Humic acid batteries derived from vermicomposts at different C/N ratios

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Abstract. Humic acid is a known fertilizer derived from decomposed organic matters. Organic wastes are normally landfilled for disposal which had contributed negatively to the environment. From waste-to-wealth perspective, such wastes are potential precursors for compost fertilizers. When worms are added into a composting process, the process is termed as vermicomposting. In this work, humic acid from vermicompost derived from campus green wastes was developed into a battery. This adds value proposition to compost instead of being traditionally used solely as soil improver. This research work aimed to study the correlation between electrical potential generated by humic acid at different Carbon to Nitrogen (C/N) ratios of vermicompost at 20, 25, 30 and 35. The temperature and pH profiles of composting revealed that the compost was ready after 55 days. The humic acid was extracted from compost via alkaline extraction followed by precipitation in a strong acid. The extracted humic acid together with other additives were packed into a compartment and termed as vermibattery. Another set of battery running only on the additives was also prepared as a control. The net voltage produced by a single vermibattery cell with Zn and PbO electrodes was in the range of 0.31 to 0.44 V with compost at C/N ratio of 30 gave the highest voltage. The battery can be connected in series to increase the voltage generation. Quality assessment on the compost revealed that the final carbon content is between 16 to 23 wt%, nitrogen content of 0.4 to 0.5 wt%, humic acid yield of 0.7 to 1.5 wt% and final compost mass reduction of 10 to 35 wt%. Composting campus green wastes carries multi-fold benefits of reducing labour requirement, generating fertilizer for campus greenery and green battery construction.

1. Introduction
Batteries are a potable form of energy and they are in demand parallel to modern lifestyle. Batteries generate electricity via electron movement from negative terminal (anode) to external positive terminal (cathode) through an electrolyte [1]. A primary battery is a single use battery whereas a secondary battery can be recharged for multiple usages. Spent batteries need a proper disposal as they contain harmful chemicals such as cadmium, lithium, mercury and nickel [2, 3]. Therefore when possible, the use of secondary battery is more preferable to reduce the disposal hazards. Nonetheless, even the simplest form of secondary battery that is acid-lead battery is environmentally hazardous. Thus, there is a need for a greener battery such as the ones derived from bio-based compounds.

Current bio-batteries generate energy from a reaction between simple starches such as glucose with enzymes instead of using harmful chemicals [4]. These batteries have many environmental advantages but lacking reliable power generation due to natural degradation of biological compounds. Bio-batteries
can potentially generate about 50 miliwatts of electricity, proving them useful for small devices application [4]. To make bio-batteries more appealing, variety of electrolytes should be developed using natural compounds like humic acid.

Humic acid (HA) is typically used as a fertilizer in agriculture and horticulture due to its rich nutrients content. It is not a single acid but rather a complex combination of many weak acids. Humic acid typically behaves as negatively charged colloid due to dissociation of carboxyl and phenolic groups of these weak acids [5]. Therefore, humic acid could potentially generate a small amount of electrical potential. Major components of natural organic matters in soil and water which includes geological organic deposits such as lake sediments, brown coals and peats are humic substances [6]. Hence, humic acid can be obtained from composting process of organic wastes.

Green wastes such as leaves, branches, grass clipping and vegetable scraps can be effectively and efficiently reduced via composting. It is a biological decomposition process of organic matters into humus through microbial activities [7]. The simplest form of composting is to pile organic wastes and leave them to break down naturally over a period of time [8]. The time required for the green wastes to degrade depends on several factors such as the Carbon (C) and Nitrogen (N) content of the raw materials, temperature, moisture content, particle size, oxygen level and piling techniques [9]. Earthworms are sometimes added to increase the efficiency of composting as well as to enhance the compost quality. Typical earthworms used include red wigglers (Eisenia fetida) and European nightcrawlers (Eisenia hortensis). Thus, the process is sometimes referred to as vermicomposting.

From vermicompost, humic substances can be separated into three different fractions which are humic acid, fulvic acid and humin [10]. Humic acid can be interpreted as liquid humus which is beneficial to plant growth [11]. It is a mixture of dibasic acids with carboxylic and phenolic groups contributing the most to the surface charge with pK values at pH 4 and pH 9 respectively [5]. At typical compost pH of 7, humic acid exists as an ampholyte with carboxylic groups becoming proton donors and phenolic groups are proton acceptors.

Karim et al. (2011) work revealed that vermicompost can produce electricity of up to 1.5 volts in just a single cell. Furthermore, it was shown that vermicompost contains high nitrate content and other essential growth elements for plants. The scope of the research however was limited to spent tea waste only [12].

Figure 1. Overview of the project.
In this work, abundant campus green wastes were utilized as compost precursors. They were added at specific Carbon to Nitrogen (C/N) ratios of 20, 25, 30 and 35 as the compost starters. Red wiggler worms were added to reduce the composting duration as well as to enhance the compost quality. Humic acid was extracted from compost at each formulation for quality and voltage analysis. It is intended for the findings to propose for an alternative to typical landfilling waste management for organics and to develop a mini bio-battery to power model cars for green-themed competition such as the annual Chem-e-car competition [13]. Figure 1 depicts the bigger picture of the project where strong emphasis is given on being green thoroughly.

2. Experimental

2.1. Materials and equipment
Dry leaves and vegetable scraps were used as the carbon and nitrogen source organics. They were collected within the Universiti Teknologi PETRONAS (UTP) campus. The raw materials were mixed at specific weight percentage (wt%) based on their suggested C and N content [14, 15]. The formulations are given in table 1. They were loaded in custom-made rotary composters accordingly. The composters were made from recycle HDPE chemical drums of 250L and 12mm thickness. They were mounted on 4-legged steel stands. Handles were installed for manual turning. Holes were made on the drum wall and on the internal spinal steel for passive aeration. Red wiggler worms were added at about 20 numbers, which is excluded from the total weight of compost because they were removed during compost harvesting. The composters were loaded at approximately 15% of the total capacity.

| Table 1. Initial compost formulations. |
|----------------------------------------|
| Batch | C source | N source | Total weight | C/N ratio |
|       | Type     | Weight (kg) | Type     | Weight (kg) | (kg)     |
| A     | Dry leaves | 0.170     | Vege   | 0.830  | 1  | 20 |
| B     | 0.270     | 0.730     | 25     |
| C     | 0.375     | 0.625     | 30     |
| D     | 0.480     | 0.520     | 35     |

2.2. Temperature and pH monitoring
Temperature and pH were recorded using WalkLab Microcomputer pH Meter TI9000 from Trans Instruments. The readings were taken once a week at six different places in the composting bins and the readings were averaged. The data were used to plot profile curves over time in order to determine the maturation period.

2.3. Total Organic Carbon (TOC) and Total Kjeldahl Nitrogen (TKN)
Samples were collected from each compost batch at six different locations in the bins and mixed in a beaker to get a good representative of the compost. For TOC, about 100 mg of the samples were treated with 10% HCl to remove inorganic substances. The samples were dried at 105°C for 3 hours in an oven prior to analysis using an Analytik Jena HT 1300. For TKN, 2g of each sample was weighed and added into a mixture of 25 ml of 97% H_2SO_4 and 10g of Kjeldahl catalyst tablets. The mixture was stirred and heated at 370°C for 1 hour using a BUCHI Digest Automat K-438. Once cooled to room temperature, each sample was distilled with 35% NaOH for 4 minutes and titrated with 0.25M H_2SO_4 to pH 4.65 using a BUCHI Auto Kjeldahl K-370 unit.

2.4. Compost harvesting and mass yield calculations
Matured composts were removed from the composters and sieved to a maximum particle size of 1 cm x 1 cm to remove odd objects and coarse particles and dried under direct 12 hours sunlight. The final mass of composts was recorded after the drying process and they are kept in tight plastic bags for further analysis. Mass yield of vermicompost and extracted humic acid were calculated in terms of weight percentage (wt%).

2.5. Humic acid extraction

2.5.1. Sample preparation. About 100 g of the composts were ground using a mortar and pestle, sieved to a maximum size of 250 µm (equivalent to US standard sieve mesh No. 60) and dried in an oven at 95°C for overnight.

2.5.2. Alkaline extraction. About 50 g of the compost was weighed and transferred into a 1 L Erlenmeyer flask. NaOH at 0.1M was added into the flask slowly while stirring until the final volume of 1 L was reached. The mixture was further stirred at 250 rpm for 6 hours. Next, the mixture was centrifuged at 5000 rpm for 15 minutes, the supernatant was collected and pellet was discarded.

2.5.3. Acid precipitation. The leached solution or the supernatant was titrated with concentrated HCl until pH 1 in an Erlenmeyer flask while stirring. The solution was left mixing to equilibrate for further 1 hour and the pH was monitored. The stirring was stopped and the HA was let to precipitate to the bottom of the flask for overnight. The solid HA particles were recovered via filtration, rinsed using distilled water and dried in an oven at 95°C for overnight. The dried mass of HA was recorded for yield calculation.

2.6. Vermibattery construction and electricity generation

Three types of battery were constructed that are a standard battery, vermibattery using vermicompost and vermibattery using humic acid. The standard battery contained only additives while vermibatteries consisted of additives together with either vermicompost or humic acid from each batch of compost. The standard battery was constructed as a control. The full formulations of the batteries are given in table 2. Simple battery cells as depicted in figure 1 (inset) were constructed with zinc and lead oxide plates as anode and cathode respectively. Voltage readings were recorded at time intervals for two consecutive days using a handheld digital multimeter.

| Additives | Weight (g) |
|-----------|------------|
| **Standard battery** | |
| 1. Activated carbon, s | 10 |
| 2. 1M H₂SO₄, aq | 60 |
| **Vermibattery** | |
| Additives 1 and 2 | 70 |
| Vermicompost of each batch, s | 50 |
| **Vermibattery** | |
| Additives 1 and 2 | 70 |
| Humic acid of each batch, s | 0.35 |
| (extracted from 50g compost) | |
3. Results and discussion

3.1. Physical observation
Moving from batch A to D, the following observations were made throughout the composting period: organics decomposed slower; rotting smell reduced; worms survived longer; composts were less watery; the final mass reduction decreased and mould presence decreased. These are typical trends of natural composting, attributed to the C and N content of the raw materials. In general, N-based organics are the elemental units for protein that promote growth while C-based organics provide energy and act as the building block for organism. Too much of N will promote ammonia gas generation, responsible for bad odour while excess of C will slow down the degradation due to lack of growth element [16]. The worms multiplied faster in batch A until a certain period which they later reduced in numbers due to lack of food. This trend diminishes in the order of batch B, C and D due to higher carbon content that can sustain worm population longer. C-based materials can be viewed as a slow-release energy provider.

3.2. Temperature and pH profiles
From figure 2, the temperature ranges from 27 to 32°C with no clear distinction of three characteristic composting phases- mesophile, thermophile and maturation. The reason is because the composters were located outdoor under a shade, which exposed them to weathering effect. The temperature range agrees to typical local temperature of 25 to 35°C. Even though the readings were taken approximately at the same time of the day, the change in weather pattern have affected the temperature profile greatly. The maturation stage cannot be reliably determined by the temperature profile due to fluctuations. However, it can be approximated at day 55 as reflected by the constant pH readings, in line with findings from many natural composting work [17-19].

Unlike the temperature profile, pH (figure 3) is not affected too much by the weather as it is mainly the result of bacterial and worms’ activity in the bins. As part of the natural process, living organisms tend to rectify the pH to a favourable condition of pH 7-8. The low initial pH reflects the natural pH of raw materials. Towards day 10, the pH increased as the result of bacterial growth in aerobic process. The increase in population and consumption of organics had resulted in higher release of organic acids and therefore lowering the pH from day 10 to 30. This trend is reflected by high presence of mould at lower pH and reduced towards the end.

After day 30, there are periods of fluctuation in the pHs until they stabilized to pH 7.5 for all the batches. This occurrence is due to “bacterial growth vs. organic acid accumulation” cycle where high population resulted in more acidic environment; hindering the bacterial growth; lowering the pH and as the population decreased; the pH was ideal again; therefore the bacteria regenerated [20]. The cycles continued until the food sources depleted towards the maturation period at day 55. Batch A can be seen to reach maturation earlier at about day 48 followed by the rest, attributed to its higher N content. These findings indicated a healthy composting pH where it is suggested that with sufficient air the pH range can naturally be maintained at 5.5 to 8.5. This condition is ideal to promote high bacterial activity and hence faster composting process [9].
3.3. TOC, TKN, HA mass yield and compost mass reduction
Compost quality was analysed via TOC and TKN as well as mass yield of humic acid. Comparison was made to the readily available vermicompost in the market. The results are tabulated in table 3.

Table 3. TOC, TKN and HA yields of Vermicomposts.

| Analysis                  | Batch A | Batch B | Batch C | Batch D | Commercial compost |
|---------------------------|---------|---------|---------|---------|--------------------|
| Initial C/N               | 20      | 25      | 30      | 35      | -                  |
| TOC (wt%)                 | 16.2    | 13.3    | 14.3    | 23.6    | 25.7               |
| TKN (wt%)                 | 2.2     | 3.3     | 3.6     | 6.5     | 2.5                |
| Final C/N                 | 33.8    | 29.6    | 28.6    | 42.1    | 10.3               |
| Weight of HA (g/50g compost) | 0.3   | 0.7     | 0.7     | 0.6     | -                  |
| Yield of HA (wt%)         | 0.7     | 1.4     | 1.4     | 1.3     | -                  |
| Initial mass (kg)         | 1       | 1       | 1       | 1       | -                  |
The final C/N ratio is the highest for batch D (42.1), followed by A (33.8), B (29.6) and C (28.6). It was expected for D to display such character due to its high initial C content (dry leaves). However, batch A with the least initial C source gave the second highest final C/N ratio, suggesting an uneven decomposition process. Many literature suggest for C/N ratio of 25 to 35 for a healthy composting activity of which outside the limits could be environmentally disadvantageous for bacteria to break down the waste [21]. Composting at extreme C/N ratios will result in uneven decomposition of C and N sources as N is always favoured naturally by the bacteria and worms.

The commercial compost has C/N ratio of only 10.3 with significantly high N content at 2.5 wt%. This indicates that the compost was prepared with a very high amount of initial N and little C sources. From business point of view, this practice is advantageous due to the ability to produce compost in a short time. However, the compost quality could be lower as the result of uneven decomposition. Batch B and C resulted in ideal compost C/N ratios as suggested by their comparable initial and final values. The finding reflects the C and N sources of the raw materials were decomposed evenly. Humic acid content in compost has a direct relation to the quality as it serves as growth promoter in plants [22]. Batch C has the highest yield of humic acid at 1.48 wt% followed by B (1.4 wt%), D (1.3 wt%) and A (0.7 wt%). These yields are considerably high compared to humic acid extracted from vermicompost of paddy straw (0.081 wt%), water hyacinth (0.053 wt%) and sawdust (0.034 wt%) [23]. Based on humic acid content, batch C with initial C/N ratio of 30 resulted in vermicompost with higher quality.

In terms of compost mass reduction, batch A scored the highest at 35 wt% while batch D is the lowest at 10 wt%. This is attributed to their initial C and N contents where N sources are consumed faster than C. From the results, it is clear that composting process is beneficial to reduce the mass of organics into nutrient-rich compost.

3.4. Voltage generation from vermibatteries

Figure 4 summarizes the voltage generation of vermibatteries using electrolytes from vermicompost (figure 4A) and humic acid (figure 4B) together with other additives. The readings after 24 hours were discarded due to the equilibrium was reached at 12 hours for vermicompost and the additives alone while 6 hours for humic acid. The voltage readings between 24 to 48 hours are within 2% differences. Comparing to the control battery running only with the additives (denoted by X), humic acid battery gave almost identical readings compared to vermicompost battery. For vermicompost battery, the presence of additives helped to serve as an electrolytic medium for ions from humic acid to flow. The solid vermicompost has provided resistance to the overall flow of the ions and therefore the voltage generation can be sustained for much longer with equilibrium voltage was reached at 12 hours (figure 4A), similar to the battery running on the additives alone.

In the case of humic acid battery, the internal resistance was removed and the active compound was utilized directly in the battery cell. Because the cell was mostly in aqueous form, it provided better flow of ions; increased surface contact with the electrodes; enhancing electrical driving force at the terminals and therefore higher voltage generated. All humic acid batteries registered initial voltage of over 3V. Due to minimal resistance, the voltage of humic acid batteries dropped rapidly until equilibrium at 6 hours (figure 4B). This improved reaction however consumed the electrodes faster. The half-cell reaction at the anode can be presented as:

\[
\text{Zn} + \text{HSO}_4^- \rightarrow \text{ZnSO}_4 + \text{H}^+ + 2e^- \\
\text{(1)}
\]
This process is known as discharging. The negative charged sulphuric ions were dissociated from \( \text{H}_2\text{SO}_4 \) used as one of the additives. Under an electric field, the negative ions moved to the negative terminal and consumed in a reaction. The \( \text{H}^+ \) protons drifted away in the electrolyte while the electrons moved to cathode. These flows of ions and electrons are attributed to an electrical potential existed in the electrolyte [24].

The other half-cell reaction at cathode or charging process can be depicted as:

\[
2\text{PbO} + 3\text{H}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{Pb}_2\text{SO}_4 + 2\text{H}_2\text{O}
\]  
(2)

The electrons deposited at the terminal causing the cation to reduce. The full-cell reaction can be expressed as:

\[
\text{Zn} + 2\text{PbO} + 2\text{H}_2\text{SO}_4 \rightarrow \text{Pb}_2\text{SO}_4 + \text{ZnSO}_4 + 2\text{H}_2\text{O}
\]  
(3)

The added sulphuric acid provided a mean of temporary recharging of the vermicbatteries until the ions were depleted. These cycles of charging-discharging have resulted in fluctuations of voltage in the cells especially at the earlier hours. The trend is more visible with vermicompost batteries due to the internal resistance provided by the solid compost. While for humic acid batteries, the bisulfate ions together with humic acid ions were much freer to flow and react.

The highest voltages generated for vermicbattery of vermicompost and humic acid were recorded for batch C at 2.9V and 3.1V respectively. Subtracting these values with the corresponding control value (2.66V) resulted in 0.24V and 0.44V of net voltage generated. Thus, it is proven that compost-derived humic acid can generate electricity, albeit a small amount.

Overall, the voltage generated from vermicompost and humic acid of batch C is marginally higher compared to the rest due to its higher humic acid content. In terms of electrolyte, humic acid can generate higher voltage but vermicompost can sustain the voltage longer. In choosing a suitable compost recipe for vermicbattery construction, ones should realize the trade-off of maximum voltage vs. durability as well as the compost quality.
Figure 4. Voltage generation of vermibatteries over time for A) vermicompost or B) humic acid as the electrolyte, with ‘X’ denotes the control.

4. Conclusion

Composting of organics is highly dependent on the C/N ratio of the raw materials with compost of high N source degraded faster. Balanced C/N ratio between initial and final were achieved at batch B and C, corresponding to C/N ratio of 25 and 30. This behaviour suggests an even decomposition of N and C sources by the worms and bacteria. Humic acid has been proven to generate a small amount of electricity with the highest net voltage production of 0.44V per 0.35g of humic acid for batch C. Vermicompost can also be used to generate comparable electricity to humic acid with an added advantage of better power durability. Batch C gave the overall ideal results in terms of compost quality, humic acid yield and voltage generation.

With the organic mass reduction of up to 35 wt%, coupled with the potential for quality compost production and prospective application as green batteries could make composting an ideal alternative than landfilling when it comes to green waste management. Future work would look into composting formulations to increase the voltage generation, experimenting with other worm species and bacteria as well as scaling-up the process.

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