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Carbon capture and biogas enhancement by carbon dioxide enrichment of anaerobic digesters treating sewage sludge or food waste

Y. Bajón Fernández [a], A. Soares [a], R. Villa [a], P. Vale [b], E. Cartmell [a,*]

[a] Cranfield Water Science Institute, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK
[b] Severn Trent Water, 2 St. John's Street, Coventry CV1 2LZ, UK

HIGHLIGHTS

- The benefits of CO_2 enrichment on anaerobic digestion were evidenced.
- Sewage sludge and food waste anaerobic digesters were examined.
- First 24 h CH_4 production increased 11–16% for food waste and 96–138% for sludge.
- A mechanism of CO_2 utilisation has been hypothesised.
- Estimated potential CO_2 reductions of 8–34% for sludge and of 3–11% for food waste.

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ABSTRACT

The increasing concentration of carbon dioxide (CO_2) in the atmosphere and the stringent greenhouse gases (GHG) reduction targets, require the development of CO_2 sequestration technologies applicable for the waste and wastewater sector. This study addressed the reduction of CO_2 emissions and enhancement of biogas production associated with CO_2 enrichment of anaerobic digesters (ADs). The benefits of CO_2 enrichment were examined by injecting CO_2 at 0, 0.3, 0.6 and 0.9 M fractions into batch ADs treating food waste or sewage sludge. Daily specific methane (CH_4) production increased 11–16% for food waste and 96–138% for sewage sludge over the first 24 h. Potential CO_2 reductions of 8–34% for sewage sludge and 3–11% for food waste were estimated. The capacity of ADs to utilise additional CO_2 was demonstrated, which could provide a potential solution for onsite sequestration of CO_2 streams while enhancing renewable energy production.

1. Introduction

Carbon dioxide (CO_2) emissions to the atmosphere need to be reduced if targets for CO_2 reduction are to be met (e.g. UK Climate Change Act, 2008). Conventional carbon capture and storage (CCS) is based on the long term storage of this compound in geological or ocean reservoirs (Xu et al., 2010). This still has high associated costs and significant limitations linked to the potential risk of leaking from storage sites (Holloway, 2007). Moreover, the need to transport the CO_2 makes the proximity of source and reservoir a limiting factor. Therefore, the implementation of CCS is more feasible in large centralised sources which benefit from the pipeline's economy of scale (Middleton and Eccles, 2013).

The UK water industry emitted over 5 million tonnes of greenhouse gases (GHG) as CO_2 equivalents (CO_2e) during 2010–2011 (Water UK, 2012), of which 56% can be attributed to wastewater treatment (DEFRA, 2008). However, the varied size and scattered

Abbreviations: AD, anaerobic digester; ANOVA, analysis of variance; CCS, carbon capture and storage; DC20, control digesters bubbled with $N_2(g)$ for 20 min; DC0.5, control digesters bubbled with $N_2(g)$ for 0.5 min; D0.3, digesters enriched with $y_{CO_2} = 0.3$; D0.6, digesters enriched with $y_{CO_2} = 0.6$; D0.9, digesters enriched with $y_{CO_2} = 0.9$; DI, deionized; DO, dissolved oxygen; GHG, greenhouse gases; H_i, Henry's constant for i; SAO, syntrophic acetate oxidation; sCOD, soluble chemical oxygen demand; TPAD, two phase anaerobic digestion; TS, total solids; UASB, upflow anaerobic sludge blanket; VFA, volatile fatty acid; VS, volatile solids; WWTP, wastewater treatment plant; k_La, volumetric liquid phase mass transfer coefficient (s^{-1}); D_L, diffusion coefficient ($m^2\,s^{-1}$); n, coefficient depending on the theory for interfacial mass transfer considered between the gas and the liquid phases; t_{95}, time to reach 95% of the equilibrium solubility (s); C^*, solubility (mg L^{-1}); C_0 concentration at time zero (mg L^{-1}); C_t, concentration at time t (mg L^{-1}); $(CO_2)_{generated}$, CO_2 generated during the entire batch digestion process (mg); $(CO_2)_{digestate}$, CO_2 dissolved in the digestate at the end of the digestion period (mg); $(CO_2)_{biogas}$, CO_2 released with the biogas (mg); $(CO_2)_{in}$, CO_2 dissolved in the material to digest after the CO_2 injection (mg).

* Corresponding author. Tel.: +44 (0)1234 758366; fax: +44 (0)1234 751671.
E-mail address: E.Cartmell@cranfield.ac.uk (E. Cartmell).

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location of organic waste and wastewater treatment plants (WWTPs), make the implementation of CCS particularly challenging in the water or waste sectors. This necessitates the development of alternative solutions for CO_2 capture and long term storage. Additionally, the increased implementation of upgrading technologies for the biogas produced in anaerobic digesters (ADs) (Weiland, 2010), results in the production of CO_2 concentrated streams. This further raises the need to develop new carbon storage or utilisation technologies applicable to the wastewater and waste sectors.

Biogenic carbon sequestration methods (e.g., microalgae, biochar) are being studied as alternatives to geological or oceanic reservoirs. However, in general, their capacity for CO_2 sequestration or their large-scale applicability needs to be further investigated (NERC, 2011). A few studies have considered the potential of CO_2 biological conversion in anaerobic processes, reporting benefits both in terms of carbon uptake and renewable energy production. Alimahmoodi and Mulligan (2008) stated a 69–86% CO_2 uptake when dissolving this gas in the influent to an upflow anaerobic sludge blanket (UASB) reactor. Salomoni et al. (2011) further confirmed the potential of CO_2 biological conversion in two phase anaerobic digestion (TPAD), and observed a 25% methane (CH_4) yield enhancement when bubbling CO_2 into the first stage. Sato and Ochi (1994) stated associated benefits of up to 30% increased specific CH_4 yields when enriching ADs treating sewage sludge with CO_2.

Therefore, the capacity of ADs to transform CO_2 into CH_4 could result in the onsite treatment of CO_2 concentrated streams and potential increases in CH_4 production. Although the benefits of CO_2 enrichment of ADs have been evidenced, the scarcity of the literature available requires further research before its full potential can be estimated. Furthermore, the increasing practice to treat food waste or mixed substrates, also needs to be considered in relation to the benefits of CO_2 enrichment.

This paper assessed the impact of CO_2 injection in batch ADs treating food waste or sewage sludge. Renewable energy production, CO_2 utilisation and digestate quality were studied. Firstly, absorption tests were completed to estimate the gas–liquid contact time required to reach CO_2 equilibrium conditions between the liquid phase and the injected gas. Secondly, the impact of CO_2 enrichment in batch ADs treating food waste and sewage sludge was assessed for CO_2 molar fractions (y_{CO_2}) of 0.3, 0.6 and 0.9 (0.4, 0.8 and 1.6 bar CO_2 partial pressures [p_{CO2}]). Lastly, the time required to recover from any initial acidification due to CO_2 injection was determined for sewage sludge by monitoring the pH of sacrificial ADs.

2. Methods

2.1. Description of the anaerobic digester equipment

Each batch AD unit consisted of a 1 L glass bottle with a four port cap (Fisher Scientific, Loughborough, UK). Two ports were used for gas injection by means of Pyrex diffusers with a porosity of 3 and 15 mm diameter (Fisher Scientific, Loughborough, UK). When running absorption tests, one port was acting as pressure release and the fourth port was blocked (Fig. 1a). When conducting CO_2 enrichment tests in ADs, one port was blocked with a 17 mm septa (Thames Restek UK Ltd., Buckinghamshire, UK), allowing gas sample extraction for composition analysis, and the last port was connected to a MilliGascounter (Litre Meter Ltd., Buckinghamshire, UK) for biogas volume recording (Fig. 1b). When running sacrificial ADs for pH monitoring, one port was used for daily sample extraction of the liquid phase. The ADs were continuously stirred and placed in a temperature controlled water bath (38 ± 0.5 °C).

2.2. Absorption tests methodology

The contact time required to ensure CO_2 equilibrium conditions between the gas injected and the sewage sludge or food waste, was estimated by conducting oxygen (O_2) absorption tests with air, and converting the results to CO_2 using diffusion coefficients, as previously suggested by Garcia-Ochoa and Gomez (2009). In order to account for the viscosity variability of food waste and sewage sludge, tests with different liquid viscosities were performed. Glycerol was used as a viscosity enhancer, because of the extensive information available of its impact on aqueous solutions (Jordan et al., 1956). Tests in deionized (DI) water with air flow rates of 0.5, 1.0 and 1.7 L min^{-1} and tests with a fixed air flow rate (1.0 L min^{-1}) and mixtures of glycerol in DI water of 10%, 30%, 50% and 70% weight (glycerol ⩾ 98%; Fisher Scientific, Loughborough, UK) were performed. The air flow rate was controlled by a mass flow controller (MFC) (Premier Control Technologies, Norfolk, UK). The dissolved oxygen (DO) was monitored using a DO probe (HACH LDO101; Camlab, Cambridge, UK) connected to a meter device (HACH HQ30d; Camlab, Cambridge, UK).

The gas to liquid mass transfer was described using Eq. (1) and corrected for the time to reach 95% of the equilibrium solubility by Eq. (2). Considering similar equations for CO_2 and O_2, and relating the volumetric mass transfer coefficients (k_La) of both gases with the ratio of their diffusion coefficients (Eq. (3)), a relationship between the times to reach equilibrium solubility with CO_2 and with O_2 was obtained (Eq. (4)). The film theory for interfacial mass transfer was considered, which states $n = 1$. The diffusion coefficients for CO_2 in water-glycerol mixtures used in Eq. (4) were 2.6×10^{-5}, 1.7×10^{-5}, 7.2×10^{-6} $cm^2\,s^{-1}$ for glycerol concentrations of 0%, 25% and 50% weight, respectively. The values used for O_2 were 3.0×10^{-5}, 3.4×10^{-5}, 1.6×10^{-5} $cm^2\,s^{-1}$ for glycerol concentrations of 0%, 25% and 50% weight, respectively. These diffusion coefficients were obtained from those reported by Brignole and Echarte (1981) and Jordan et al. (1956), for CO_2 and O_2, respectively, after correction for a temperature of 38 °C as per Díaz et al. (1987).

$$\ln\left(\frac{C^* - C_t}{C^* - C_0}\right) = -k_La \cdot t \tag{1}$$

$$\ln(0.05) = -k_La \cdot t_{95} \tag{2}$$

$$(k_L\ a)_{CO_2} = (k_L\ a)_{O_2} \cdot \left[\frac{(D_L)_{CO_2}}{(D_L)_{O_2}}\right]^n \tag{3}$$

$$(t_{95})_{CO_2} = (t_{95})_{O_2} \cdot \frac{(D_L)_{O_2}}{(D_L)_{CO_2}} \tag{4}$$

where k_La: volumetric liquid phase mass transfer coefficient (s^{-1}), D_L: diffusion coefficient ($m^2\,s^{-1}$), n: coefficient depending on the theory for interfacial mass transfer considered between the gas and the liquid phases, t_{95}: time to reach 95% of the equilibrium solubility (s), C^*: solubility (mg L^{-1}), C_0: concentration at time zero (mg L^{-1}), C_t: concentration at time t (mg L^{-1}).

2.3. Methodology for enriching the digesters with CO_2

Batch ADs treating food waste or sewage sludge were operated with an inoculum to substrate volatile solids (VS) ratio of 2:1 and a working volume of 700 ml. Macerated and digested food waste were collected from a full scale UK AD site treating 30,000 tonnes of organic waste per year. Thickened waste activated sludge (WAS) and digested sewage sludge were collected from a full scale UK WWTP serving a 2.5 million population equivalent.

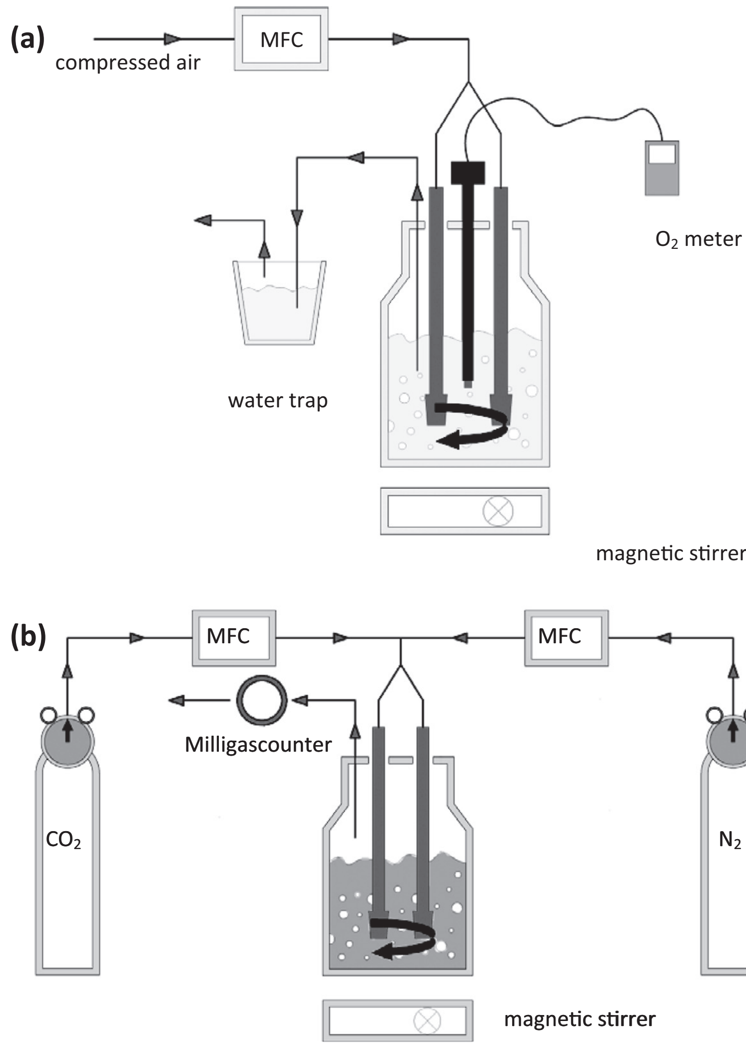

Fig. 1. Schematic representation of the experimental rig used (a) for the absorption tests and (b) for the operation of ADs enriched with CO_2.

The material in each AD was enriched with a different p_{CO2} before starting the digestion process, (Table 1). Mixtures of CO_2 and nitrogen (N_2) were used to regulate the p_{CO2}, and only N_2 was used in the control units. The N_2 and CO_2 were supplied from gas cylinders (BOC, Manchester, UK) and were controlled by MFCs (Premier Control Technologies, Norfolk, UK).

Table 1
Gas injection conditions used for enrichment with CO_2 of the material to digest in batch ADs.

	y_{CO_2} [a]	DC[e] 0.00	D0.3[f] 0.30	D0.6[g] 0.60	D0.9[h] 0.89
Food waste	p_{CO2}[b] (bar)	0.0 ± 0.0	0.4 ± 0.0	0.8 ± 0.1	1.6 ± 0.3
	n[c]	2	2	2	2
Sewage sludge	p_{CO2} (bar)	0.0 ± 0.0	0.5 ± 0.1	n/a	1.7 ± 0.0
	n	3	3	n/a	2
Sacrificial AD	p_{CO2} (bar)	0.0 ± 0.0	0.4 ± 0.1	n/a	1.3 ± 0.2
	n	6[d]	3	n/a	3

[a] CO_2 molar fraction.
[b] CO_2 partial pressure.
[c] Number of replicates.
[d] Three ADs bubbled with nitrogen for 0.5 min and three for 20 min.
[e] Control digester.
[f] Digesters enriched with $y_{CO_2} = 0.3$.
[g] Digesters enriched with $y_{CO_2} = 0.6$.
[h] Digesters enriched with $y_{CO_2} = 0.6$.

The duration of the CO_2 injection was determined from the results of the absorption tests. The control ADs for food waste and sewage sludge were bubbled with N_2 from 5 up to 20 min to ensure that any increase in performance was not due to an initial improved mixing of substrate and inoculum.

Lastly, sacrificial ADs treating sewage sludge were operated under the same conditions (Table 1) and their pH evolution was monitored daily. The effect of the N_2 injection time on the initial conditions of the control ADs was studied by operating two types of sacrificial controls: bubbled with N_2 for 0.5 min and 20 min. A gas flow rate of 1.0 L min^{-1} was used in all the reactors.

2.4. Analytical methods

The materials were analysed on commencement and at the end of the AD operation for soluble chemical oxygen demand (sCOD), total solids (TS) and VS (APHA, 2005). To obtain the solid free fraction, samples were centrifuged in a Falcon 6/300 refrigerated centrifuge (MSE UK Ltd., London, UK) at 4700g and 19 °C for 20 min, and the supernatant was centrifuged again for 40 min under the same conditions. The final supernatant was vacuum filtered through 1.2 μm pore size glass microfiber filters GF/C (Whatman™, Kent, UK) and then through 0.45 μm pore size syringe-drive filter units (Millipore™, Billerica, United States).

The volume of gas produced and its composition were recorded daily by means of MilliGascounters (Litre Meter Ltd., Buckinghamshire, UK) and a CSi 200 Series Gas Chromatograph (Cambridge Scientific Instruments Ltd., Witchford, UK), respectively.

The CO_2 generated during the entire batch digestion process was calculated as per the following mass balance, which was compared for control and test ADs to estimate the reduction of CO_2 emissions:

$$(CO_2)_{generated} = (CO_2)_{digestate} + (CO_2)_{biogas} - (CO_2)_{in} \quad (5)$$

where: $(CO_2)_{digestate}$: CO_2 dissolved in the digestate at the end of the digestion period (mg). Obtained with the headspace concentration of digestate samples allowed to reach equilibrium conditions with the gas phase and Henry's law, $(CO_2)_{biogas}$: CO_2 released with the biogas (mg), at 20 °C and 1 atm, $(CO_2)_{in}$: CO_2 dissolved in the material to digest after the CO_2 injection (mg). Calculated based on Henry's law, considering the partial pressure of each injection (Table 1) and assuming CO_2 solubility of 1071 mg L^{-1}.

Statistically significant differences between ADs were identified through an analysis of variance (ANOVA), where the AD performances (e.g., CH_4 yield, daily CH_4 production) were the dependent variables and y_{CO_2} or p_{CO2} were the factors. Statistica software version 11 (StatSoft Ltd., Bedford, UK) was used.

3. Results and discussion

3.1. Estimation of gas–liquid contact time to achieve CO_2 equilibrium during enrichment

The results from the absorption tests demonstrated that equilibrium of the liquid phase with O_2 in air was achieved in 2–4 min for all the air flow rates and viscosities tested. The diffusion coefficients for CO_2–water–glycerol and O_2–water–glycerol reported by Brignole and Echarte (1981) and Jordan et al. (1956) were used, after correction for mesophilic temperatures as per Díaz et al. (1987). A ratio of diffusion coefficients of O_2 to CO_2 of 1.2, 2.0 and 2.3 was obtained for glycerol concentrations of 0%, 25% and 50% weight, respectively, demonstrating that the gas–liquid contact time required with CO_2 was 1.2–2.3 times higher than with O_2. Considering Eq. (4) and an O_2 to CO_2 diffusion coefficients ratio of 2.3, a gas–liquid contact time over 9 min was required to reach equilibrium conditions with the CO_2 enriched gas, for the system in place. Due to the scarcity of published diffusion coefficients for high glycerol concentrations, food waste and sewage sludge, and due to the added complexity of the bicarbonate equilibrium in ADs, a safety factor was applied. A CO_2 injection time of 20 min was used when enriching with CO_2 the materials to digest in the test ADs.

This methodology and equilibrium time were validated by injecting CO_2 enriched streams into sewage sludge and food waste, and monitoring the pH change. In both cases a gas injection of 20 min ensured that equilibrium conditions were achieved.

From the sacrificial ADs operation (Fig. 2), the duration of N_2 injection on the control ADs significantly affected the initial pH, with longer injection times (20 min) increasing the pH by 0.9 units. Therefore, it was concluded that the starting pH of the ADs bubbled with N_2 for only 0.5 min, was more comparable to that measured in the test ADs before CO_2 injection.

3.2. Assessment of digestion performance: renewable energy enhancement and digestate quality

Biogas and CH_4 production data are summarised in Table 2 and Fig. 3. All the ADs enriched with CO_2 and treating food waste obtained higher CH_4 yields than the controls. More specifically, the ADs enriched with $y_{CO_2} = 0.9$ achieved a 13% improvement (p-value of 0.04) on CH_4 yield, whilst an 8% and 5% increase (p-value of 0.15 and 0.29, respectively) was observed for ADs bubbled with $y_{CO_2} = 0.3$ and $y_{CO_2} = 0.6$, respectively. During the first 24 h after CO_2 injection, the increase in daily CH_4 production was 14%, 11% and 16% for $y_{CO_2} = 0.3, 0.6 and 0.9$, respectively ($p$-value of 0.03, 0.06, 0.02, respectively) (Table 2).

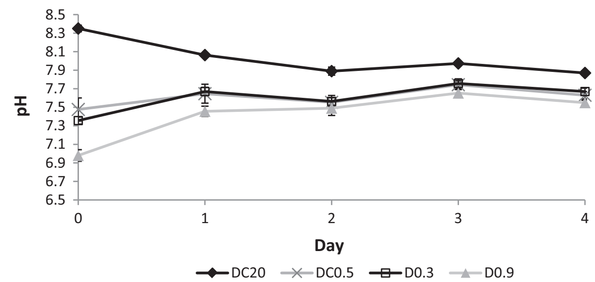

Fig. 2. pH evolution in sacrificial ADs treating sewage sludge. The data at day zero represent the pH after the gas injection. *DC20*: control digesters bubbled with N_2 (g) for 20 min, *DC0.5*: control digesters bubbled with N_2 (g) for 0.5 min, *D0.3*: digesters enriched with $y_{CO_2} = 0.3$, *D0.6*: digesters enriched with $y_{CO_2} = 0.6$, *D0.9*: digesters enriched with $y_{CO_2} = 0.9$. The error bars represent the standard deviation between replicates.

Despite the increase in the final yield, there were no significant differences in the distribution of the CH_4 production over time for food waste ADs (Fig. 3a). During the first 48 h of digestion, the control units achieved 47 ± 3% of their final CH_4 yield, which was similar to that of the test reactors: 49 ± 0%, 48 ± 0% and 46 ± 2%, for $y_{CO_2} = 0.3, 0.6, 0.9$, respectively.

Conversely, the test ADs treating sewage sludge experienced an increase of 96% and 138% (p-value of 0.007 and 0.001, respectively) in the CH_4 production 24 h after the CO_2 injection, when enriched with $y_{CO_2} = 0.3$ and $y_{CO_2} = 0.9$, respectively. However, this initial boost was not maintained throughout the batch digestion period, leading to no benefit in the final CH_4 yield when compared with the control ADs (Table 2). Therefore, there was a significantly different distribution of the CH_4 production of control and test sewage sludge ADs over time (Fig. 3b). The test ADs achieved over 60% of the CH_4 yield during the first 48 h of the digestion process, whilst the control ADs attained less than 40% (Table 2).

Since the material to digest was enriched with CO_2 only at the start of the digestion process, lower CH_4 yield improvements than the 30% achieved by Sato and Ochi (1994) or the 25% reported by Salomoni et al. (2011) when injecting CO_2 periodically into ADs, were observed. However, if the enhancement in the sewage sludge ADs over the first 48 h following CO_2 enrichment was considered, significantly higher benefits were achieved in this study. Nevertheless, the comparison with previous studies was limited because of the difference of substrates treated and reactor type used (i.e., continuous or batch, single or two phased, UASB or AD).

The ADs enriched with higher CO_2 concentrations achieved greater enhancements, with the exception of $y_{CO_2} = 0.6$ when treating food waste, which led to similar benefits than $y_{CO_2} = 0.3$. For the two substrates treated, the best performance was obtained when using $y_{CO_2} = 0.9$ (p_{CO_2} of 1.6–1.7 bar). This finding differs from the study of Sato and Ochi (1994), who reported an optimum performance at $y_{CO_2} = 0.6$ and related the reduction in yield at higher concentrations with a possible drop in pH. Again the comparison of the results is limited, since only data of the CO_2 concentrations were reported in that study whilst the amount of CO_2 dissolved is determined by the p_{CO2}. Moreover, different alkalinities (buffering capacities) in the material to digest would lead to a different impact of the CO_2 injection in the pH.

In this study, no difference in the pH of the digestate of tests and controls for any of the substrates treated was observed (Table

Table 2
pH at start and end of the digestion process, batch ADs performance and removal efficiencies. Format as average ± standard deviation.

	Food waste					Sewage sludge			
	Mixture to AD	DC[a]	D0.3[b]	D0.6[c]	D0.9[d]	Mixture to AD	DC[a]	D0.3[b]	D0.9[d]
Liquid phase									
pH	7.6 ± 0.0	8.4 ± 0.0	8.4 ± 0.0	8.4 ± 0.0	8.4 ± 0.0	7.2 ± 0.0	7.7 ± 0.0	7.7 ± 0.1	7.7 ± 0.0
Removal efficiencies									
TS (%)	–	16.6 ± 0.7	17.2 ± 0.2	16.0 ± 0.5	17.3 ± 1.1	–	19.2 ± 0.1	25.2 ± 1.2	18.6 ± 0.5
VS (%)	–	26.1 ± 0.1	25.6 ± 0.1	25.4 ± 1.8	26.0 ± 0.8	–	27.2 ± 0.0	32.6 ± 0.4	26.5 ± 0.4
sCOD (%)	–	22.7 ± 6.4	33.2 ± 12.9	16.1 ± 3.3	21.7 ± 2.3	–	29.9 ± 4.6	43.3 ± 6.7	34.9 ± 8.3
Biogas and methane yields									
CH_4 yield (ml CH_4 (g VS)$^{-1}$)	–	172 ± 12	186 ± 8	182 ± 1	195 ± 6	–	101 ± 2	94 ± 2	103 ± 10
% of the CH_4 yield achieved during the first 48hours of digestion	–	47 ± 3	49 ± 0	48 ± 0	46 ± 2	–	39 ± 10	63 ± 4	61 ± 7
Biogas yield (ml biogas (g VS)$^{-1}$)	–	267 ± 13	281 ± 8	279 ± 3	303 ± 9	–	183 ± 8	171 ± 4	189 ± 5
% of the biogas yield achieved during the first 48 h of digestion	–	52 ± 3	53 ± 0	53 ± 0	52 ± 1	–	37 ± 7	61 ± 3	62 ± 4
Average CH_4 content in the biogas (%)	–	68 ± 1	70 ± 1	69 ± 1	69 ± 0	–	57 ± 1	56 ± 1	55 ± 2
Enhancement of ADs enriched with CO_2									
Increase in normalised CH_4 yield (%)	–	–	8.0	5.5	13.3	–	–	−6.6	2.2
Increase in CH_4 production during the first 24 h (%)	–	–	14.4	11.1	16.3	–	–	95.9	137.9
Increase in biogas yield (%)	–	–	5.1	4.5	13.2	–	–	−6.3	3.5

[a] Control digester.
[b] Digesters enriched with $y_{CO_2} = 0.3$.
[c] Digesters enriched with $y_{CO_2} = 0.6$.
[d] Digesters enriched with $y_{CO_2} = 0.9$.

2), which confirmed that the initial acidification associated with CO_2 injection was overcome during the digestion process. Moreover, the lowest pH achieved in the sacrificial ADs after bubbling sewage sludge with CO_2 during 20 min, was 7.0 ± 0.1 (Fig. 2), which is above the pH of 6 stated as inhibitory by Gerardi (2003).

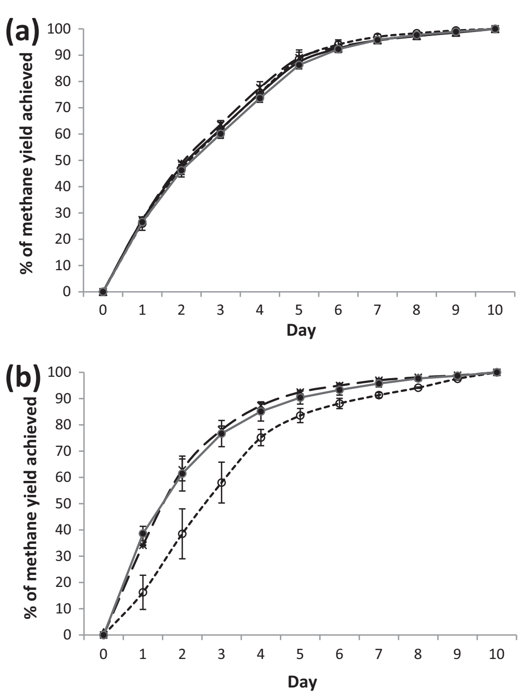

Fig. 3. Distribution of the methane production over time, as percentage of the methane yield achieved by each day of the digestion process, when treating food waste (a) and sewage sludge (b). *DC*: digesters control, *D0.3*: digesters enriched with $y_{CO_2} = 0.3$, *D0.6*: digesters enriched with $y_{CO_2} = 0.6$, *D0.9*: digesters enriched with $y_{CO_2} = 0.9$. The error bars represent the standard deviations.

Similar solids removals for the units enriched with CO_2 and the controls were observed, with the exception of sewage sludge ADs enriched with $y_{CO_2} = 0.3$, where the VS removal increased by 20% (Table 2). Sato and Ochi (1994) reported no benefit in the VS removal when enriching periodically with CO_2 in laboratory scale ADs (6 L) treating WAS. However, the same study observed an increase of solids reduction from 39.7% to 45.4% when digesting mixed sludge (primary and WAS) in pilot-scale units with periodic CO_2 injection.

In all the ADs treating sewage sludge and enriched with CO_2, the sCOD removal during the entire batch digestion period was enhanced. The removal of sCOD reached 43.3 ± 6.7% and 34.9 ± 8.3% when enriching with $y_{CO_2} = 0.3$ and $y_{CO_2} = 0.9$, respectively, whilst 29.9 ± 4.6% was recorded for the control units. Only on ADs bubbled with $y_{CO_2} = 0.3$ was observed an increased sCOD removal when digesting food waste (Table 2).

3.3. CO_2 utilisation in the batch digesters

The benefits in carbon footprint were initially quantified with a CO_2 mass balance (Eq. (5)) of the batch ADs, which considered the CO_2 dissolved in the material to digest after the enrichment, the CO_2 dissolved in the final digestates and that released with the biogas. The first two terms were estimated for equilibrium conditions with the p_{CO_2} of each injection (Table 1) or the headspace concentration, respectively, and assuming CO_2 solubility of 1071 mg L^{-1}. The CO_2 in the biogas was obtained from the daily monitoring data of biogas production and composition.

The mass balance allowed a preliminary comparison between the carbon footprint of the batch ADs enriched with CO_2 and the control units. The contribution of each of the reactions in which CO_2 was produced or consumed was gathered in the overall CO_2 emission term, as similarly reported by Alimahmoodi and Mulligan (2008).

The comparison between control and test ADs suggested CO_2 overall reductions of 8% and 34% for sewage sludge ADs enriched with y_{CO_2} of 0.3 and 0.9, respectively. Similarly, benefits of 3%, 10% and 11% were estimated for food waste ADs enriched with y_{CO_2} of 0.3, 0.6 and 0.9, respectively. If scaled-up, these carbon benefits associated with CO_2 enrichment of ADs, could significantly contribute towards the target to reduce GHG emissions at least an 80% by 2050 compared to 1990 (Climate Change Act, 2008). However, the benefits of CO_2 enrichment in the GHG emissions of ADs needs to be further investigated and quantified.

The complexity of the reactions taking place in ADs makes high the uncertainty regarding the mechanism of action by which the CO_2 could be utilised and bioconverted to CH_4. Besides, part of the CO_2 could have been transformed into other species (e.g., ammonia bicarbonates) rather than converted to CH_4, which further hinders stating a single mechanism of CO_2 utilisation. Alimahmoodi and Mulligan (2008) attributed the benefits to the encouragement of the hydrogenotrophic route for CH_4 production. On the contrary, Francioso et al. (2010) sustained that CO_2 boosts the volatile fatty acids (VFA) formation by combining with reducing compounds in the early stages of the digestion process according to the Wood–Ljungdahl pathway. In this study, CO_2 enrichment resulted in different CH_4 production patterns over time for food waste and sewage sludge ADs, which can help to hypothesize a CO_2 mechanism of action.

The initial increase in CH_4 production was significantly more pronounced when treating sewage sludge than when treating food waste, as stated before in terms of the production over the first 24 h (Table 2). Several studies have reported an inhibition of the acetoclastic methanogens at high ammonia concentrations (Banks et al., 2011, 2012; Borja et al., 1996; Rajagopal et al., 2013; Schnürer and Nordberg, 2008; Walker et al., 2011), making the hydrogenotrophic methanogenesis the dominant route for CH_4 formation. This has been demonstrated for food waste ADs, where the hydrolysis of proteins leads to inhibitory levels of ammonia (Banks et al., 2008; Chen et al., 2008; Mata-Alvarez, 2003; Schnürer and Nordberg, 2008; Siles et al., 2010; Walker et al., 2011). In this study, total ammonia concentration in digestates was around $4\ g\ L^{-1}$ NH_4–N in food waste ADs, which was higher than the $3\ g\ L^{-1}$ NH_4–N reported as completely inhibitory (Rajagopal et al., 2013) for the acetoclastic route of CH_4 formation. Thus, it is considered that the main mechanism of CH_4 production in the food waste ADs was hydrogenotrophic methanogenesis preceded by syntrophic acetate oxidation (SAO).

If the acetoclastic route is considered to be inhibited, the more moderate improvement of the CH_4 yield in food waste ADs could be due to the CO_2 being reduced by hydrogenotrophic methanogens. If only partly inhibited, the acetoclastic pathway could have been enhanced, leading to moderate benefits since it would have a much lower contribution to the CH_4 formation than the commonly accepted 70% (Conrad, 1999).

The ammonia content in the digestates of sewage sludge ADs ($1.1\ g\ L^{-1}$ NH_4–N) did not reach inhibitory levels, hence it is likely that both mechanisms of CH_4 formation were active when digesting this substrate. Consequently, the increased CH_4 formation in the sewage sludge ADs may be due to the enhancement of the acetoclastic pathway of CH_4 formation, likely due to an encouragement of the Wood–Ljungdahl mechanism in which CO_2 is reduced and acetate is formed (Müller, 2003; Ragsdale and Pierce, 2008). Salomoni et al. (2011) reported a 25% increased specific CH_4 yield when injecting CO_2 into the first stage of a TPAD treating sewage sludge. Since an efficient phase separation was stated, an injection into the first stage was also attributed to an encouragement of the acetogenic metabolism.

For both substrates the benefits were more emphasized during the first 48 h of digestion, which may be due to the CO_2 having being utilised to the levels prior to the enrichment or to other substrate limitation. The recovery from any initial acidification during the first 24–48 h of digestion (Fig. 2) may indicate that CO_2 was utilised up to the levels prior to the enrichment. This could support the possibility of CO_2 enrichment by periodic injections, which could potentially maintain the benefits observed over the 24 h period following CO_2 enrichment throughout the digestion process. However, the pH evolution is due to a combination of reactions (e.g., VFA formation/consumption) and not only due to CO_2 utilisation, therefore further testing would be required.

4. Conclusions

The effect of CO_2 enrichment of ADs was investigated for food waste and sewage sludge. An enhancement of CH_4 production was observed, demonstrating the potential of ADs to utilise additional CO_2. When treating food waste, CO_2 enrichment increased the CH_4 yield by up to 13%. For sewage sludge, CH_4 production increases of 96–138% were obtained during the first 24 h of digestion. Associated CO_2 reductions of 3–11% for food waste and 8–34% for sewage sludge were estimated. The different substrate response to CO_2 observed could indicate that CO_2 enrichment enhanced the acetoclastic pathway of CH_4 formation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.02.010.

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