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pH-Based Control of Anaerobic Digestion to Maximise Ammonium Production in Liquid Digestate

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Abstract: A typically overlooked by-product of the anaerobic digestion process is the liquid digestate. The digestate is generally high in valuable nutrients like nitrogen, potassium, and phosphorus, which are essential for plant growth. This indicates that digestate can be an effective fertilizer. In this study, the pH of the anaerobic digestion process was controlled at three different set points (6, 7, and 8) for three different substrates (banana peels, cow dung, and red lentils) in order to determine the ammonium release characteristics at each set point. This was achieved by using two different set-ups; one set-up, named the daily dosing set-up (DDS), incorporated pH corrections once a day, and the other set-up, named the continuous dosing set-up (CDS), corrected the pH every minute. It was discovered that a pH of 7 is the optimal set point for both ammonium release as well as the gas production rate. In terms of a comparative analysis between precise pH control being performed every minute and pH control that was performed once a day, there were differences present in the gas production profiles with the CDS providing enhanced rates compared to the DDS. However, there was a negligible difference in the ammonium release rate.

Keywords: anaerobic digestion; digestate; fertilizer; ammonium; pH

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1. Introduction

Anaerobic digestion is a process whereby microorganisms break down waste materials into simpler compounds, while simultaneously producing a biogas that is typically high in methane and carbon dioxide content (60–70% methane and 30–40% carbon dioxide) with trace amounts of hydrogen sulphide and some water vapour [1]. Methane, in particular, is a highly desirable product because it is an energy dense fuel that can be easily stored [2]. The energy potential of this process cannot be overstated; the Environmental and Energy Study Institute estimates that a feed of one ton of biowaste generally translates to an electricity yield of 250 kWh [3]. This process has been exploited magnificently by countries throughout the European Union in recent years. Countries, such as Germany, Spain, and The Netherlands, have anaerobic digestion plants that convert organic waste (primarily food waste, green waste, and agricultural waste) into biogas. As recently as 2020, the European Biogas Association reported that there were approximately 20,000 biogas and biomethane units in operation (a striking increase from roughly 10,000 units in 2010); this amounted to 191 TWh of total energy production, which, in turn, accounted for around 4.6% of the European Union's gas consumption. However, this sector is expected to increase fivefold by 2050, with estimates suggesting that the energy production from biogas plants could be as high as 1000 TWh, which would account for around 30–40% of the EU's total gas consumption [4–6].

However, a typically overlooked by-product of the anaerobic digestion process is the digestate. The digestate is the material that remains after the anaerobic digestion process. The digestate is generally high in valuable nutrients, such as nitrogen, potassium, and phosphorus, all of which are considered essential for plant growth [7,8]. This indicates that digestate has the potential to be an extremely effective fertiliser. The digestate is

comprised of solid and liquid phases. Solid digestate is routinely used by farmers as livestock bedding or composted with minimal processing [9]. Liquid digestate, on the other hand, has seen a vast increase in usage by farmers as a fertilizer that can be applied on farmlands because of its high macronutrient concentration. The nitrogen that is available in the liquid digestate is generally in the form of either ammonium or ammonia, depending on the pH of the solution [10]. Anaerobic digestion may produce 1.5–6.5 g/L of nitrogen in the liquid digestate, with around 60–80% of that nitrogen typically being ammonium [10–12], however, the ammonium content in the digestate generally depends on the type of feedstock that is used, with protein-rich feedstock customarily providing higher ammonium content in the digestate. This indicates that liquid digestate could be suitable as a fertilizer for soilless agriculture [10].

Soilless agriculture is a possible solution to the myriad of problems that are currently plaguing the agricultural sector. Not only does this approach save on both land and water, but it also has the added advantages of having better control over the nutrients and water that are delivered to the plants, thus making it easier to grow healthy plants consistently [13,14]. However, similar to conventional farming, soilless agriculture remains largely dependent upon harmful mineral fertilisers, although admittedly in smaller quantities [15].

There has been surprisingly limited research done on the use of liquid digestate in soilless agriculture; this is in large part due to the fact that organic fertilisers tend to be poisonous to plants [16]. However, there has been a recent surge in the number of researchers who are interested in liquid digestate as a fertiliser, with varying degrees of success. Some researchers argue that the use of digestate in hydroponics leads to poor plant growth—this poor growth is typically attributed to low concentrations of plant-available macronutrients, such as phosphorus and sulphur, in the liquid digestate, as well as ammonia phytotoxicity [16–18]—whereas other researchers argue that the use of digestate in hydroponic systems has a beneficial effect on plant growth [19–22]. However, it should be noted that an auxiliary step was utilised in most of the cases that reported beneficial plant growth; this step typically involved converting the ammonium from the digestate to nitrates before the fertiliser was introduced to the hydroponic unit. This is because plants can absorb nitrogen as either ammonium or nitrate, however, the total uptake of nitrogen usually consists of a combination of the two. Although plants may be able to utilise ammonium for growth, they typically prefer a higher concentration of nitrates than ammonium in standard nutrient solutions [23].

In this study, the emphasis is placed on the production of liquid digestate in anaerobic digestion. Conventionally, the liquid digestate was only seen as a minor by-product from the anaerobic digestion process and little emphasis was placed on the mineralisation rates within the digester. Given the major growth occurring in the soilless agriculture sector and the need for more sustainable fertilisation strategies in these food production processes, liquid digestate has been promoted to a more prominent topic in the circular production of human nutrition. In this regard, it is important to understand the rate and extent of fertilizer production in the anaerobic digestion process. This will aid in the design of novel digester processes, where liquid digestate is selectively removed in order to counter ammonia inhibition while simultaneously optimising fertilizer production. Accordingly, this study scrutinises the ammonia production rates in batch digestation under different pH control strategies in order to gain more insight on the time-dependent mineralisation characteristics of the process.

Three different substrates were investigated in this study (cow dung only, cow dung with banana peels, and cow dung with red lentils). These feeds were chosen so that the pH control system could be tested against feedstock that are more prone to producing large amounts of ammonium, as well as those that are not, in order to determine if there would be a difference in the control characteristics depending on the substrate. Substrates that were comprised of red lentils only or banana peels only were not investigated in this study because these substrates typically require microbial seeding, such as cow manure, or a sample from an existing anaerobic digester at the beginning of the anaerobic digestion process [24].

2. Materials and Methods

Two different set-ups were used for the experiments performed over the course of this study. The first was a batch set-up constructed for manual dosing once a day, and the second set-up included continuous dosing with the aim of controlling the pH on a minute-to-minute basis; these set-ups were named the daily dosing setup (DDS) and continuous dosing setup (CDS), respectively.

2.1. Materials

The cow dung was collected from the University of Pretoria Experimental Farm located on the Hillcrest campus. The cow dung was sourced from dairy cows. The pH was controlled by using a 1 M solution of NaOH and a 1 M solution of HCl. Imbo red lentils (500 g) and Cavendish bananas were procured from a local supermarket. Deionised water was also acquired from the University of Pretoria laboratories. The feed material for the CDS was the same as those used in the DDS experiments. However, the pH was controlled by using a 0.25 M solution of NaOH and a 0.25 M solution of HCl.

2.2. Analysis

A DLAB single-channel adjustable pipette was used to extract samples from the Schott bottles. An Agilent Technologies Cary 60 UV-vis spectrophotometer was used to analyse the samples for ammonium. A Bluelab® pH probe connected to LabVIEW (Laboratory virtual instrument engineering workbench), was used for pH measurements. A Radwag PS 8000/X digital lab scale was used to measure the mass of the chemicals and initial masses of the feedstocks required in the experiments.

The initial mass of each feed was measured by a Radwag PS 8000/X digital lab scale. The pH was measured using a Haoshi H101 pH electrode. The temperature inside the reactors was measured by a Maxim DS18B20 temperature sensor. The pH was controlled by using a precision peristaltic pump and an intelligent stepper controller. The pump, stepper controller, pH, and temperature sensors were all coupled to an Arduino MEGA 2560.

Each digestate sample was analysed using a Merck Spectroquant ammonium test, and then to measure the absorbance of the mixture of the sample, an ultraviolet–visible spectrophotometer was used with the wavelength set at 690 nm. The absorbance could then be related to ammonium concentration through a previously calibrated ammonium absorbance-concentration curve. The samples were taken by opening the lid of the digester and drawing the sample with the pipette and then closing the lid after extracting the sample.

2.3. Apparatus

An Orbital shaker-incubator ES-20/60 was used as the main vessel for the DDS experiments. The incubator had enough space for six 250 mL Schott bottles. An 8 mm hole was drilled into each bottle's lid in order to allow for gas capturing with a tube. The gas was captured with six 500 mL graduated cylinders that were inverted and submerged in water; the gas production rate could then be correlated with the water displaced in the cylinders over the course of the experiment. A schematic of this apparatus is shown in Figure 1.

Two identical reactors were constructed for the CDS experiments. Each reactor required an acrylic tube with an outside diameter of 110 mm, an inside diameter of 104 mm, and a height of 140 mm, and a square plexiglass base (200 × 200 × 10 mm). A Daihan Scientific digital hotplate stirrer MSH-20D was used to control the temperature and mix the digester contents with a stirrer bar. The reactors were constructed by attaching the clear acrylic tubes to the square base using magma bond (C1). The lid for each of the reactors was a PVC end cap with an inside diameter of 110 mm, and PTFE tape was placed in the space between the lid and the tube providing an air-tight seal. The lids had various holes drilled through them allowing for sampling, charging, temperature control, a gas outlet, and pH control. The gas was captured in the same fashion as the DDS experiments. The

peristaltic pumps were used to regulate the pH inside the reactors. The pH electrodes and the pumps were coupled to an Arduino MEGA 2560 in order to employ an on/off control scheme to achieve the desired set-point. A schematic of this apparatus is shown in Figure 2.

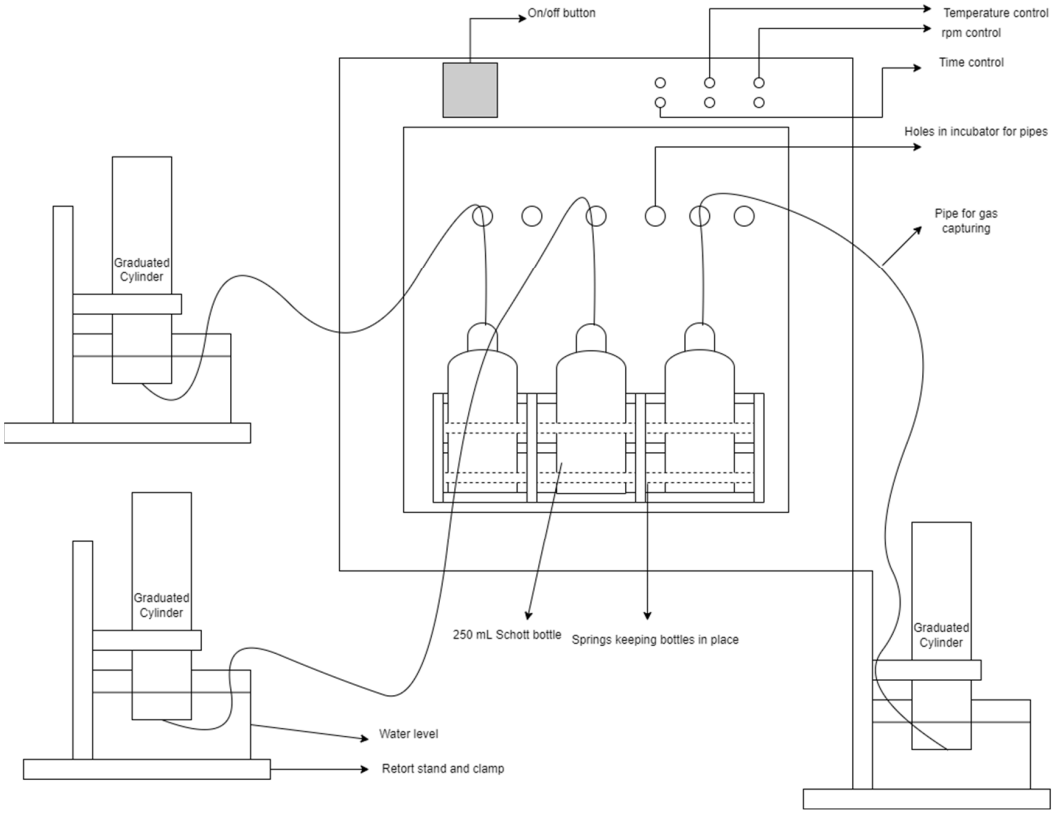

Figure 1. A schematic of the DDS.

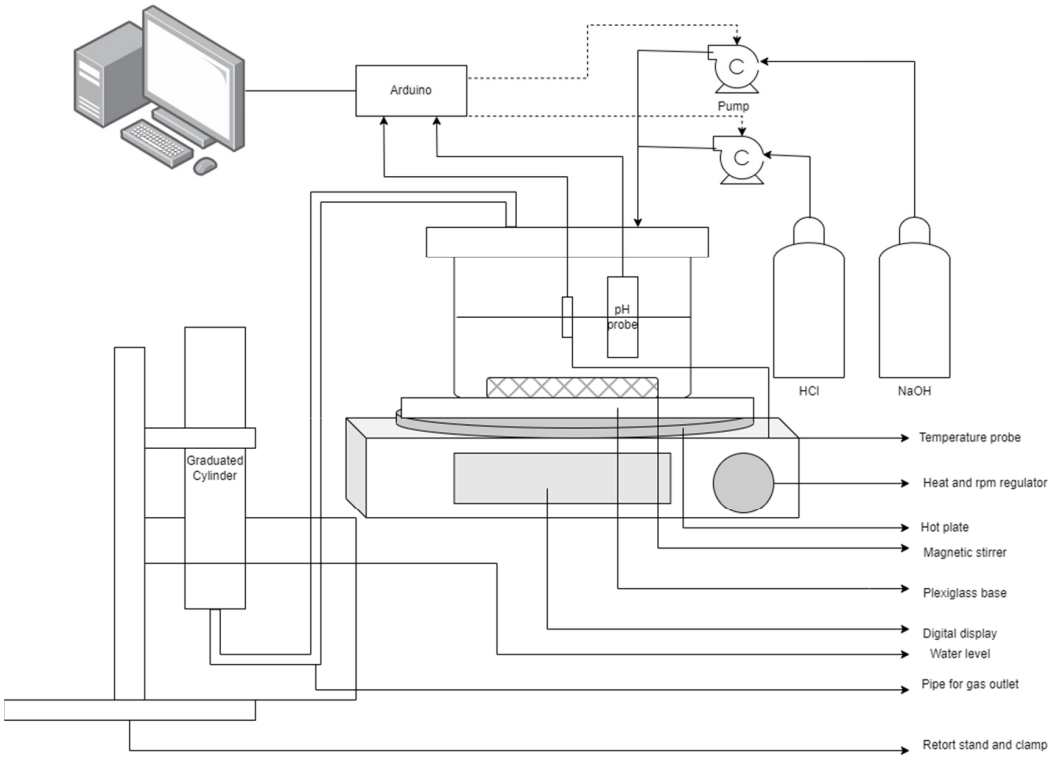

Figure 2. A schematic of the CDS.

2.4. Experimental Procedure

Firstly, for the DDS experiments, three banana peels (each with a mass of 100 g) were dried in an oven for 24 h at 70 °C to determine the dry mass to wet mass ratio of the banana peels. The average moisture content of the banana peels was found to be 85% on a mass basis which correlates well with literature [25,26]. The full results from these tests are given in Table 1. Six 250 mL Schott bottles were used for each experiment.

Table 1. Wet masses, dry masses, and moisture content of each banana peel sample tested.

	Wet Mass (g)	Dry Mass (g)	% Moisture
Sample 1	103	16.3	84.2
Sample 2	100	14.4	85.6
Sample 3	98	15.7	83.9
Average	100	15.5	84.6

Three separate feeds were then prepared for each experiment. Each feed was prepared such that the total solids in each bottle would be 5% of the total mass and that the dry mass ratio between the feedstocks would be 1:1, as this is considered the optimum mixing ratio for co-digestion [27]. The first feed was prepared with 52.5 g of cow manure and 105 mL of deionized water. The second feed was prepared with 26.25 g of cow dung, 26.25 g of banana peels, and 105 mL of water. The third feed was prepared with 26.25 g of cow dung, 3.94 g of dry red lentils and 130 mL of water. The value for the moisture content of cow manure that was used for the experiments was 85%, as this is generally the value that is found in literature [28,29].

The starting masses of 7.88 g (dry basis) of each type of feedstock were then blended and placed in the 250 mL Schott bottles and placed into a shaker incubator at a specified rpm of 150 and a temperature of 35 °C for the duration of each experiment. Each feed had a duplicate bottle for each pH condition. The pH in each bottle was measured and adjusted daily with a standard solution of 1 M NaOH or 1 M HCl as necessary, depending on the experimental requirements. The ammonium concentration in each bottle was measured on days 0, 1, 5, 9, 13, 17, and 21 by extracting a 2 mL sample from each bottle.

For the CDS experiments, only two of the feeds were considered—the cow dung only and cow dung and banana peel feed. Each feed was prepared such that the total solids in each flask would be 5% of the total mass, however, due to the reactors being slightly larger in volume, the initial masses of each feed had to change. This change in initial masses was such that the probes could be submerged in the solution without interfering with the stirrer bar. The first feed was prepared with 175 g of cow dung and 350 mL of deionized water. The second feed was prepared with 87.5 g of cow dung, 87.5 g of banana peels, and 350 mL of deionized water.

The feedstock was placed in each reactor at a specified rpm of 150 and a temperature of 35 °C for the duration of each experiment. The pH and dosing data was captured for every minute of each experiment, and the ammonium concentration in each bottle was measured on days 0, 1, 5, 9, 13, 17, and 21 by extracting a 2 mL sample from each reactor.

Once the experiment started, the Arduino would be activated. The Arduino received signals from the pH meter and the temperature probe that were captured in a text file, and these signals were then used to control both the pH and temperature in the reactors. The Arduino was linked to two peristaltic pumps with each pump connected to a 0.25 M NaOH and 0.25 M HCl solution, respectively. These pumps were actuated depending on the pH set point required for the experiment. A simple on/off control was employed for the pH control, with a signal being received every minute during the experiments, meaning that the pumps could be actuated every minute to control the pH. For experiments that did not require pH control, the pumps were deactivated, however, the pH and temperature data were still captured in a text file.

3. Results

Two types of experiments were performed over the course of this study. The first was performed with pH correction once a day, the set-up used to perform these experiments was named the daily dosing set-up (DDS). A second comparative experiment was designed to determine the effect of continuous dosing as opposed to dosing once a day; this experiment recorded pH data every minute with the aim of controlling the pH of the solution on a minute-to-minute basis, the set-up used to perform these experiments was named the continuous dosing set-up (CDS). The experiments that were performed over the course of this study are summarized in Table 2.

Table 2. A summary of all the experiments performed. Two ticks indicate that the experiment was performed for both the CDS and DDS, one tick indicates that the experiment was only performed for the DDS.

Feed	pH 6	pH 7	pH 8	No pH Control
Banana peels and cow dung	✓✓	✓✓	✓✓	✓✓
Cow dung only	✓✓	✓✓	✓✓	✓✓
Lentils and cow dung	✓	✓	✓	✓

3.1. The DDS

In the first experiment, there was no acid or base dosing. This was done to determine the digestion characteristics of each feedstock to better understand the influence each feedstock had on the pH. The pH characteristics of each feed are shown in Figure 3.

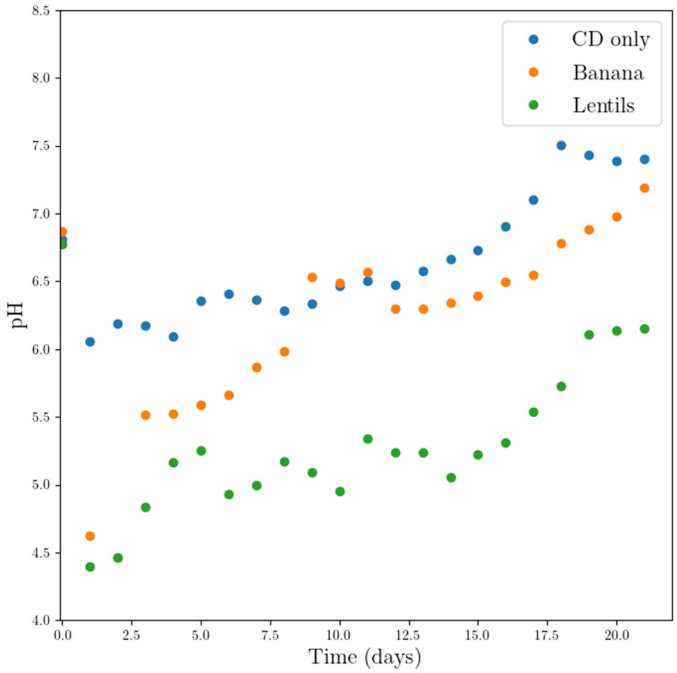

Figure 3. pH characteristics of each feedstock with no pH adjustments for the DDS. CD, cow dung.

Figure 3 depicts a sharp initial decrease in the pH on the first day, then a steep incline in the pH on the second day, and then a steady increase in the pH until a plateau is reached in all the different feedstocks at around day 18. There is a noticeable difference in the pH of the lentil feedstock compared to the cow dung only and banana feedstocks. This could be attributed to the fact that the feed is protein-rich, and as such it was expected to produce far more ammonium than the other two feedstocks [10,30]. The production of ammonium typically correlates with the first two steps of the anaerobic digestion process (hydrolysis and acidogenesis), and these first two steps generally occur at lower pH values than the

rest of the process [31–33], which explains why the pH of the lentil feedstock was notably lower than that of the other two feedstocks.

The lentil substrate was also the only substrate that was cooked before being placed in the reactors. This may be considered as a thermal pre-treatment step in the process. Thermal pre-treatment is a universally accepted method of augmenting the anaerobic digestion process because it accelerates the degradation of the substrate, which provides an easily digestible fraction of the substrate [34–37]. Another major difference between the three substrates is the fact that lentils contain much less lignocellulosic material compared to the other two substrates. Lignocellulosic biomass, especially the lignin content, has been reported as having an inhibitory effect on the anaerobic digestion process due to the complexity of the biomass structure [38–41]. Lentils typically contain 1.2 to 1.8% of lignin, whereas cow dung and banana peels range from 8–14% and 8–15%, respectively [42–47]. Figure 4 shows the acid/base dosing of each feed at the different pH set points.

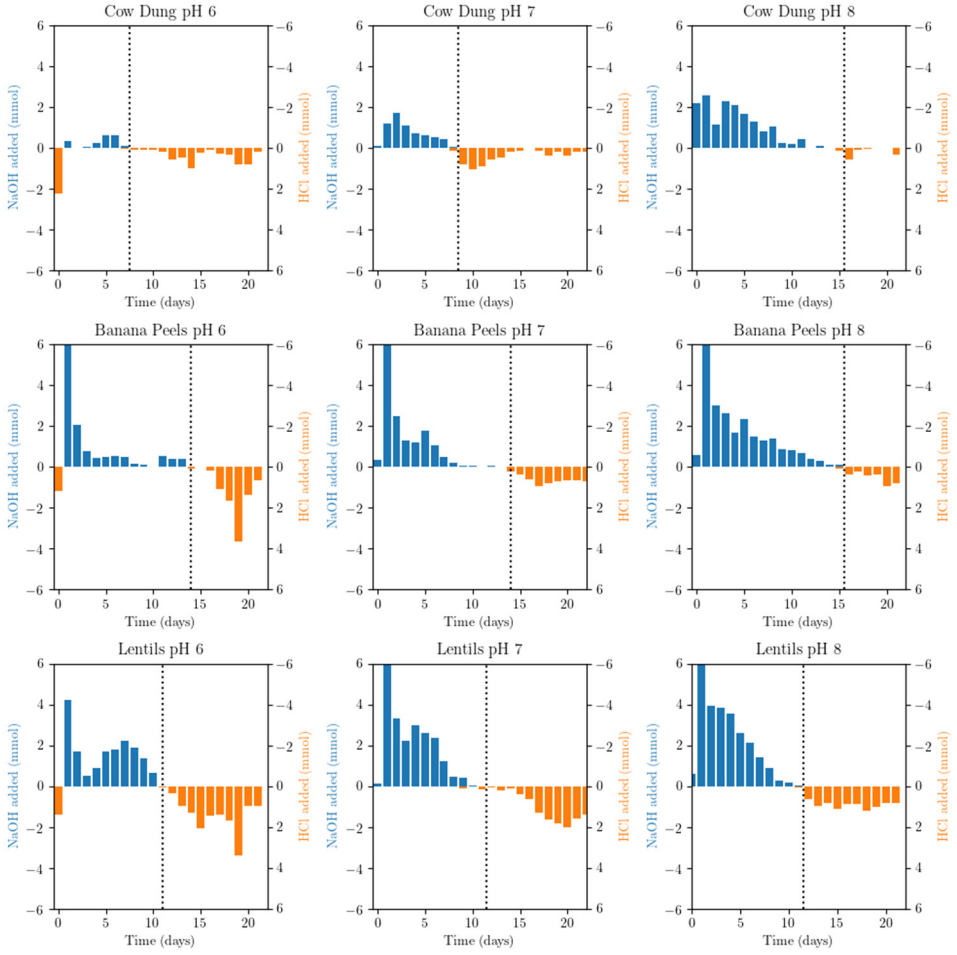

Figure 4. A comparison of the acid/base dosing of each feed at the different pH set points for the DDS. The blue represents the amount of sodium hydroxide added, the orange represents the amount of hydrochloric acid added. The dotted line represents the switchover point for each experiment (i.e., when HCl had to be dosed instead of NaOH).

From Figure 4, it can be seen that the runs at a higher pH set point require more sodium hydroxide to reach the set point, however, the time taken to reach the switch point (when hydrochloric acid must be added instead of sodium hydroxide to maintain the set point) does not vary significantly with each feed. The switch point indicates a change in regime for the process. It is noted from Figure 4 that at a pH of 8, the cow dung and banana peel feeds take much longer to reach their switchover point. This could be attributed to the fact that the anaerobic digestion process is sub-optimal at such a relatively high pH.

Typically, the process of anaerobic digestion prefers pH values between 6.8 and 7.2 [48–50]. These two substrates had almost identical switch points for the experiments performed at pH values of 6 and 7. However, the cow dung substrate had a faster switch point compared to the banana peel substrate at these pH values. Figure 4 also illustrates how the lentil substrate showed little variation in the switch point characteristics compared to other two substrates. Figure 5 shows the ammonium concentrations of each feed at different pH set points.

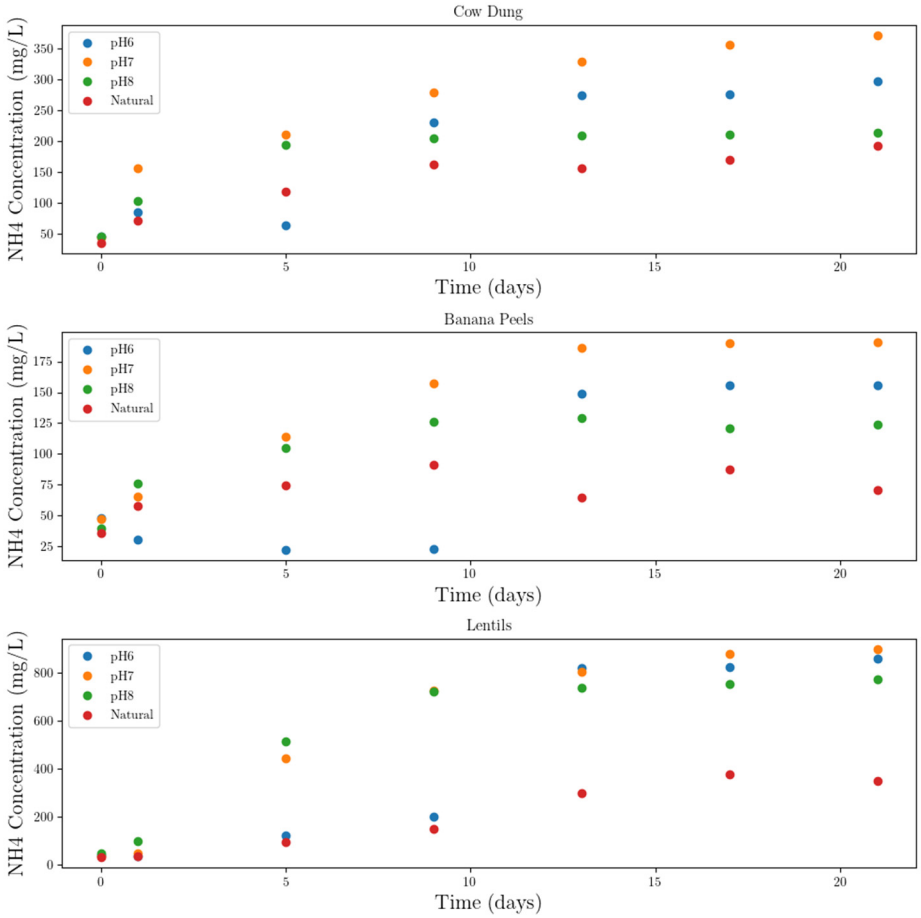

Figure 5. The ammonium concentrations of all of the feeds for the experiments performed in the shaker incubator at different pH values for the DDS. Each concentration value is an average of the two repeats that were performed for each feed and pH value.

Figure 5 demonstrates that a pH of 7 is generally preferable for all the feeds in terms of the amount of ammonium released, although it could be argued that the differences in concentrations for the lentils are negligible. This figure also shows how the ammonium that is released in the lentil feedstock is much higher than the other two feeds; this could be attributed to the fact that the lentil feedstock contains more protein compared to the other two feedstocks and as such it was expected that it would release the largest amount of ammonium (as previously proposed) [10]. Although the pH 7 run was optimal for ammonium release in all the feeds, the significant advantage it had over the other set points in the cow dung and banana peel substrates is less pronounced in the lentil substrate, where much more nitrogen was released. This is likely an indication that the readily digestible protein fraction of a protein-rich feed is insensitive to pH compared to the more complex lignocellulosic feeds.

More significant insight can be drawn from Figure 5. Firstly, the pH control aided in extracting ammonium from the feedstock into the liquid. The optimal pH was 7, the higher pH provided the lowest amount of ammonium released, and the ammonium concentrations

for the experiments performed at a pH of 6 were only marginally better than those of the pH 8 experiments. An explanation for these results can be obtained from anaerobic digestion theory: anaerobic digestion has four processes (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) [51,52], of which the first steps are typically at a lower pH and the final step is generally at a higher pH value, and these steps are sequential at the start of the process. It is widely accepted that the optimal pH is around 6.8–7.2 for optimal digestion [48–50], which explains why the ammonium concentrations for the experiments performed at pH values of 7 and 8 are similar at the beginning but then starts to plateau for pH 8. In contrast, the lower pH run stagnates the production of ammonium at the beginning of the run as the lower pH stunts the process. This can also be seen with the gas production, where the gas production is much slower at the beginning of the process for the experiments at a pH of 6 compared to the other runs (except for the natural run). Figure 5 also shows that the run with no pH control performed poorly compared to the pH-controlled runs. If one considers that the gas production from the natural runs was much lower than the controlled runs, and this fact coupled with Figure 3 shows why the no pH control run had not reached the optimal pH range by the end of the run. It is plausible that this could be the reason for the decrease in ammonium and gas production. The uncontrolled experiments consistently produced the least amount of ammonium for each substrate, indicating that pH control is important for ammonium release in anaerobic digestion.

Since there seems to be a correlation between the pH control and ammonium concentration, a composite figure of the ammonium and cumulative sodium hydroxide added for each pH set point was made. This is seen in Figure 6.

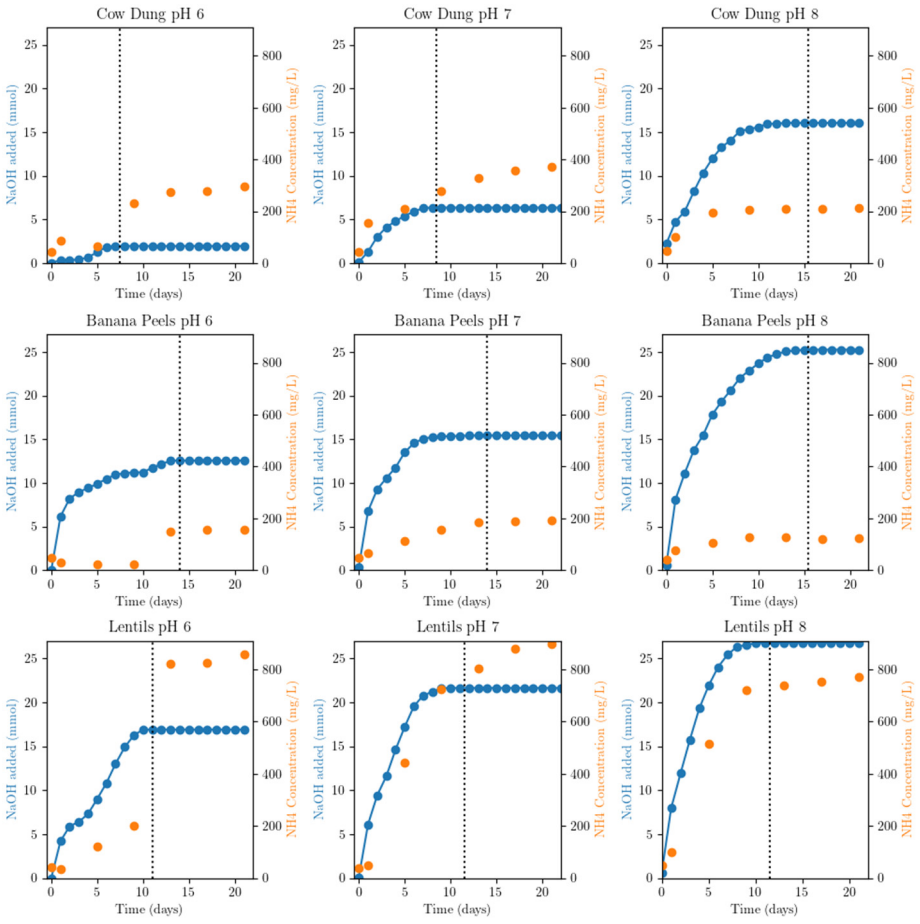

Figure 6. A composite figure of the cumulative sodium hydroxide dosing and the ammonium concentration on each y-axis respectively for the DDS. The orange markers represent the ammonium concentrations, and the blue markers represent the cumulative sodium hydroxide dosing. The NaOH added is in mmol.

Figure 6 shows a clear increase in the sodium hydroxide required as the pH set point increases for each pH-controlled run. This figure also shows that the difference in the dosing amount of sodium hydroxide between the banana peel and lentil substrates is relatively low despite the vast differences in the ammonium concentrations, which indicates that the additional amino acid breakdown that is required for the lentil substrate does not have in influence on acidifying the mixture.

Figure 6 further displays a sharp increase in ammonium concentrations after the switch point for the experiments performed at a pH of 6. This indicates that the ammonium release is initially inhibited at a lower pH. However, when one examines the results seen in Figure 7, it is evident that the gas production at pH 6 is inhibited at the beginning of the experiment. This makes it apparent that the lower pH has an inherent inhibitory effect on the anaerobic digestion process as whole.

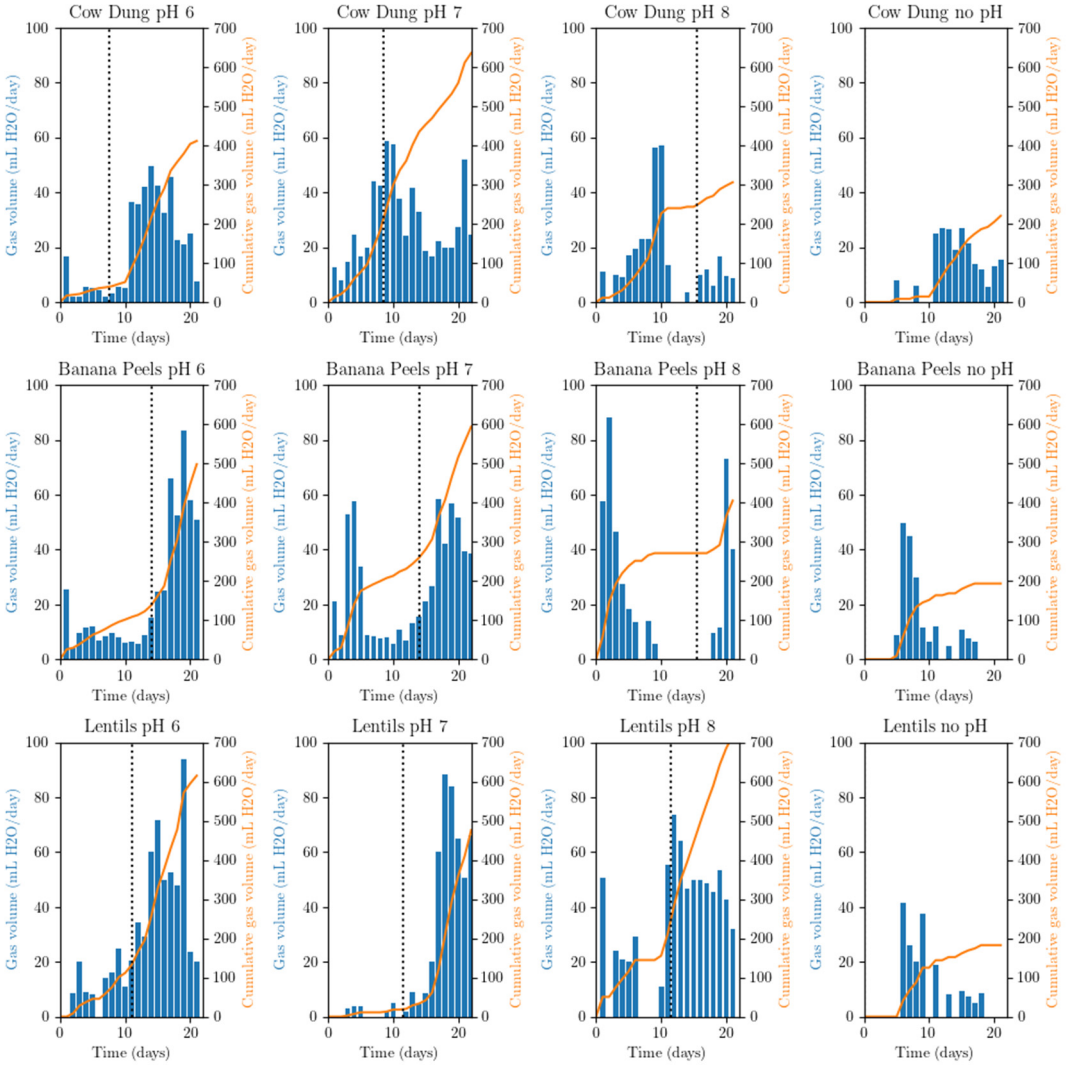

Figure 7. Gas volumes produced by each feed at different pH set points for the DDS. The orange line represents the cumulative water displaced over time, whereas the blue represents daily water displacement.

Figure 7 shows the gas production of each feedstock at different pH set points.

Figure 7 shows how the uncontrolled pH experiments were comprehensively outperformed in terms of gas production by the experiments that had pH control. The uncontrolled pH experiments typically had a relatively large lag phase at the beginning of the experiments in which no gas was produced, whereas the pH-controlled experiments typi-

cally started producing gas much earlier. The pH-controlled experiments also consistently produced more gas than the experiments without pH control.

Figure 7 shows that the gas production is left skewed at a lower pH value (i.e., the mean gas produced is less than the median), indicating that perhaps the lower pH hinders the anaerobic digestion process slightly more than the other pH set points, whereas the higher pH value produces gas more sporadically compared to the other two set points. A pH of 7 seems to be the optimal for most of the feeds. The natural run seems to corroborate these findings: at the beginning of each natural run the pH was still relatively low resulting in limited gas production, but when the pH started approaching neutral values, the gas production picked up, thus indicating that the lower pH stunts the gas production of the process.

Figure 7 also shows clear evidence of an accelerated gas production after the switch point is reached. There is an inflection in the cumulative gas production that almost perfectly correlates to the switch point in all the pH-controlled experiments. This inflection is not present in the natural runs, which gives further credence to the fact that the acceleration in gas production is correlated to the switch point.

3.2. CDS vs. DDS

Figure 8 shows the comparison of the cumulative dosing of sodium hydroxide in a system that was controlled by continuous dosing through online measurements versus the shaker flasks that were controlled by measuring the pH every day and dosing accordingly.

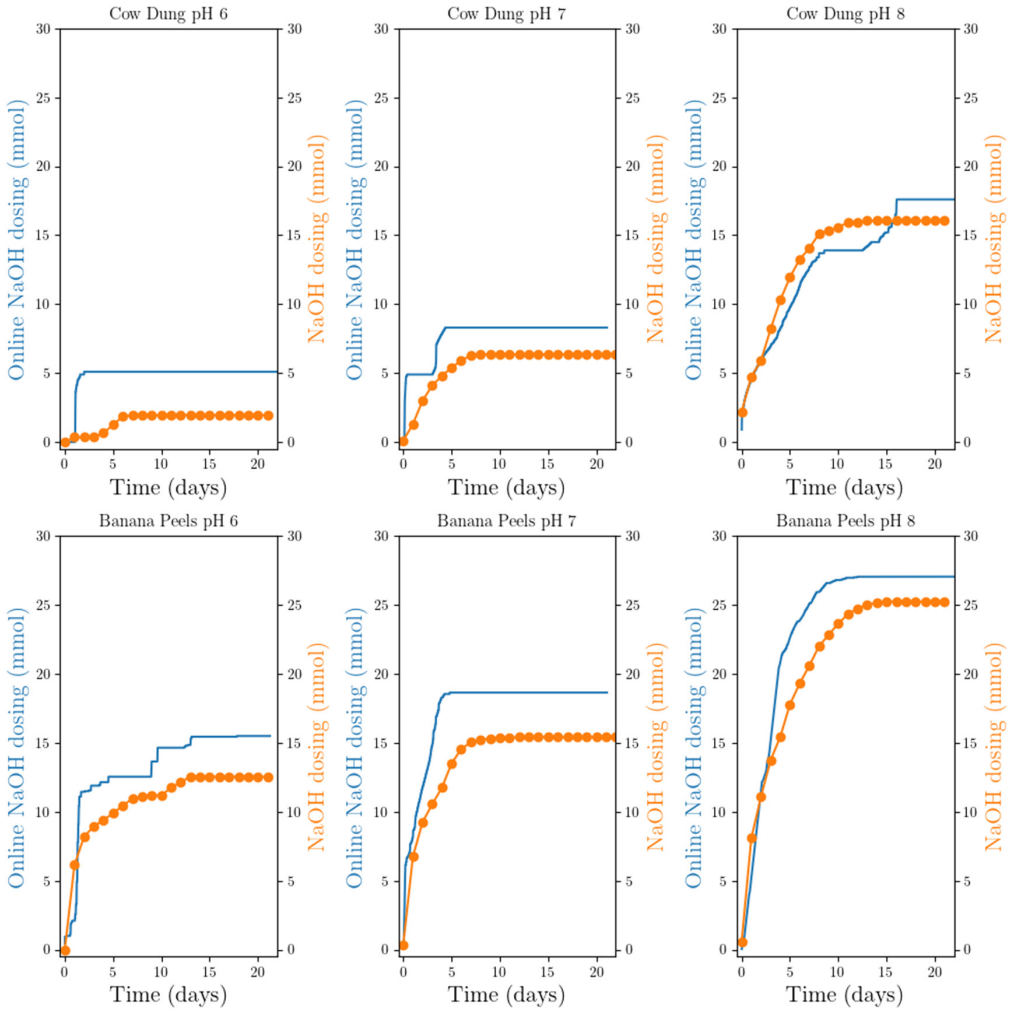

Figure 8. A comparison of the cumulative dosing of NaOH for the CDS vs. the DDS at different pH set points. The orange represents the DDS whereas the blue represents the CDS.

Figure 8 illustrates that the CDS typically provided peaks of sodium hydroxide much earlier than the DDS. It is also clear that the CDS generally has a higher peak than that of the DDS. This could be because the CDS has a much better pH control strategy than the DDS. Since the pH is measured every minute in the CDS, it has more stringent pH control over the solution, meaning that it doses more frequently than the DDS, which explains why there is generally more sodium hydroxide dosed in the CDS experiments compared to the DDS experiments. The average values of NaOH added for the CDS and DDS at different pH set points are shown in Table 3.

Figure 9 shows the comparison between the ammonium concentrations of the CDS vs. DDS experiments.

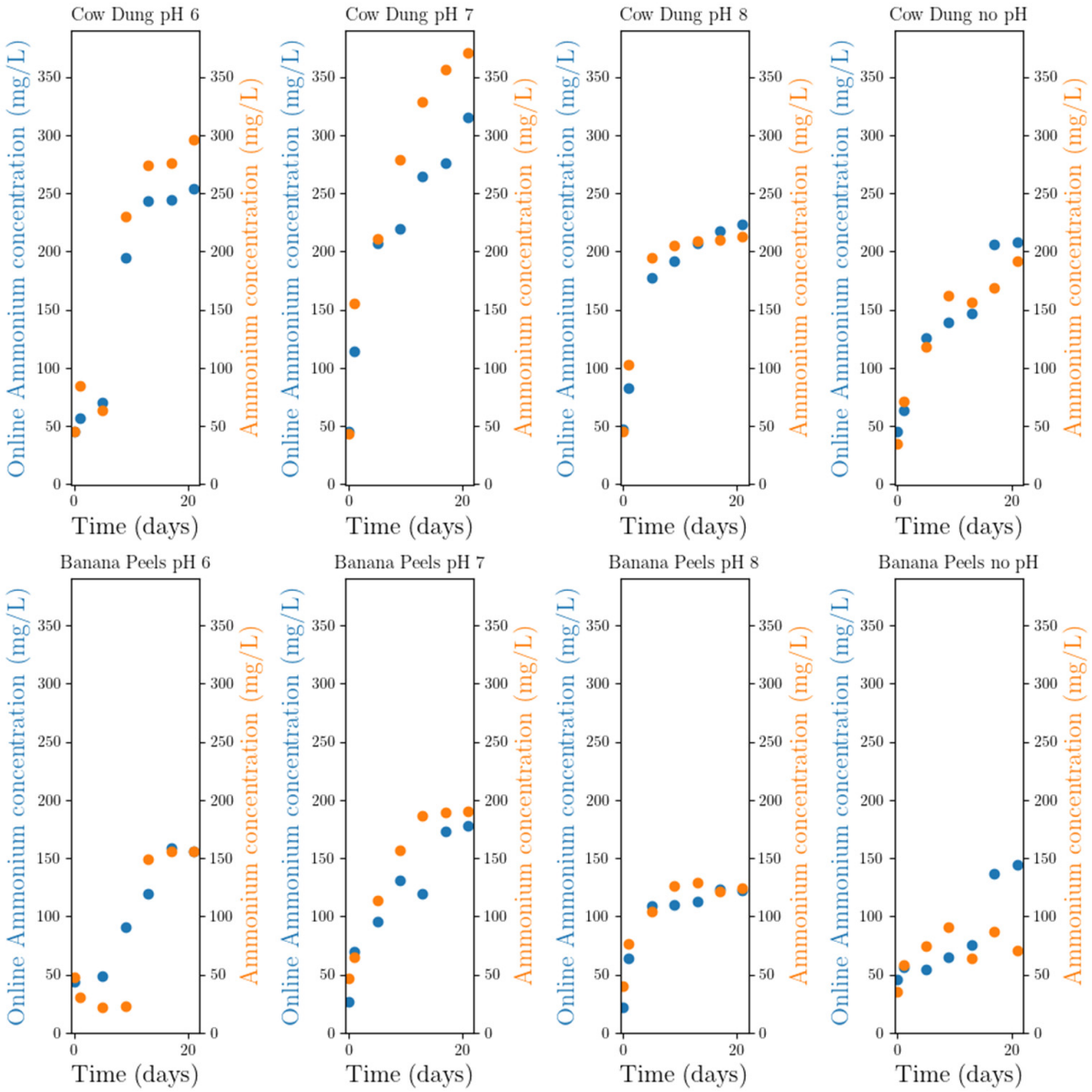

Figure 9. A comparison of the ammonium concentrations for the CDS vs. the DDS at different pH set points. The orange represents the DDS whereas the blue represents the CDS.

Table 3. Average amount of NaOH added for CDS and DDS at different pH set points.

Feed	pH 6 (mmol)	pH 7 (mmol)	pH 8 (mmol)
Banana peels and cow dung—CDS	15.5	18.7	27.1
Banana peels and cow dung—DDS	12.6	15.4	25.3
Cow dung only—CDS	6.9	8.3	18.7
Cow dung only—DDS	2.0	6.4	16.1

Figure 9 shows that the difference in ammonium production between the two systems is negligible. However, the increase in ammonium concentrations in the CDS runs is slightly more consistent than that seen in the DDS runs. This is seen especially in the pH 6 experiments: the ammonium increased at a steady rate with continuous dosing, whereas the DDS provided a much steeper increase in ammonium concentrations over a smaller period. The average ammonium concentration values for CDS and DDS at different pH set points are given in Table 4.

Table 4. Average ammonium concentrations for CDS and DDS at different pH set points.

Feed	pH 6 (mg/L)	pH 7 (mg/L)	pH 8 (mg/L)	No pH Control (mg/L)
Banana peels and cow dung—CDS	156	178	122	144
Banana peels and cow dung—DDS	156	190	124	70
Cow dung only—CDS	254	315	223	208
Cow dung only—DDS	297	371	213	192

Figure 10 shows the gas production of the CDS versus the DDS runs. The most notable differences between the two different set-ups is that there seems to be more periods in which the gas production stagnates for the DDS runs, whereas the gas production seems to be more consistent for the CDS runs. The gas production typically increases steadily for the CDS runs, whereas there seems to be more frequent periods in which gas production stagnates for the DDS runs. This could be attributed to the fact that the methanogens (bacteria responsible for methane production) are typically sensitive to pH fluctuations [53]. These pH fluctuations are inherently more drastic in the DDS because pH corrections were only performed once per day, whereas pH corrections were performed every minute in the CDS. The delay in pH corrections in the DDS resulted in more drastic pH fluctuations compared to the CDS, which thus disrupts the methanogenic bacterial activity. The average values for the gas produced by the CDS and DDS at different pH set points are given in Table 5.

Table 5. Average gas produced for CDS and DDS at different pH set points.

Feed	pH 6 (mL)	pH 7 (mL)	pH 8 (mL)	No pH Control (mL)
Banana peels and cow dung—CDS	793	735	643	374
Banana peels and cow dung—DDS	498	595	405	194
Cow dung only—CDS	576	825	532	324
Cow dung only—DDS	411	611	306	220

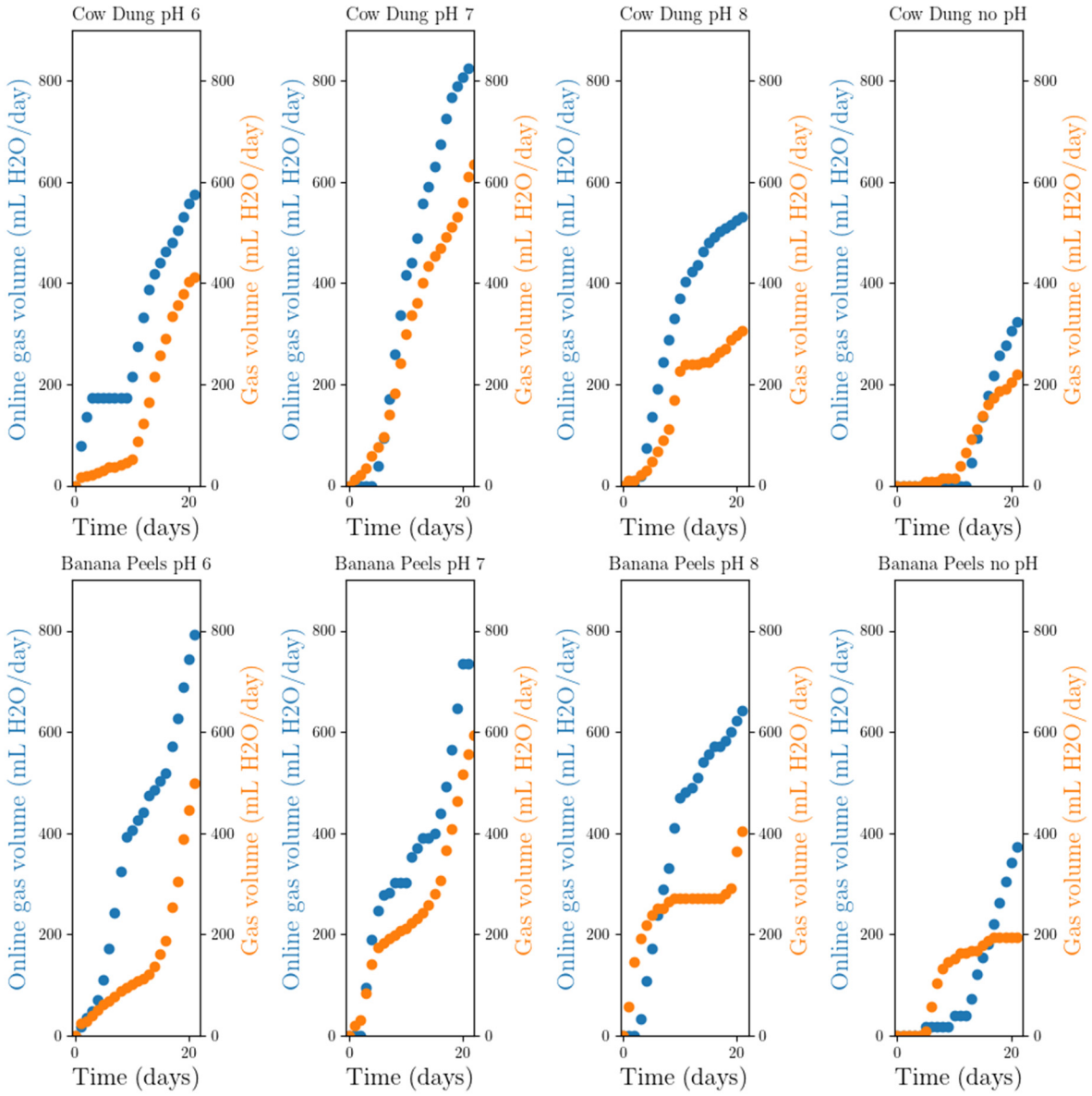

Figure 10. A comparison of the cumulative amount of water displaced by the gas created for the CDS vs. the DDS at different pH set points. The orange represents the DDS whereas the blue represents the CDS.

4. Discussion

It is evident that pH control has a profound effect on the ammonium release rate as well as the gas production rate. A pH of 7 is clearly the optimal set point for both ammonium release as well as the gas production rate. The results also show that the substrate that contained a larger amount of easily accessible protein (lentils) produced significantly more ammonium compared to the more lignocellulosic substrates that were tested. In addition, it was noted that the enhanced ammonium concentrations from the protein-rich substrate did not significantly affect the amount of base required for neutralization.

The substrate had a strong influence on the pH switch point from base to acid dosing. The actual pH set point had a significant effect on the switch point on the protein-lean substrates. However, the differences in pH values are largely insignificant for the protein-rich substrate indicating that the additional amino acid breakdown that is required for the lentil substrate does not have in influence on acidifying the mixture.

There appeared to be an inherent inhibitory effect on both gas and ammonium production associated with a low pH at the beginning of the anaerobic digestion process. This inhibitory effect was not observed at higher pH values. The switch point was observed to be crucial in terms of gas production. There was a clear acceleration in the gas production observed after the dosing switch point.

In terms of the comparative analysis between the CDS and the DDS, there were differences present in the gas production profiles, with the CDS providing enhanced rates compared to the DDS. There was a negligible difference in the ammonium release rate between the different set-ups, which indicates that precise pH control has a more pronounced effect on the methanogenesis phase of anaerobic digestion compared to the hydrolysis, acidogenesis, and acetogenesis steps.

5. Conclusions

The results obtained from the study suggest that operating an anaerobic digester at a pH of 7 allows for the optimum production rate of ammonium and maximum amount of nitrogen extracted. Controlling the process at a lower pH stagnates the anaerobic digestion process at the beginning of the process, whereas controlling the process at a higher pH causes the process to stagnate towards the end of the run.

It was also clearly illustrated that the CDS performed better (when considering gas production) than the DDS, while making an insignificant impact on ammonium release. This was attributed to the delay in pH corrections in the DDS, which resulted in more drastic pH fluctuations compared to the CDS. This delay disrupts the methanogenic bacteria activity. The ammonium release, in contrast, appears to be less sensitive to the pH fluctuations.

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