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ASSESSING THE POTENTIAL ROLE OF ANAEROBIC DIGESTION ON BIODEGRADABILITY OF COPPER TREATED BIOMASS

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ABSTRACT

Bach anaerobic digestion was carried out under mesophilic condition at the temperature of 37^{0}C and retention time of 30 days. Two sets of cultures were prepared in 500 ml capacity incubation bottles. The first set contained required amount of pre-adsorption feedstock and the second set with post-adsorption feedstock containing 50 mg/l of copper. The feedstocks are corn cob, mango peel waste, rice husk and seaweed (Ascophyllum nodosum sp.). The results show that in the raw feedstocks the amount of the total solids progressively decreases with time from 25.98 g/l at Time zero (t = 0) to 14.45 g/l in 30 days for corn cob, however, in the spent corn cob more of the total solid was lost from 26.78 g/l to 9.39 g/l during the same period. Similar trend of total solid reduction were observed in Mango peel, Rice husk and Seaweed regardless of the metal content of the spent feedstocks. While there were variations in the trend of volatile solid reduction, it was clear that the effect of metals within the concentration of 50 mg/l on the entire anaerobic process was insignificant. This study concludes that anaerobic digestion process is a viable option for effective degradation of waste biomass.

Keywords: Anaerobic digestion, Waste, Copper, Heavy metal

INTRODUCTION

One of the prime environmental concerns is the global warming which caused climate change. Rapid increase in human population and industrializations has exacerbated the threats of climate change and significantly put high demand on energy utilisation (Talebnia *et al*, 2010). The concern over greenhouse gas emissions and dwindling oil reserves has focused debate and research effort on finding alternative sources of energy.

Nigerian economy is dominated by technologies that rely on fossil energy (petroleum, coal, natural gas) to produce fuels, power, chemicals and materials. Other developing economies also met their energy needs with the use of petroleum and other fossil fuels which has resulted in drastic increased in the level of green house gas emission, especially carbon dioxide (CO_2) in the atmosphere (Twidell and Weir, 2006; Gnansounou, 2010; Taylor, *et al*.,2010; Talebnia *et al*, 2010). Consequently, this has accelerated the transition from energy system based on fossil fuels to renewable energies, especially, when scientific evidences continued to document the accelerating threats of climate change as a result of unsustainable utilization of non-renewable energy sources (Miguel, 2009). A number of researches have documented the viability of biomass in the renewable energy generation. Thus, renewable energy is now widely believed to be the future and green waste has been considered to be a promising sustainable feedstock for actualizing the aspiration of global energy security (Jegannathan *et al*, 2009). While bio-ethanol is produced from the fermentation process, biogas is a product of anaerobic digestion (AD) of the biomass materials (Horn, 2000; Twidell and Weir, 2006; Jegannatha *et al*, 2009).

Biomass such as agricultural wastes, municipal wastewater and green wastes present a promising renewable energy opportunity that could provide an alternative to the use of fossil resources. However, presence of toxic metals has been a source of concerns to the anaerobic digestion process. The effect of metals on anaerobic digestion process has been documented (Alkan et al, 1996; Chiu-Yen Lin, 1993; Zheng-Bo Yue et al, 2007). Anaerobic digestion has been the traditional method for separating sludge from municipal wastewater for ultimate disposal in landfill. However, the concentration of toxic metals contained in the sewage sludge is the determining factors governing its rate of agricultural application (Wong and Cheung, 1996). Moreover, Mata-Alvarez (2003) reported that toxic compounds could be degraded anaerobically depending on the technology applied and makes it an important option of waste management strategy worldwide.

AD consists of several interdependent, complex sequential and parallel biological reactions in the absence of oxygen, during which the products from one group of microorganisms serve as the substrates for the next, resulting in transformation of organic matter mainly into a mixture of methane and carbon dioxide (biogas) (Anthony and Wilson, 2009). Biogas is the product of complete digestion of biomass in the absence of oxygen. The reactions below show the various stages of anaerobic digestion process.

Acidogenic Fermentation of Glucose

$$C_6H_{12}O_6 \longrightarrow CH_3(CH_2)_2COOH + 2CO_2 + 2H_2 \quad \text{(i)}$$

$$C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2H_2O \quad \text{(ii)}$$

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2H_2 + 2CO_2 \quad \text{(iii)}$$

Acetogenic Oxidation Reaction

$$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + CO_2 + 3H_2 \quad \text{(iv)}$$

Methanogenic Reactions

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad \text{(v)}$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O \quad \text{(vi)}$$

(Adopted from Chanakya *et al.*, 2006).

In this light of the above, four organic feedstocks; Corn cob, Mango peel, Rice husk and Seaweed (*Ascophyllum nodosum)* have been considered in this study to evaluate their biodegradability using anaerobic digestion process with the aim of converting them to usable materials and assess the effect of toxic metal ions on the degradation process.

MATERIALS AND METHODS

Sample Collection and Preparation

The seaweed (*A. nodosum*) was collected at the Broughty Ferry beach, Dundee, Scotland. The mango fruit was obtained commercially and the peel carefully removed manually, which was then air dried over night (T 22 ºC ± 2 ºC) for 24 hours. Rice husk was collected from a local rice mill in Kura, Kano state. Corn cob from edible zeamase was obtained from a local farmer.

Seaweed was washed separately with tap water to remove the sand and stones entangled in the sample. The seaweed and other feedstocks were dried separately in the oven at 105°C for 24 hours. Each of the four samples was blended into a powder using a commercial blender

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and further reduced to finer particles of 0.5mm particle-size using Fritsch Rotor Speed Mill-Pulverised 14 and stored separately in clearly-labelled transparent containers.

Preparation of Raw and Spent Feedstocks

Two sets of feedstocks were prepared in this study. The first set consists of four raw feedstocks (Corn cob, Mango peel, Rice husk and Seaweed) devoid of any metal treatment and were used in their natural forms after washing, drying and pulverising. In the second set, same feedstocks were separately dosed with 50 mg/l of copper solution and labelled spent feedstock.

Seed Inoculums

The anaerobic digester sludge (seed inoculums) was obtained from mesophilic anaerobic digester at a Wastewater Treatment Plant in Hatton Dundee, Scotland in the United Kingdom.

Preparation of Non-Growth Medium

Non-growth medium was prepared for the anaerobic digestion process using the following compounds; KH_2PO_4, K_2HPO_4, $MgSO_4.7H_20$, $CaCl_2$, $FeCl_3$, KCl, $CoCl_2$ and $NiCl_2$ (Table 1). The required amount of each of the reagents was carefully measured using top digital high precision balance. The medium provided the essential nutrients required by the microorganisms (Horn, 2000).

Preparation of Culture for Batch Digesters

10 g of each of the four raw feedstocks was weight into the first four 500 cm^3 incubation bottles, followed by adding 110 cm^3 of seed inoculum and make up to 400 cm^3 with non growth medium. The same procedure was adopted for the spent feedstocks in the second sets of four 500 cm^3 capacity bottles and the blank contain only seed sludge and the medium as shown in Table 2.

Anaerobic Digestion Studies

The anaerobic digestion was carried out under mesophilic condition at the temperature of 37 ^0C and 30 days retention time. The method of digestion employed for this study was wet digestion (Attal *et al.*, 1992; Ortega *et al.,* 2008).

1000 mg/l Copper

This was prepared by dissolving 1.000 g of copper metal (Cu) in a minimum volume of (1:1) HNO_3 in a 100 cm^3 beaker. The resultant solution was quantitatively transferred into a clean dried 1liter volumetric flask and diluted to mark with 1% (v/v) HNO_3 (Perkin Elmer, 1996). This solution was transferred into cleaned plastic bottles, labelled and kept for further use. Working standard solution of the metal was prepared using dilution ratio as follows;

$$C_1V_1 = C_2V_2$$

Where;

C_1 = Concentration of the stock solution (mg/l).

V_1 = Volume of stock solution required to make the dilute solution (ml).

C_2 = Concentration of required dilute solution (mg/l).

V_2 = Volume of dilute solution required (ml).

Physicochemical Analysis

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The physicochemical analysis was carried out by measuring 20 cm^3 of homogenized samples from the incubation bottles at different time interval. The sample was collected in the following times interval (in days) t = 0, 1, 2, 3, 4, 7, 10, 13, 19, 25 and 30 for the volatile solids (VS) determination. During the time intervals, the pH of each of the sample was also determined. The pH values were monitored using a pH meter (Hanna Educational pH Meter HI 208). Moisture content and volatile solid were measured gravimetrically by drying at 105 ^0C for 24 hours and incineration at 540 ^0C for 3 hour respectively. All other parameters were determined according to standard procedure set by APHA, 1992.

Table 1. Non growth medium

S/N		*Needed Concentration (g/l)*
1	KH_2PO_4	27
2	K_2HPO_4	35
3	$MgSO_4.7H_2O$	0.05
4	$CaCl_2$	0.05
5	$FeCl_2$	0.05l
6	KCl	0.05l
7	$CoCl_2$	0.01
8	NiCl2	0.01

Table 2. Composition of cultures in batch digesters

S/N	*Feedstock*	*Amount of Feedstock (g)*	*Amount of Inoculum (cm^3)*	*Non growth Medium (cm^3)*
1	Corn cob (pre-adsorption)	10	110	290
2	Mango peel (pre-adsorption)	10	110	290
3	Rice husk (pre-adsorption)	10	110	290
4	Seaweed (pre-adsorption)	10	110	290
5	Corn cob (post-adsorption)	10	110	290
6	Mango peel (post-adsorption)	10	110	290
7	Rice husk (post-adsorption)	10	110	290
8	Seaweed (post-adsorption)	10	110	290
9	Blank	-	110	290

RESULTS AND DISCUSSION

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Reduction of Total Solids and Volatile Solids Concentration with Time

Both the total solids and volatile solids present in the samples were determined at Time intervals (t = 0. 1, 2, 3, 4, 7, 10, 13, 19, 25 and 30 day) during the anaerobic digestion process. Table 3 shows the variation in concentration of total solids from Time 0 – 30 days in both the raw and spent feedstocks under study. In the raw feedstocks the amount of the total solids progressively decreases with time from 25.98 g/l at Time zero (t = 0) to 14.45 g/l in 30 days for corn cob, however, in the spent corn cob more of the total solid was lost from 26.78 g/l to 9.39 g/l during the same period. Similar trend of total solid reduction were observed in Mango peel, Rice husk and Seaweed regardless of the metal content of the spent feedstocks. At t = 0, the total solid was 30.42 g/l in the pre-adsorption mango peel. While it was expected to reduce as a result of the metabolic activities of bacteria, the value was raised to 34.44 g/l on the second day. This might be due to over flow of the suspended solid material from the incubation bottle during the daily measurement of the culture. Since the culture was a composite mixture of three different materials and the measurement was done manually, such variation in the amount of total solid and volatile solid is likely. Thus, it was recurrent in all the feedstocks across the total solid and volatile solid as shown in table 3 and 4. However, there was generally significant reduction of both total and volatile solid from t = 0 to t = 30.

The variations in volatile solid reduction are presented in Table 4. The volatile solids represent the biodegradable fraction of total solids which account for all the solids available for bioconversion to methane and other gases during the anaerobic digestion process. Volatile solid reduction also followed similar pattern with the total solid as shown in Table 4. There was gradual loss of the volatile solid in the raw Seaweed feedstock from 19.36 g/l to 4.63 g/l at t = 0 and t = 30 days respectively.

Table 3. Variation of Total Solids (TS) with Time in Various Sample of Feedstock

Time (Day)	*Corn Cob (g/l)*		*Mango peel (g/l)*		*Rice Husk(g/l)*		*Seaweed(g/l)*		*Blank (g/l)*
	Raw	*Spent*	*Raw*	*Spent*	*Raw*	*Spent*	*Raw*	*Spent*	
0	25.98	26.78	30.42	31.56	21.06	20.73	31.67	31.36	10.67
1	18.13	17.71	31.44	26.43	18.24	18.17	29.77	30.36	8.21
2	22.27	23.76	34.44	25.97	17.87	16.9	29.38	30.73	7.38
3	19.57	21.55	25.66	24.27	16.78	13.78	24.36	26.75	5.11
4	17.25	13.18	21.64	21.66	13.76	9.73	19.28	21.6	3.84
7	23.66	21.94	24.73	23.08	16.08	11.72	28.18	26.27	3.96
10	22.1	24.08	32.82	27.7	16.2	13.03	27.31	24.93	3.75
13	25.26	23.16	27.84	27.95	15.42	13.59	26.57	25.18	5.52
19	26.5	24.07	30.82	26.05	15.37	14.08	24.77	28.48	7.59
25	17.62	11.53	21.05	20.55	12.93	9.16	19.04	18.56	3.23
30	14.45	9.39	18.94	18.67	10.25	8.94	17.53	17.72	3.01

Table 4. Variation of Volatile Solids (VS) with Time in Various Sample of Feedstock

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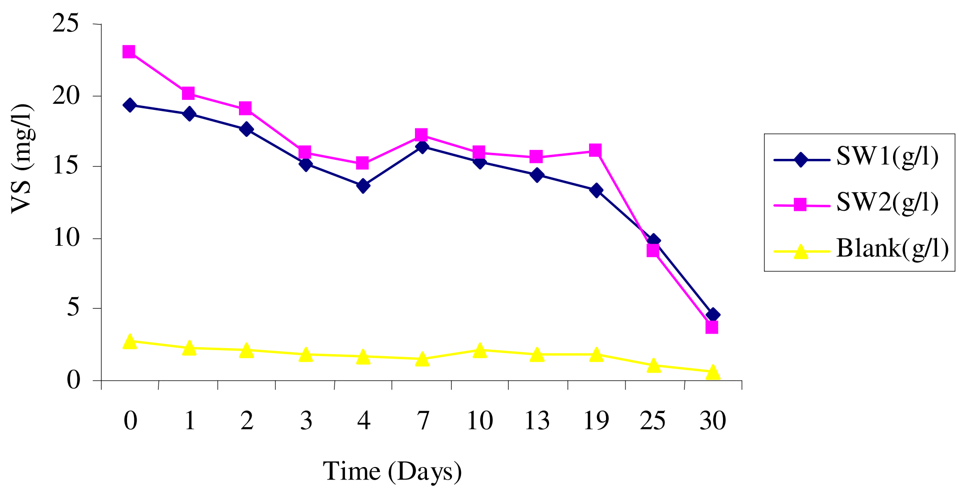
Time (Day)	Corn Cob (g/l)		Mango peel (g/l)		Rice Husk(g/l)		Seaweed(g/l)		Blank (g/l)
	Raw	*Spent*	*Raw*	*Spent*	*Raw*	*Spent*	*Raw*	*Spent*	
0	18.34	18.89	22.76	23.29	12.16	11.03	19.36	23.02	2.81
1	11.93	11.97	22.68	18.88	10.38	10.01	18.72	20.07	2.37
2	16.1	17.13	22.55	17.2	9.54	8.23	17.71	18.95	2.1
3	12.91	16.71	15.64	16.49	9.32	7.05	15.18	16	1.9
4	13.52	10.76	15.31	17.36	8.73	5.69	13.65	15.15	1.64
7	16.13	14.76	16.09	15.19	10.24	6.92	16.39	17.23	1.51
10	14.88	17.17	19.71	18.92	7.79	7.31	15.38	16.01	2.08
13	14.44	14.9	16.57	18.41	8.54	6.86	14.48	15.63	1.89
19	13.53	12.21	16.75	20.49	6.7	6.12	13.27	16.11	1.91
25	10.86	7.55	13.76	13.32	6.02	5.24	9.84	8.98	1.02
30	6.54	4.03	6.48	5.97	3.85	3.17	4.63	3.73	0.61



Appendix 1. Reduction of volatile Solid (VS) in Seaweed

The data of table 3 and 4 were analysed and presented in appendix 1 - 4, which show the overall trend in reduction of the volatile solid. The graphs in appendix 1 show progressive volatile solids reduction with time during the anaerobic digestion in both raw and spent seaweed. There was a significant reduction in the amount of volatile solids in the first 5 days which could be attributed to the corresponding rapid hydrolysis of the readily biodegradable fraction of the feedstocks as supported by available literature (Akunna *et al.,* 2007). This rapid reduction in volatile solids occurred in seaweed despite the metal content of the post adsorbent feedstock (appendix 1).

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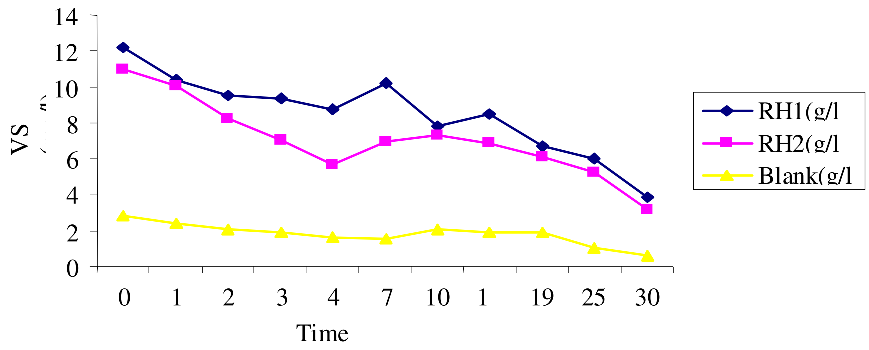
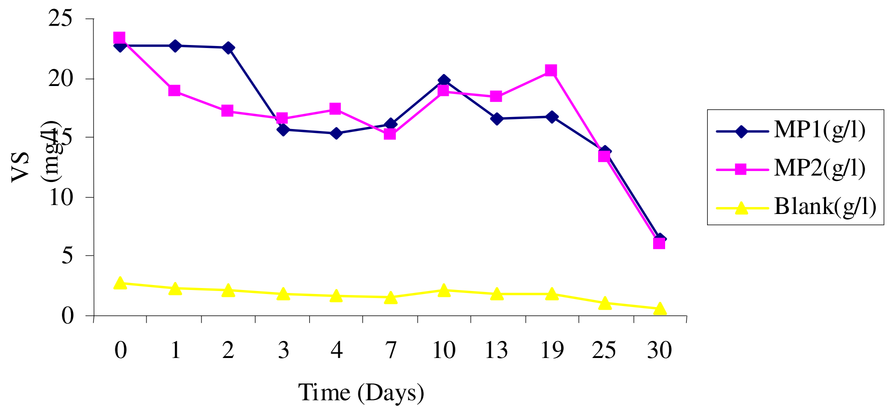
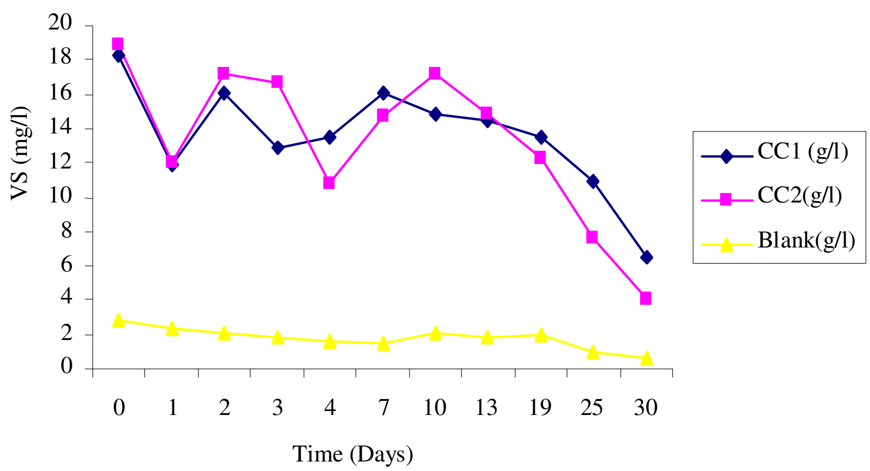


Appendix 2. Reduction of volatile solid in Rice husk



Appendix 3. Reduction of volatile solid in Mango peel



Appendix 4. Reduction Reduction of volatile solid in Corn cob

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Although, studies have shown that heavy metals could disturb the anaerobic digestion process (Robert *et al.*, 1989), but it was observed that there was insignificant differences in volatile solids reduction in both raw and spent feedstocks. However, higher reduction was observed in the raw rice husk and mango peel as indicated in appendix 2 and 3 respectively. These results show that the metal content in the spent feedstocks do not have significant impact on the reduction pattern of both total solids and volatile solids. However, there were variations in the trend of reduction as indicated in appendix 1 – 4.

CONCLUSION

This study concludes that anaerobic digestion process is a viable option for effective degradation waste biomass. The study shows that the effect of metals on total solid and volatile solid was insignificant and effective anaerobic digestion of all the feedstocks tested in this study could be achieved regardless of metal concentration of up to 50mg/l. It was also shown that the metals content of the feedstocks were concentrated in the slurry by-product of the anaerobic digestion process and thus, become easier for recovery.

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