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Controlled experiment contradicts the apparent benefits of the Fenton reaction during anaerobic digestion at a municipal wastewater treatment plant

Ahmet E. Uman, Joseph G. Usack, José L. Lozano and Largus T. Angenent

ABSTRACT

A previous study had reported that the Fenton reaction at full scale increased the digestibility of thickened sludge in a digester. The authors of the study had observed a positive effect on biogas productivity, but without a control. Here, we evaluated this result by investigating the anaerobic treatment characteristics of fresh, thickened sludge in an experimental design with a control. To accomplish this, two identical continuously stirred anaerobic digesters (CSADs) were operated in parallel at mesophilic conditions. We also included anaerobic settlers to mimic the full-scale plant and to accomplish sludge recycling. We fed fresh, thickened sludge to both setups once every other day, but performed the Fenton reaction with only the experimental system by adding H_2O_2 to the recycled biosolids from the anaerobic settler. We observed very large fluctuations in biogas production due to ever-changing characteristics of the thickened sludge both on a daily and seasonal basis. Regardless, the two setups performed almost identically with: 1) chemical oxygen demand removal efficiencies of $63.8 \pm 2.9\%$ and $62.1 \pm 3.2\%$; and 2) biogas productivities of 0.280 and 0.279 L $CH_4 \cdot g^{-1}$ volatile solids for the experimental (with Fenton) and control (without Fenton) CSADs, respectively. These results indicate that the use of a Fenton reaction did not affect biogas productivities.

Key words | anaerobic digestion, biogas, Fenton reaction, thickened sludge, wastewater treatment

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INTRODUCTION

Water, energy, and food demands, along with their impacts on climate change, have increased the need and importance of resource recovery all over the world. Wastewater is being considered as a source of water, energy, and nutrients, such as nitrogen (N) and phosphorus (P) (Guest *et al.* 2009), stimulating innovation within the field of environmental engineering. For more than 100 years, wastewater treatment facilities have used the waste activated sludge (WAS) process to achieve a high-quality effluent. However, the process requires considerable energy inputs due to aeration, which could reach 40–60% of the total energy requirements of a treatment facility (Gikas 2017). Environmental engineers have posed the question whether the organic material in the wastewater could be used as the only source of energy to power a treatment facility (McCarty *et al.* 2011). Anaerobic digestion has already been used for many years as a secondary treatment technology to recover energy and stabilize

WAS. Typically, the energy is recovered from the sludge that is produced at the facility by: (1) settling primary sludge from domestic wastewater; and (2) growing and settling secondary sludge (WAS). This combined sludge is further settled and is referred to as thickened sludge. One possibility to improve the recovery of energy is to increase the digestibility of this sludge. In the USA, many domestic wastewater treatment facilities deploy a two-stage anaerobic digestion system for thickened sludge treatment with a continuously stirred anaerobic digester (CSAD) followed by an anaerobic settling tank (Appels *et al.* 2008).

Anaerobic digestion is a biological process with different groups of microbes that degrade complex organic molecules as a consortium. Hydrolysis is the first stage in the degradation and for difficult-to-degrade complex substrates, such as WAS, it is often the rate-limiting step in anaerobic digestion. To accelerate the hydrolysis of sludge and to ultimately

enhance the biogas productivity (i.e., yield) and solids removal efficiency, several pretreatment methods have been utilized. The mechanism for improving the digestibility of sludge is to make the intracellular material accessible by cell membrane breakage. The methods include: (1) biological methods, such as temperature-phased anaerobic digestion (Han & Dague 1997); (2) mechanical methods, such as ultrasound and maceration (Khanal *et al.* 2007; Cho *et al.* 2014); (3) thermal methods, such as thermohydrolysis (Bougrier *et al.* 2008; Pilli *et al.* 2015; Li & Yu 2016); (4) thermochemical methods, such as hydrothermal liquefaction (Posmanik *et al.* 2017; Angenent *et al.* 2018); and (5) chemical methods, such as ozone (O_3) and alkali treatment (Bougrier *et al.* 2006; Cho *et al.* 2014).

Instead of calcium hydroxide ($Ca(OH)_2$), sodium hydroxide ($NaOH$), magnesium hydroxide ($Mg(OH)_2$), or potassium hydroxide (KOH) as chemical additions for alkali sludge pretreatment (López Torres & Espinosa Lloréns 2008), hydrogen peroxide (H_2O_2) has also been added to pretreat lignocellulosic biomass with the Fenton reaction before anaerobic digestion (Michalska *et al.* 2012). The application of H_2O_2 itself is not effective, but rather a strong oxidative power is triggered by the presence of other substances to generate hydroxyl radicals (•OH) and hydroperoxyl radicals (HO_2•), which are some of the most reactive chemical species known (Bishop *et al.* 1968). Iron(II) and H_2O_2 can generate •OH directly, while iron(III) and H_2O_2 can generate HO_2• directly, and then •OH after another reaction of the formed iron(II) and more H_2O_2 (Bishop *et al.* 1968). Other chemical species that can form radicals with H_2O_2 are O_3 and ultraviolet light (Neyens & Baeyens 2003). A study by Lozano (2010) reported the application of the Fenton reaction to recycled biosolids from the anaerobic digester to improve the digestibility of sludge at a wastewater treatment facility, and he reported an increase in biogas production of 13%. Because this had been implemented in a full-scale treatment plant, however, it was not possible to include a control. Similar results, especially increased biosolid disintegration, have also been reported in other studies (Cacho Rivero *et al.* 2006; Eskicioglu *et al.* 2008; Shahriari *et al.* 2012), which further substantiates the effectiveness of certain oxidative treatments. However, so far, only short-term, laboratory-scale experiments using batches of uniform wastewater sludge have been employed. These experiments would not capture the potentially important role of daily or seasonal changes in sludge composition on the long-term effectiveness of oxidative treatment.

Here, our objective was to conduct a controlled experiment to determine whether treating recycled biosolids with the Fenton reaction would augment biogas production and solids destruction as previously reported. Moreover, to account for sludge variability and to better mimic full-scale conditions, we operated two pilot-scale anaerobic digester systems during a 280-day period at a real wastewater treatment facility, using fresh thickened sludge taken directly from the thickening unit.

MATERIALS AND METHODS

System setup and inoculum

Two CSADs were operated at mesophilic conditions ($32 \pm 1\,°C$) with an effective volume of 45 L each (Figure 1(a)). Mixing was achieved by circulating 1.04 L·min^{-1} of the head
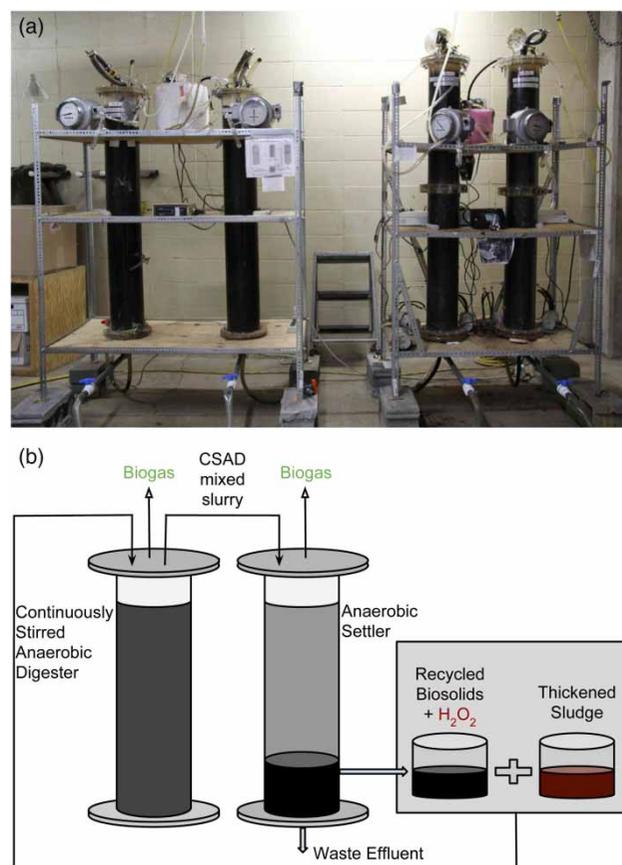
Figure 1 | Setup of the 45-L continuously stirred anaerobic digester (CSAD) and anaerobic settler with biosolids recycling: (a) picture of pilot-scale CSADs on the right and anaerobic settlers on the left; (b) schematic of the pilot-scale CSADs. The grey box shows the substrate preparation procedure. The influent mixtures for both the experimental and control system consisted of recycled biosolids and fresh, thickened sludge. For the experimental system, the H_2O_2 was first added to the recycled biosolids to complete the Fenton reaction before being fed to the CSAD.

space biogas from top to the bottom of the CSADs by using peristaltic pumps (Cole-Parmer; Vermon Hills, IL, USA). Two anaerobic settlers were built similar to the CSADs except that mixing and heating were omitted. These anaerobic settlers were operated at room temperature ($25 \pm 1\ ^\circ$C). One CSAD was placed in series with one anaerobic settler to achieve two identical two-stage systems. The CSADs and anaerobic settlers were inoculated by filling them with active biomass containing $9.57 \pm 0.1\ \mathrm{g \cdot L^{-1}}$ volatile solids (VS) from the full-scale CSAD of the Ithaca Area Waste Water Treatment Facility (IAWWTF).

Influent composition and experimental conditions

To mimic the influent composition of the full-scale system, fresh, thickened sludge, consisting of primary sludge, secondary sludge, tertiary sludge, and additional co-substrates, such as septage, alkaline hydrolysate (Usack & Angenent 2015), acid whey (Xu *et al.* 2018), and de-icing fluid (Gruden *et al.* 2001), was taken from the thickening unit of the IAWWTF immediately before feeding. This thickened sludge was then combined at a 1:1 ratio (v/v) with the recycled biosolids that had been decanted from the anaerobic settler of the pilot-scale system (Figure 1(b)). A total volume of 6 L of this influent mixture was fed every other day to each of the two CSADs, resulting in a hydraulic retention time (HRT) of 30 days for the CSAD and 60 days for the total system. Both experimental and control systems were operated under identical operating conditions during Phase I (Days 0–179). During Phase II (Days 180–219), 2.2 mL of 50% H_2O_2 was added into the recycled biosolids of the anaerobic settler to obtain a 0.03% (v/v) concentration. After manual mixing and an approximate 10-min reaction time to complete the Fenton reaction, the recycled biosolids and the fresh, thickened sludge were added to the CSADs. During Phase III (Days 220–280), the H_2O_2 amount was increased 10 times to obtain a 0.3% (v/v) concentration.

Monitoring parameters and analytical methods

Every alternate day, biogas production (Actaris Meterfabriek, Delft, the Netherlands), CSAD temperature, effluent pH (AB15+, Fisher-Scientific, Pittsburg, PA, USA), and ambient pressure and temperature were monitored. Biogas production was corrected for ambient temperature and pressure to 25 °C and 101.6 kPa. Alkalinity, ammonium (Model Orion 95-12; Thermo-Scientific, Waltham, MA, USA), soluble chemical oxygen demand (SCOD), total chemical oxygen demand (TCOD), total volatile fatty acids

(TVFAs), total solids (TS), and VS analyses were performed for the influent and effluent of the CSADs and anaerobic settlers. Biogas composition was measured using a gas chromatograph (SRI Instruments 8610C, Lehigh Valley, PA, USA), which was equipped with a thermal conductivity detector and a packed column (0.3-m HaySep-D packed Teflon; Restek, Bellefonte, PA, USA).

Biochemical methane potential analysis

The biochemical methane potential (BMP) method for measuring the methane production yield of the substrate with an increasing application of H_2O_2 was performed according to Posmanik *et al.* (2017). For substrate preparation, varying percentages (i.e., 0, 0.037, 0.19, 0.37, 0.55, 0.74, and 1.85% (v/v)) of H_2O_2 was added into the recycled biosolids from the anaerobic settler of the control pilot-scale bioreactor setup (no H_2O_2 addition). To avoid inhibiting the methanogens within the BMP analysis, H_2O_2 was allowed to react with the recycled biosolids for 2 h. Next, fresh, thickened sludge from the thickeners at the IAWWTF was then added to the mixture at 1:1 (v/v) to mimic the same conditions compared to the pilot-scale anaerobic digestion system. The resulting solution of recycled biosolids with H_2O_2 and thickened sludge from the WWTP was then added to the empty 250-mL media bottles. Subsequently, the nutrient solution, which included required trace elements and nutrients (Posmanik *et al.* 2017), was added to the bottles. Finally, the inoculum, which consisted of the effluent from the pilot-scale CSAD, was added to the bottles. The inoculum:substrate ratio was 2:1 (VS basis). Control bottles only included the nutrient solution and the inoculum. All bottles were flushed with nitrogen, sealed, and stored at 32 °C for 30 days. Biogas volume and content measurements were made periodically using a wet-syringe method and gas chromatography (HP Hewlett Packard 5890 Series II, Palo Alto, CA, USA).

RESULTS AND DISCUSSION

The two bioreactor systems, consisting of a CSAD followed by an anaerobic settler, achieved similar biogas production, chemical oxygen demand (COD) removal efficiencies, solids removal efficiencies, and ammonia concentrations during the identical operating conditions and feeding strategies of Phase I (Table 1; Figure 2). Both systems showed equally variable performance parameters that were proportional to the always-changing influent composition. The influent

Table 1 | Summary of average performance data or average effluent concentrations for experimental and control CSADs during the entire operating period

Parameter	Form	Units	Experimental			Control		
			Phase I	Phase II	Phase III	Phase I	Phase II	Phase III
Biogas production rate	–	L·d^{-1}	11.99 ± 5.9[a] (n = 90)	11.87 ± 5.4 (n = 14)	10.21 ± 3 (n = 31)	11.92 ± 6[a] (n = 90)	11.59 ± 5.5 (n = 14)	10.36 ± 3 (n = 31)
COD concentration	TCOD	g·L^{-1}	17.93 ± 0.6 (n = 20)	18.75 ± 0.5 (n = 4)	20.04 ± 0.9 (n = 4)	17.18 ± 0.62 (n = 20)	18.77 ± 0.71 (n = 4)	19.82 ± 0.41 (n = 4)
	SCOD	mg·L^{-1}	272.4 ± 13.7 (n = 21)	256.9 ± 10.3 (n = 5)	287.1 ± 12.2 (n = 5)	269.9 ± 10.6 (n = 21)	262.3 ± 9.8 (n = 5)	257.9 ± 14.1 (n = 5)
COD removal efficiency	TCOD	%	58.9 ± 7.7 (n = 20)	63.75 ± 2.9 (n = 4)	68.10 ± 11.2 (n = 4)	62.63 ± 8.7 (n = 20)	62.12 ± 3.2 (n = 4)	60.81 ± 16.7 (n = 4)
	SCOD	%	79.60 ± 9.5 (n = 21)	86.80 ± 8.2 (n = 4)	91.75 ± 1.2 (n = 4)	79.70 ± 9.8 (n = 21)	84.64 ± 8.5 (n = 4)	91.02 ± 1.5 (n = 4)
TVFA concentration	–	mg·L^{-1}	55.2	70.6	51.2	45.2	54.05	55.2
Ammonia concentration	N	mg·L^{-1}	728.4	945.4	778.4	726.8	910.7	745.8
Solids concentration	TS	g·L^{-1}	18.42 ± 0.11 (n = 10)	21.25 ± 0.14 (n = 4)	18.23 ± 0.37 (n = 5)	18.89 ± 0.69 (n = 10)	22.03 ± 0.09 (n = 4)	17.86 ± 0.11 (n = 5)
	VS	g·L^{-1}	10.68 ± 0.12 (n = 10)	11.69 ± 0.12 (n = 4)	9.68 ± 0.18 (n = 5)	11.10 ± 0.62 (n = 10)	12.26 ± 0.05 (n = 4)	9.57 ± 0.09 (n = 5)
Solids removal efficiency	TS	%	56.53 ± 5.4 (n = 10)	57.54 ± 2.0 (n = 4)	58.52 ± 6.4 (n = 5)	59.12 ± 5.3 (n = 10)	55.51 ± 2.3 (n = 4)	53.23 ± 13.8 (n = 5)
	VS	%	61.05 ± 4.9 (n = 10)	63.98 ± 3.0 (n = 4)	61.84 ± 7.0 (n = 5)	62.74 ± 4.8 (n = 10)	60.52 ± 2.1 (n = 4)	56.13 ± 15.7 (n = 5)
Alkalinity	CaCO$_3$	mg·L^{-1}	3,750	3,680	3,640	3,690	3,700	3,620
pH	–	–	7.09 ± 0.21 (n = 90)	6.91 ± 0.12 (n = 14)	6.92 ± 0.16 (n = 31)	7.11 ± 0.17 (n = 90)	6.93 ± 0.14 (n = 14)	6.94 ± 0.15 (n = 31)

[a]First 30 days excluded for both CSADs. In addition, a correction factor of 0.704 L·d^{-1} was subtracted from all the data through days 30–180 for only the experimental CSAD due to an experimental error in biogas production measurement. Error bars represent the standard deviation of the measurements.

TCOD concentration for the fresh thickened sludge was particularly variable, in the range 11–38 g·L^{-1} (Figure 2(b)), which is partly caused by constant changes in the relative proportion of primary sludge, secondary sludge, tertiary sludge, and additional co-substrates. The TCOD concentration of the combined thickened sludge and recycled biosolids was also variable, in the range 29–68 g·L^{-1}. Considering the high variably of the influent, it is notable that such a high level of consistency between the bioreactor systems was achieved (Figure 2). The CSADs were responsive to these fluctuations and produced equally varying biogas production rates in accordance with the changing COD loading rates (Figure 2(a)–2(c)), while the anaerobic settlers produced very little biogas (i.e., approximately 2% of that produced by the CSADs).

The concentrations of ammonia and TVFAs, which are break-down products of hydrolysis, could be inhibitory to anaerobic digestion when their concentrations are higher than approximately 4,500 mg N·L^{-1} for total ammonia (De Baere *et al.* 1984) and 1,000 mg·L^{-1} for TVFAs (Speece 1996). For our study, the ammonia concentration remained within the recommended range for anaerobic digestion and did not exceed these limits (Figure 2(d); Table 1). The TVFA concentrations remained below 75 mg·L^{-1} (Table 1), resulting in relatively low SCOD concentrations throughout the entire operating period of approximately 250 mg·L^{-1} (Figure 2(c)). Alkalinity was measured as calcium carbonate (CaCO$_3$) and was used to observe the stability of the CSADs. An alkalinity level of 2,530–5,890 mg CaCO$_3$·L^{-1} was observed during the operating period for the CSADs (Table 1). The evaluation of all these concentrations in combination with a neutral pH (Table 1) indicates that stable conditions were maintained during the entire operating period.
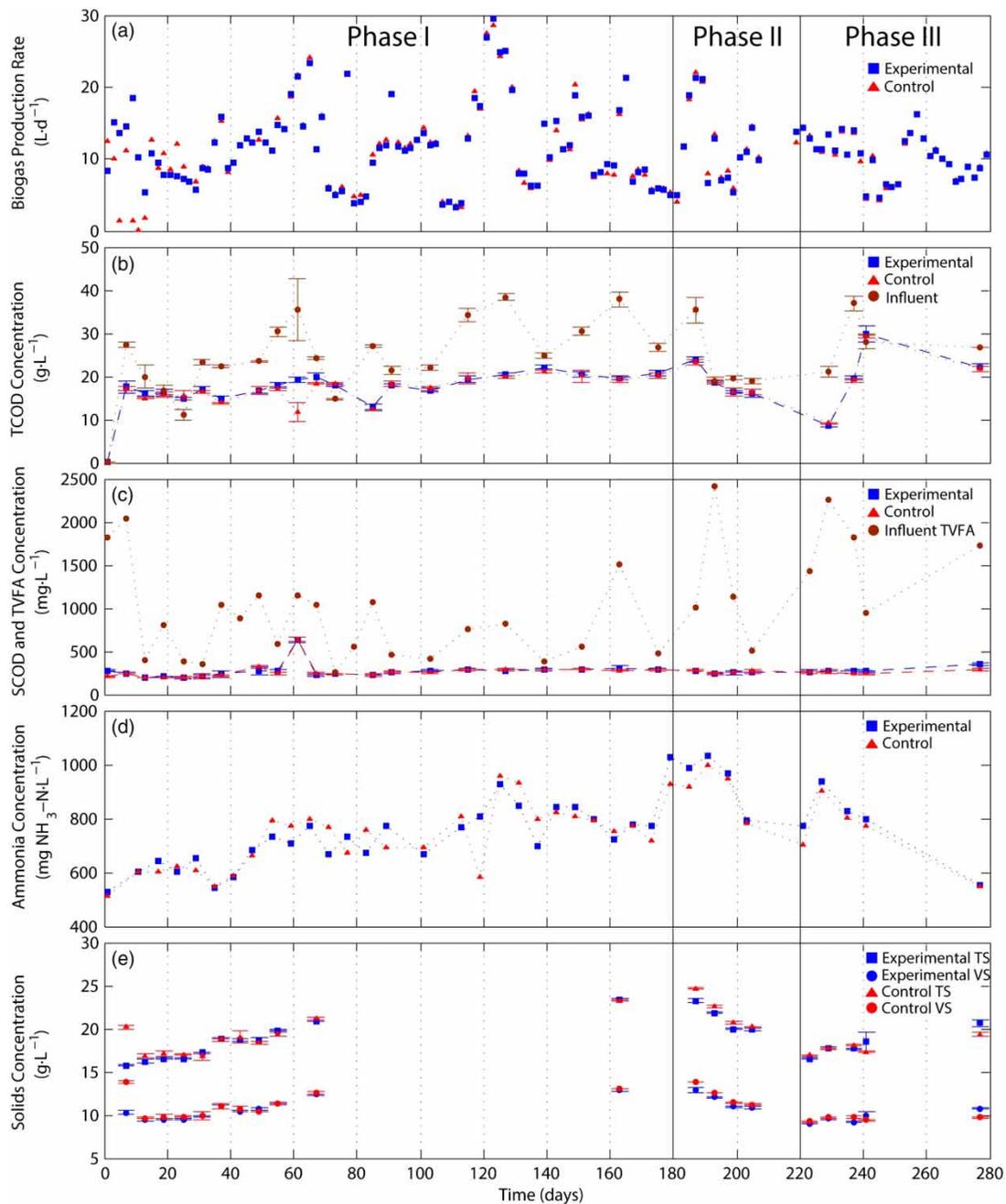
Figure 2 │ Operating and performance data for the CSADs: (a) biogas production rate; (b) TCOD concentration of influent and effluent; (c) SCOD concentration of effluent and TVFA concentration of influent; (d) ammonia concentration of effluent; (e) solids concentrations of effluent. Phase I: no H_2O_2 added; Phase II: 0.03% (v/v) H_2O_2 added into the recycled biosolids of the experimental system; Phase III: 0.3% (v/v) H_2O_2 added into the recycled biosolids of the experimental system. Error bars represent the standard deviation of the measurements.

We had anticipated similar performance parameters between both bioreactor setups during Phase I when they were operated identically. Other studies had already observed similar performances and community structures for identical operating conditions between bioreactors (Vanwonterghem *et al.* 2014; Werner *et al.* 2014). It was a surprise to us that this consistency between experimental and control bioreactor setups was also observed during Phases II and III when H_2O_2 was applied. The average biogas production rates remained similar at 11.87 and 10.21 L·d^{-1} for the experimental CSAD and 11.59 and 10.37 L·d^{-1} for the control CSAD during Phases II

and III, respectively (Figure 2(a); Table 1). A paired sample *t*-test comparing the biogas production rates between the experimental and control CSADs throughout the entire operating period showed no statistical difference at an *α*-value of 0.05, resulting in a *p*-value of 0.93. The overall hydrolysis was similar, resulting in the same TCOD concentrations of 18.75 ± 0.5 and $20.04 \pm 0.9 \text{ g·L}^{-1}$ for the experimental CSAD and 18.77 ± 0.71 and $19.82 \pm 0.41 \text{ g·L}^{-1}$ for the control CSAD during Phases II and III, respectively (Figure 2(b)). SCOD concentrations of the effluents from the CSADs were rather stable and showed no change in Phases II and III or between experimental and control CSADs (Figure 2(c)). Finally, the ammonia and solids concentrations were also similar, showing that hydrolysis was not different between the bioreactor setups (Figure 2(d) and 2(e)). Stable ammonia and solids concentrations were also observed in two similar studies conducted by Cacho Rivero *et al.* (2005, 2006). The dosing rates of H_2O_2 in these studies (i.e., 0.5, 1.0, and 2.0 g $H_2O_2 \cdot \text{g}^{-1}$ volatile suspended solids), were considerably higher than the dosing rate used in this study, which

suggests H_2O_2 availability is not an important determinant of oxidative treatment effectiveness.

With the equal performances for the CSADs for the experimental and control systems after placing the Fenton reaction in the digester sludge line for the test system only, the possibility could have emerged that the performance for the anaerobic settler within the experimental setup was improved. However, we did not observe this shift in importance in treatment performance for the experimental system compared to the control system (Figure 3). Based on TCOD concentration (Figure 3(a)), SCOD concentration (Figure 3(b)), and ammonia concentration (Figure 3(c)) in the effluent of the anaerobic settler, we did not observe a consistent difference in the treatment performance before and after the Fenton reaction application for the experimental system (between Phase I and Phase II); nor did we observe such a difference between the experimental and control system. We have already discussed that the non-heated and non-mixed anaerobic settlers did not perform much of the treatment in terms of biogas production. This also holds true for hydrolysis, because the ammonia
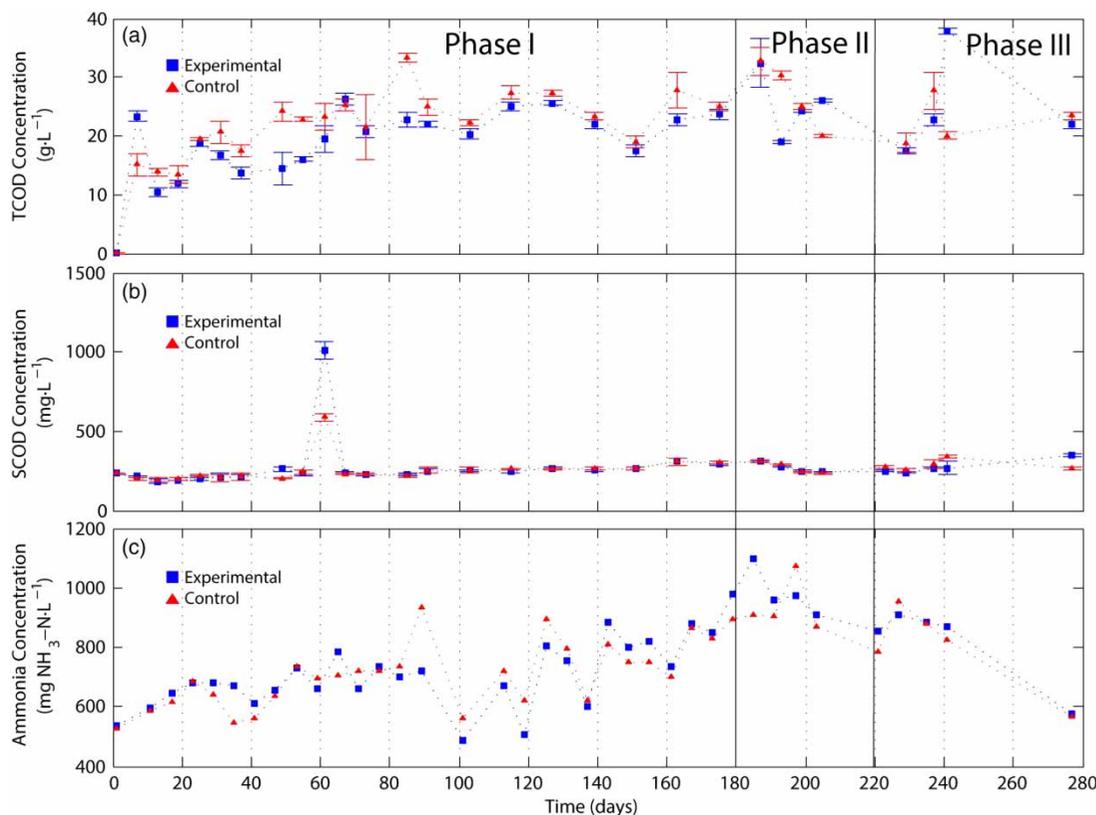

Figure 3 | Performance data during the operation period for anaerobic settlers: (a) TCOD concentration; (b) SCOD concentration; (c) ammonia concentration. Phase I: no H_2O_2 added; Phase II: 0.03% (v/v) H_2O_2 added into the recycled biosolids of the experimental system; Phase III: 0.3% (v/v) H_2O_2 added into the recycled biosolids of the experimental system. Error bars represent the standard deviation of the measurements. For (c) we did not use zero at the origin of the *y*-axis to better compare the ammonia concentrations.

concentrations were not considerably different between systems at the end of the operating period (Phase III in Figure 3(c)).

H$_2$O$_2$ addition, therefore, did not cause any noticeable performance change for the overall experimental system when compared to the overall control system during either Phase II or III. However, H$_2$O$_2$ addition to the recycled biosolids material did increase its SCOD concentration, resulting in a different recycled biosolids between the experimental and control system (Figure 4(a)). The SCOD concentration for the H$_2$O$_2$-treated recycled biosolids was approximately 1.5 times higher than that of the untreated biosolids during Phase II (Figure 4(a)). The SCOD concentration was approximately two times higher for the treated recycled biosolids compared to the untreated recycled biosolids after a 10 times higher concentration of H$_2$O$_2$ was applied during Phase III (Figure 4(a)). These increases in SCOD concentration are within the range of values observed in other studies, such as between the ~20–40% increase observed by Shahriari et al. (2012) and the ~400%

increase observed by Eskicioglu et al. (2008). The higher concentrations of SCOD occurred because of the formation of free radicals as a result of the Fenton reaction, with a noticeable and immediate foam formation when applied to recycled biosolids. Yet, while the free radicals increased the speed of disintegration of some particulate solids in the recycled biosolids, the relatively long HRT of the CSADs rendered this effect inconsequential, providing ample time for regular hydrolysis in the first-stage bioreactor to take place.

Also, in a previous pretreatment study of a mixture of primary and secondary sludge, the application of ultrasound to the fresh sludge had increased the SCOD concentration considerably, but the combination of ultrasound and H$_2$O$_2$ application did not result in a further increase in SCOD concentration compared to the ultrasound treatment alone. The H$_2$O$_2$ application of fresh sludge without ultrasound treatment had increased the SCOD concentration slightly (Grönroos et al. 2005). Of course, the sludge quality is important and treatment before or after anaerobic digestion
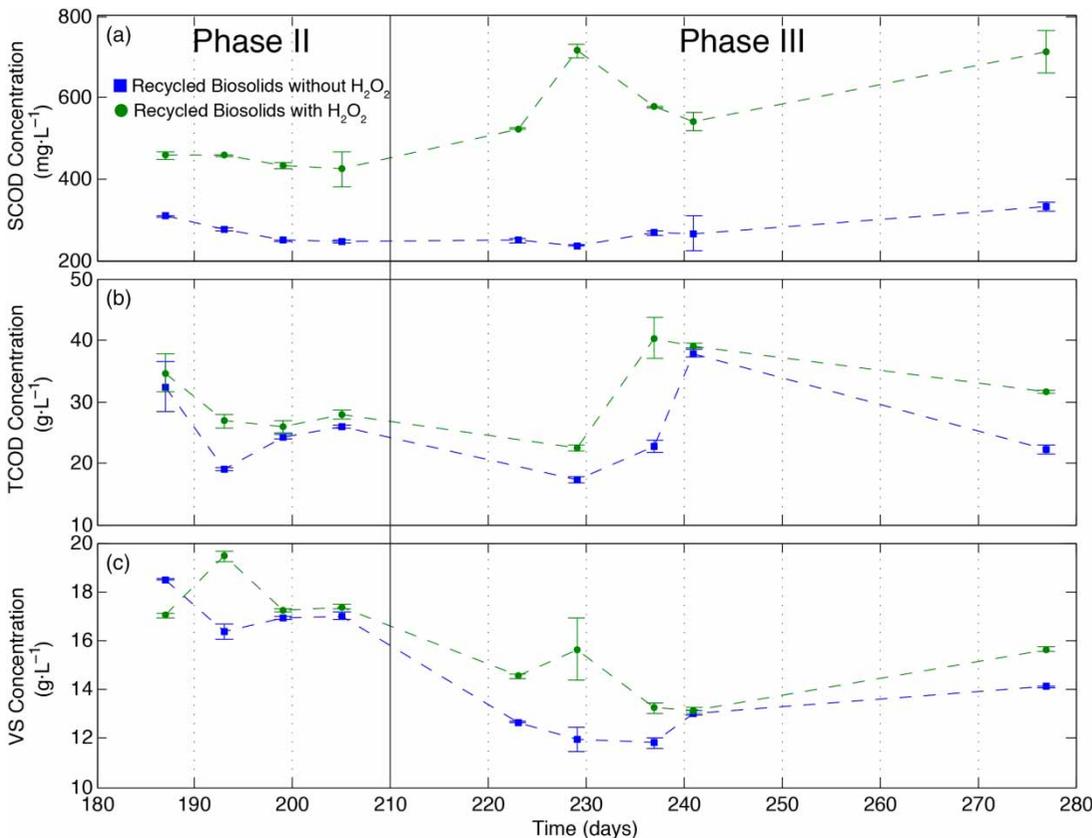

Figure 4 │ Effluent characteristics of the recycled sludge with and without H$_2$O$_2$ during the operating period for recycled biosolids: (a) SCOD concentration; (b) TCOD concentration; (c) VS concentration. Phase II: 0.03% (v/v) H$_2$O$_2$ added into the recycled biosolids of the experimental system; Phase III: 0.3% (v/v) H$_2$O$_2$ added into the recycled biosolids of the experimental system. Error bars represent the standard deviation of the measurements. To more clearly show the differences for the recycled sludge, we did not use zero at the origin of the y-axes.

treatment would result in a different outcome. Bougrier et al. (2008) already discussed that if the sludge is readily biodegradable, the oxidative pretreatment would not be as effective. That is why we treated the recycled biosolids with H_2O_2 after digestion.

Regardless of the higher concentration of SCOD in the recycled biosolids, the biogas production rates did not improve with H_2O_2 treatment in our study. These findings are in agreement with a previous study during which H_2O_2 was also added to recycled biosolids for a one-stage mesophilic anaerobic digester (37 °C, 8 L of active volume). This previous study also included treatment of a mixture of primary and secondary sludge in their anaerobic digesters and the authors did not observe enhanced biogas production with H_2O_2 addition (Cacho Rivero et al. 2006). However, when they pretreated the recycled biosolids with heat at 90 °C and applied H_2O_2, a significant increase in biogas production rate was reported (Cacho Rivero et al. 2006). Here, we did not test the heating step, because the heating of large quantities of sludge was deemed uneconomical.

The BMP test also showed no significant difference in the ultimate biogas and methane production yield for the recycled biosolids when the H_2O_2 concentration was increased (Figure 5(a)–5(c)). At the end of a 30-day incubation period, the total methane production was between 14.8 ± 2.2 and 18.9 ± 2.3 mL for the seven treatments (0, 0.037, 0.19, 0.37, 0.55, 0.74, and 1.86% for $n = 2$, 3, 3, 3, 3, 3, and 3, respectively) (Figure 5(b)). The difference between the varying H_2O_2 samples and the control was insignificant, resulting in p-values of 1.0, 0.45, 0.76, 0.57, 0.70, and 0.59 (t-test at an α-value of 0.05). Thus, the bioreactor and the BMP results were in agreement in terms of the ultimate biogas and methane yields, and in addition showed that applying more H_2O_2 would not have led to a different outcome.

While the biogas productivity was not enhanced, a higher TS removal efficiency was observed in our study for the experimental CSAD compared to the control CSAD. For example, at the end of Phase III, the TS removal efficiency was 58.5% and 53.2% for the experimental and
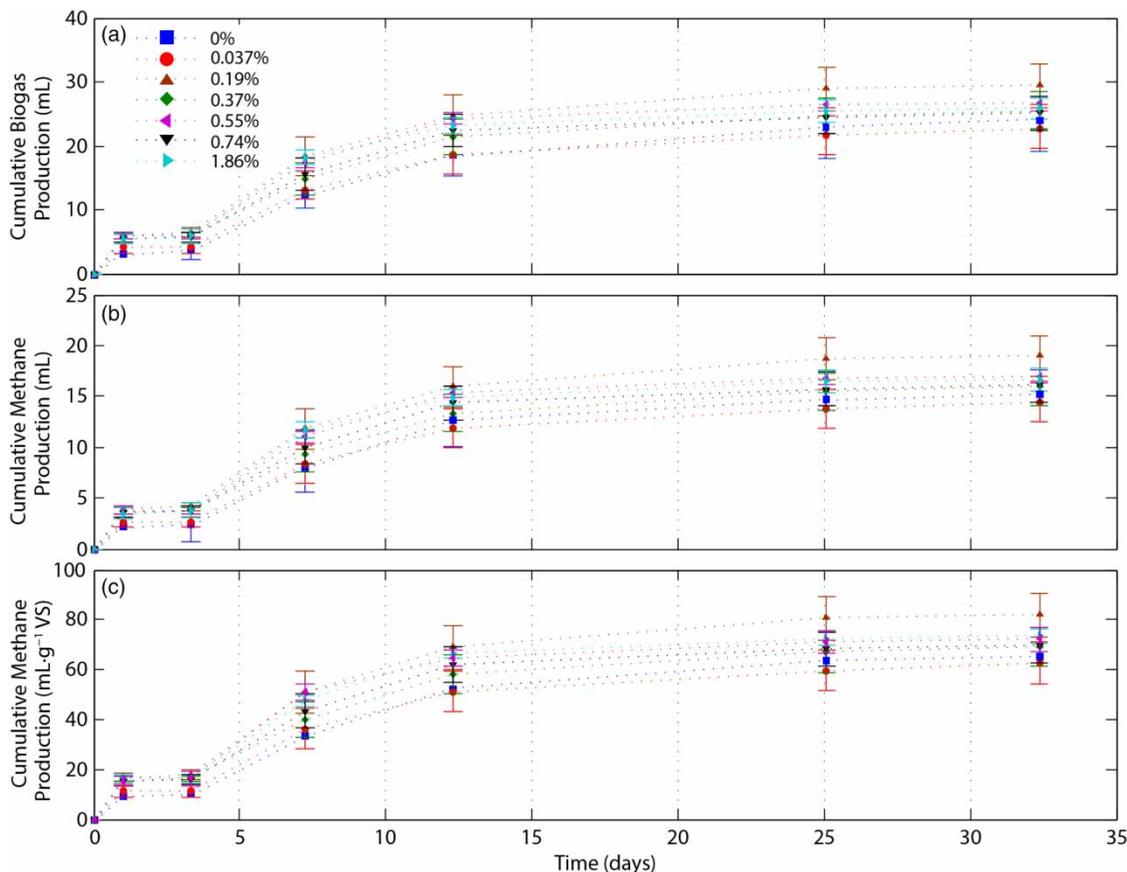
Figure 5 | Biochemical methane potential of varying H_2O_2 samples: (a) cumulative biogas production; (b) cumulative methane production; (c) cumulative methane production when corrected for biomass concentration. Error bars represent the standard deviation of the measurements.

control CSADs, respectively (Table 1). The TS concentrations for both CSADs were similar throughout the entire operating period (between 17.9 and 22.0 g L^{-1} in Table 1), and the different TS removal efficiency must have, therefore, been affected by the higher TS concentration in the recycled biosolids. Indeed, the TCOD and solids concentration for the recycled biosolids from the experimental settler were higher than from the control settler (Figure 4(b) and 4(c)). H_2O_2 was reported to increase the dewaterability and settleablity, which in this circumstance was the likely reason for the increase in solids concentrations from the experimental settler compared to the control settler (Kim *et al.* 2009).

We were unable to replicate the 13% increase in biogas production and 11.5% reduction in biosolids which was previously reported by Lozano (2010) from a full-scale implementation of the Fenton reaction. We believe that the temporal fluctuations of the biosolids quality in the thickeners at the IAWWTP are so large that observed changes in gas production could have been caused by variation in sludge characteristics, rather than improved digestibility. These results highlight the difficulty of evaluating performance changes in full-scale wastewater treatment facilities following process modifications. Moreover, it emphasizes the importance of performing controlled reactor experiments at either laboratory or pilot scale prior to full-scale implementation.

CONCLUSIONS

We verified here that anaerobic digestion is a highly stable and predictable system once it reaches pseudo steady-state conditions and exhibits similar performances under identical operation conditions. We observed that two identical CSAD systems were able to achieve the same variable performances and responses during continuous variations in the influent quality. We also confirmed that the addition of H_2O_2 to recycling biosolids after anaerobic digestion has the potential of accelerating the disintegration and hydrolysis rates of the biosolids itself, but that it had no effect on biogas production rates in our anaerobic digesters, which were characterized by a relatively long HRT of 30 days. An earlier observed increase in biogas production rate in a full-scale wastewater facility without a control was likely an artifact of the highly variable operating conditions and resulting performances (both daily and seasonally).

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