Closing the loop in agricultural waste management: co-smouldered digestate ash as alkalinity and trace element supplement for anaerobic digestion

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Berry cultivation results in discharge of large quantities of high organic strength putrescible solid waste which potentially contributes to environmental degradation, making it imperative to assess options for its sustained management. Anaerobic digestion (AD) could be an ideal option when the target is energy generation, however, the technology could be limited by its high alkalinity requirement or need for trace elements (TEs) supplementation. Overcoming these limitations in an economic viable way could entail replacement of synthetic additives with recycled by-product waste, which in line with the philosophy of circular economy could facilitate the recovery of energy from berry agriculture generated waste (Davis et al, 2016). Thus, this study evaluated the process performance of the AD of berry fruit waste (BFW) when ashes from co-smouldered digestate and coir is added as alkalinity and TEs supplement.

Berry waste was collected from SunnyRidge® farm (Queensland, Australia). The inoculum was granular sludge from a brewery wastewater treatment plant. The dosed ash was obtained from smouldering of a mixture of 73% coco-coir waste and 27% digestate from AD of berry fruit and plant waste. **Tab. 1** and **2** shows the analytical characteristics of the substrate and inoculum, and the essential elements in the digestate, coir and co-smouldered digestate ash, respectively.

Triplicate assays were performed in batch systems following I/S of 2 (in volatile solids), using serum bottles (160 mL) sealed and placed in a heated room (35 ± 0.5°C), after creating anaerobic conditions. Controls include (i) inoculum and substrates only – for determination of minimum total alkalinity concentration (TAC) for AD of BFW from $NaHCO_3$ and alkalinity potential of the ash, (ii) inoculum, substrate and $NaHCO_3$ **-** for the effect of ashes as TEs source. The alkalinity and TE potential of the ash were evaluated by supplementing ash (22.574 g/Kg ash) of equivalent TAC to that of the minimum evaluated from $NaHCO_3$, and by dosing ash (0.012 – 7.574 g/Kg ash) of varying concentrations of specific essential TEs (Co, Fe, Ni, Se), respectively. TAC refers to alkalinity of inoculum and the additives.

Table 1. Analytical characteristics of substrate and inoculum

Sample	pH	Moisture content (%)	Total solids (g/Kg)	Mineral solids (g/Kg)	Volatile solids (g/Kg)	Total nitrogen (wt %)	Total carbon (wt %)	C/N ratio
Berry Fruit	3.1 ± 0.1	85.1	149 ± 4.0	15 ± 1.0	135 ± 5.0	0.108 ± 0.003	6.58 ± 0.14	61
Inoculum	5.1 ± 0.1	96.1	38.8 ± 2.3	4.7 ± 0.5	34.1 ± 2.1	ND	ND	ND

Table 2. Essential elements in the digestate, coir and coir-digestate ash

	Se	Ca	Cu	Fe	K	Mg	Mn	Na	Co	Ni	S	Zn
Digestate	35	5824	70	76598	18824	2906	36	14999	8	64	71494	909
Coir	19	8514	39	2815	2606	1960	364	365	0.4	0	6043	64
Coir-digestate ash	0.5	21548	114	21587	24478	7642	625	13476	8.6	41	10454	1588

The result (not shown) of the assays to ascertain the minimum alkalinity for the AD of BFW with $NaHCO_3$ showed an acidification (pH (5.2 ± 0.1) and IA/PA (> limit) of the control with no added $NaHCO_3$, resulting to a low cumulative methane production (CMP) of 51 mL CH_4/g VS ± 2. pH (7 – 8) and IA/PA (< 0.8) are generally considered limit for stable AD process (Drosg, 2013). However, as more $NaHCO_3$ was added to the system, stability was established. The CMP values were approximately 6 and 5 times more than that from the control for TAC of 1500 mg $CaCO_3$/L and other tested TACs (2000, 3000 and 4250 mg $CaCO_3$/L), respectively. However, TAC of 1500 mg $CaCO_3$/L revealed a tendency for acidification, while 3000 and 4250 mg $CaCO_3$/L could be excessive, as there was no significant difference in the CMP. Overall, the results revealed that TAC of 2000 mg $CaCO_3$/L from dosed $NaHCO_3$ of 745 mg $CaCO_3$/L could be considered the appropriate minimum alkalinity required to ensure correct AD of the BFW.

Ash supplementation as alkalinity buffer revealed a stable digestion process, with final pH and IA/PA (**Table 3**) within the acceptable range for a stable AD process **(**Drosg, 2013). However, as compared to the control the ash dosage of 22.574 g/kg (745 mg $CaCO_3$/L) had a detrimental effect to the AD system, reducing the CMP by -36%, possibly due to the concentration level of certain metals in the ash (**Table 2**). For example, Fe, a crucial co-enzyme for methanogenic conversion of CO_2 to CH_4 is found to be in excess levels (487 mg/L) compared to the concentration of 1 – 10 mg/L recommended for AD systems (Schattauer et al., 2011). Nevertheless, the dosed ash increased the MPR, by +92% as compared to the control, which would have resulted from the synergistic effect between Ni and Co, which are within recommended range for AD (Kida et al, 2001) and are known to accelerate initial exponential rates (Linville et al., 2016).

Table 3. Methane production and characterization of the digestate from AD of BFW with ash buffer (mg $CaCO_3$/L)

	Control 2000 (0)	$NaHCO_3$ 2000 (745)	Ash 2000 (745)
Cumulative methane production (mL$_{STP}$ CH_4/g VS)	161 ± 50	272 ± 3	103 ± 18
Methane production rate (mL$_{STP}$ CH_4/ (g VS.h))	7 ± 2	0.72 ± 0.1	13.5 ± 3.8
pH	6.4 ± 0.8	7.2 ± 0.2	7.9 ± 0.1
Alkalinity ratio (IA/PA)	0.94 ± 0.79	0.38 ± 0.29	0.58 ± 0.12
Total Alkalinity (mg $CaCO_3$/L)	563 ± 88	1458 ± 72	1208 ± 72
sCOD (mg O_2/L)	184 ± 23	81 ± 4	394 ± 33

The result of the experiments to assess the ash potential to provide essential TE (Fe, Co, Ni, and Se) at much lower ash dosages (**Table 4)** shows a relatively stable process, with similar pH and corresponding alkalinity at all conditions except the highest dosage of 7.574 g/kg. Correspondingly, the IA/PA decreased at increasing dosage of ash, with the lowest dosage of 0.012 g/kg being at the upper stability limit, thus, prone to instability. As compared to the control, the CMP decreased at increasing ash dosage, with 7.574 g/kg ash having the highest effect of -23.5%. However, ash dosage of 7.574 g/kg ash increased the MPR by +15.3%, while ash dosages of 0.012, 0.306 and 1.52 g/kg decreased the MPR by -7.5%, -1.9% and -10.4%, respectively. These effects could be attributed to the varying concentrations of essential TEs required for AD, i.e., Se, Co, Ni and Fe in the different dosages of ashes. For example, in all ash dosage, Se was observed to be within the stimulatory concentration of < 0.04 mg/L. However, Co and Ni were less than the recommended concentration for AD processes of 0.03 < Co < 19 mg/L and 0.03 < Ni < 27 mg/L (Romero-Güiza et al., 2016) for ash dosages of 0.012 g/kg ash (0.0001 mg Co/L, 0.0005 mg Ni/L) and 0.306 g/kg ash (0.003 mg Co/L, 0.013 mg Ni/L), respectively. On the contrary, 7.574 g/Kg ash contained Co (0.07 mg/L), Ni (0.31 mg/L), and Se (0.004 mg/L) in appropriate levels, except for Fe (163 mg Fe/L) which was in excess, hence, the probable increase in MPR at this higher dosage of ash. In general, ash supplementation had a detrimental effect on the CMP, however, high dosages of ash could be beneficial for higher methane recovery at a given time (MPR) from either a buffered or none buffered AD of BFW, thus, could be recommended for closing the loop in berry agriculture waste management when reactor volume reduction dominates the economics of the AD system deployment.

Table 4. Characterization of the digestate from AD of BFW with ash as TE source (g/kg)

	Control (0)	0.012 (0.4)	0.306 (10)	1.520 (50)	7.574 (250)
CMP (mLSTP CH4/g VS)	149 ± 23	145 ± 24	130 ± 10	127 ± 13	114 ± 9
MPR (mLSTP CH4/ (g VS.h))	11.2 ± 1.6	10.3 ± 1.3	11 ± 1	10 ± 0.8	13 ± 3
pH	7.0 ± 0.1	7.1 ± 0.1	7.1 ± 0.1	7.2 ± 0.1	7.6 ± 0.0
Alkalinity ratio (IA/PA)	0.66 ± 0.05	0.77 ± 0.05	0.71 ± 0.04	0.27 ± 0.06	0.18 ± 0.07
Total Alkalinity (mg CaCO3/L)	967 ± 104	942 ± 63	825 ± 66	1900 ± 90	3442 ± 63
sCOD (mg O2/L)	139 ± 22	155 ± 8	148 ± 18	115 ± 18	173 ± 23

Alkalinity contained in dosed ashes (mg $CaCO_3$/L) is in parenthesis

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