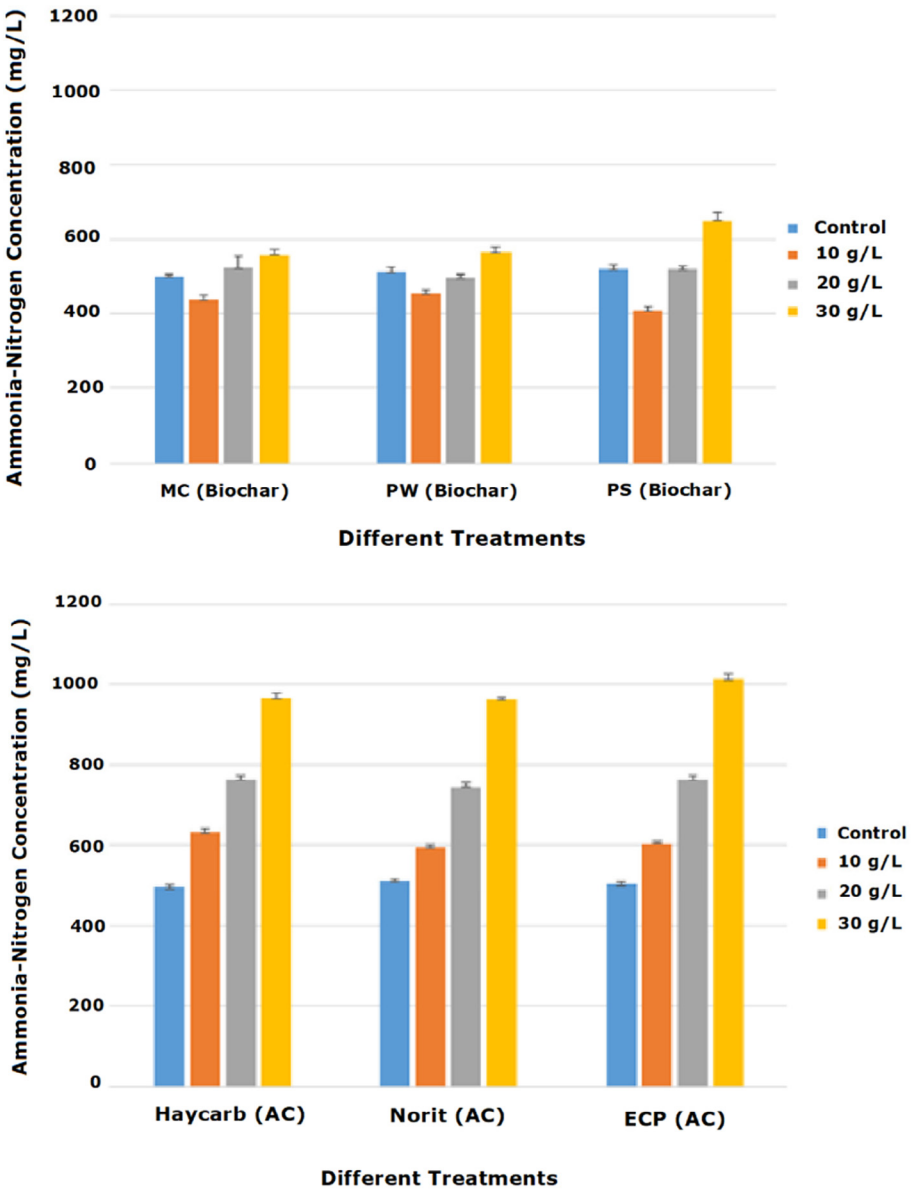

Fig. 6. Ammonia nitrogen concentration after AD of OFMSW using biochar (a) and AC (b) additives.

3.4. Ammonia nitrogen formation

When OFMSW is dominated by protein-rich materials and high loads of such materials are added to AD, especially at a commercial scale, a considerable amount of ammonia nitrogen can be formed, which can result in process inhibition [49]. Typically, degradation of amino acids during acidogenesis releases ammonia in media which would be toxic for methanogenic bacteria [50].

From Fig. 6 it can be seen that biochar can adjust ammonia nitrogen in media and keep the concentration at a safe level for microorganism activity. In contrast, increasing the dosage of AC increased the ammonia nitrogen concentration significantly.

By using biochar for all the sources, the concentration dropped when just 10 g/L of biochar was used, but, for the higher concentration of biochar, again the ammonia nitrogen concentration increased. However, there was not a marked difference between the highest (650 mg/L) and the lowest (500 mg/L) as compared to AC-treated samples. It was demonstrated that biochar samples could potentially absorb ammonia when used on agricultural land to diminish the environmental impacts of chemical fertilisers [51]. This property of biochar could therefore also potentially contribute to controlling the levels of ammonia nitrogen.

Comparing the results of accumulated biogas generation and ammonia nitrogen concentration can justify the choice of optimum concentration of biochar additives. It was found that adding biochar up to 30 g/L (except PS biochar) resulted in higher degradation and more biogas generation, without reaching inhibition of ammonia nitrogen compared to the control sample.

The difference between ammonia nitrogen concentrations using 10 g/L and 30 g/L of biochar can be explained by the fact that a higher amount of biochar promotes more degradation and, as a result, more ammonia nitrogen can be released. However, a higher amount of biochar can adsorb most of the released ammonia nitrogen. Accordingly, for the lowest amount of biochar, the rate of adsorption was probably higher than the rate of degradation. In another study conducted by Gao et al. (2019) on municipal sewage digestion, similar results were reported. It was found that when ammonia nitrogen concentration was more than 500 mg/L, the methane production rate decreased significantly due to the inhibition of high ammonia nitrogen. The results showed that even a negligible increase in ammonia nitrogen can cause a

Table 4
pH and soluble COD changes during AD process.

Sample type			pH	Final soluble COD (mg/L)
Digested OFMSW without additive			7.11 ± 0.05	36202 ± 465
Digested OFMSW with biochar additive	PW	10 g/L	7.63 ± 0.06	35479 ± 712
		20 g/L	7.72 ± 0.05	33211 ± 523
		30 g/L	7.94 ± 0.05	31752 ± 543
	PS	10 g/L	7.64 ± 0.08	30690 ± 254
		20 g/L	7.88 ± 0.06	31255 ± 390
		30 g/L	8.15 ± 0.09	35753 ± 568
	MC	10 g/L	7.55 ± 0.08	32212 ± 545
		20 g/L	7.89 ± 0.06	32756 ± 333
		30 g/L	7.83 ± 0.06	33555 ± 432
Digested OFMSW with activated-carbon additive	Norit	10 g/L	6.92 ± 0.09	27560 ± 157
		20 g/L	6.40 ± 0.12	37600 ± 356
		30 g/L	6.19 ± 0.09	39555 ± 212
	Haycarb	10 g/L	6.53 ± 0.14	33160 ± 422
		20 g/L	6.36 ± 0.08	36220 ± 167
		30 g/L	6.23 ± 0.05	37112 ± 549
	ECP	10 g/L	7.08 ± 0.07	29865 ± 212
		20 g/L	6.52 ± 0.12	38950 ± 312
		30 g/L	6.17 ± 0.13	40120 ± 674

significant negative effect [52].

In this study it was found that that he highest concentration of ammonia nitrogen amongst biochar additive samples (650 mg/L) was produced when PS-biochar was used. This high concentration of ammonia nitrogen resulted in the lowest biogas generation as methanogenesis microorganisms are sensitive to high range of ammonia nitrogen concentration.

Unlike the biochar-added samples, there was a significant variation of ammonia nitrogen between the AC-treated samples and the control sample, ranging from 496 mg/L to 1016 mg/L which, in some traces, had an inhibitory effect. AC has been widely used as an efficient adsorbent, especially to remove odours or fumes. However, the nonpolar surface diminishes its capacity to adsorb polar ammonia [53]. There are a few studies which have shown the effect of AC on ammonia nitrogen [53]. However, there have been inconsistencies in the reported data with no correlation found in the published results. The result of this study showed that

Hansen et al. (1997) reported that using 1.5% (w/w) of AC for a sample with 6 g/L initial ammonia concentration increased the biogas generation. They concluded that an increase in biogas generation was due to the adsorption effect of conductive AC [54]. Poirier et al. (2017) found that the addition of 10 g/L AC decreased the lag phase of AD and did not improve biogas generation. They concluded that AC was more effective in improving methanogenesis kinetics because of its conductive property compared to ammonia adsorption [55].

The results from this study are in agreement with the results of previous studies suggesting that improvement in biogas generation using 10 g/L AC is due to the conductive role of AC samples instead of adsorption of ammonia. According to this explanation, by increasing the concentration of AC, the degradation will be increased and consequently more ammonia will be released and AC cannot adsorb the accumulated ammonia. Under the effect of excess ammonia, the cumulative biogas generation reduces. As can be seen in Table 3, the lowest second stage weight loss was obtained when 30 g/L of AC was used. The second stage is the most critical stage of degradation. As more degradation of organic compounds occurs, more ammonia nitrogen is produced. However, AC is unable to adsorb this excess ammonia nitrogen due to its non-polar surface characteristics. The excess ammonia nitrogen can negatively affect the methanogenesis bacteria.

The change in pH during the AD process can also indicate the variations in ammonia nitrogen concentration. For all the samples before digestion, pH was adjusted at 7.5 to create the same condition for all treatments. After digestion, pH was 7.1 for the control sample. For biochar added samples, the change in pH was between 7.6 and 8.1 (Table 4). Previous studies showed that using biochar can increase the buffering capacity of the digestion process [39,40,56]. For the AC additive treatments, almost all digested samples showed a pH less than 7. The study conducted by Chen et al. (2016) on digested food waste at different pH ranges from 7.2 to 4.6 confirmed that ammonia nitrogen tends to increase by decreasing the pH [57].

COD removal efficiency is another important parameter which can explain the degradation process. After digestion, COD was 35% for the control sample. The highest COD removal efficiency (51%) was achieved using 10 g/L Norit AC additive. In contrast, the lowest COD removal efficiency (28%) was obtained using 30 g/L ECP-AC additive after 10 days. For AC additive samples, it was found that low pH and high ammonia nitrogen concentration can alleviate soluble COD removal efficiency according to Table 4. Decreasing in COD removal efficiency for the high concentration of AC can contribute to high levels of ammonia nitrogen which is reported before by Gao et al. (2019) [52]. For biochar additive samples, COD removal efficiency was between 36% and 45%, indicating fewer changes compared to AC additives.

4. Conclusions

Thermogravimetric analysis, in conjunction with ammonia nitrogen analysis, can be used to better explain the impact of carbonaceous additives on the AD process. It was found that introducing AC and biochar additives to the anaerobic media can improve the performance of the digestion process. DTG results confirmed that using 20 g/L biochar can significantly increase the rate of anaerobic digestion reactions. Using 10 g/L AC additive (Norit) resulted in the maximum (51%) leachate COD removal efficiency. The findings of this study suggest that biochar can adsorb ammonia nitrogen better than AC due to its polar surface compared to AC with nonpolar-surface characteristics. In average, 1000 mg/L of ammonia nitrogen was produced by applying 30 g/L AC additives, whereas for control sample approximately 500 mg/L ammonia nitrogen was produced. High concentrations of ammonia nitrogen have a significant impact on the AD. As a result, biogas generation potential can be affected considerably.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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