

COMPOSTING OF MUNICIPAL SLUDGE - RIVERHEAD WASTEWATER TREATMENT FACILITY

JINGJING LING, HE ZHANG, TAHIR HUSAIN,
ZHIWEN ZHU & KHOSHROOZ KAZEMI

MEMORIAL UNIVERSITY
FEBRUARY 2017

2014-15 HARRIS CENTRE - MMSB WASTE
MANAGEMENT APPLIED RESEARCH FUND

Acknowledgements

The support provided by the Harris Centre at Memorial University in the form of the Harris Centre - MMSB Waste Management Applied Research Fund is highly appreciated. Appreciation is also extended to the Corner Brook Pulp and Paper Limited for providing waste material for this project.

Executive Summary

A significant amount of biosolids is generated by the Riverhead Wastewater Treatment Facility (RHWTF) every year. Although biosolids have the potential to be transformed into compost through the composting process, the usual practice is to dispose them into landfills. Composting helps stabilize the organic matter in the biosolids (Oleszczuk, 2008), and the heat generated during the thermophilic phase also kills pathogens. The organic content of the sludge will be converted into stabilized humic substances through mineralization and, hence, the volume of the sludge is significantly reduced (Gouxue et al., 2001). These composted biosolids, once applied to the soil, can accelerate plant growth, improve soil moisture retention, increase organic matter in the soil, and control erosion of the topsoil (Liang et al., 2003). Since the RHWTF-generated biosolids have a very low carbon to nitrogen (C/N) ratio (8:1), they are usually landfilled. The fly ash (FA) generated from Corner Brook Pulp and Paper (CBPP), however, has a high carbon content; its addition to biosolids could increase the C/N ratio of biosolids. Therefore, the main objective of this study is to investigate the potential application of locally available carbon-enriched ash from CBPP in improving the quality of biosolids generated by RHWTF, which serves the City of St. John's, Mount Pearl, and Paradise.

Two parallel experiments were conducted under the same conditions: CBPP fly ash (CBPP FA) was added to one reactor; the other, without CBPP FA, was used as a control unit. The results of these two reactors can be compared to determine the capability of wood ash as a stabilizer. Seven kilograms of digested wastewater sludge was weighed and added to both reactors, and two kilograms of fish waste processed in a food processor was also added to both reactors. An additional 500 grams of CBPP FA was added to one reactor. The samples were turned twice a day to keep air flow of systems. The samples of 30 grams each were taken every three days over a 30-day period.

The C/N ratio and germination index (GI) are two parameters used to evaluate the stability and maturity of a compost. From the results of C/N ratio, it is clear that the addition of fly ash can significantly increase the C/N ratio. However, the C/N ratios for two types of compost over a 30-day period have similar trends and slopes, which indicates that adding fly ash may not accelerate the composting processes. Both of the two types of compost materials have a slight C/N ratio change, indicating that the composting of each is quite slow.

The GI results reveal that both composts are not adequately mature. Extending composting time is necessary. Compared with biosolids-only compost, the addition of fly ash hinders seed germination. Therefore, a further study is suggested to investigate the phytotoxic compounds in the fly ash.

Table of Contents

Acknowledgements	2
Executive Summary	3
1 Introduction.....	7
1.1 Sludge.....	7
1.2 Composting.....	8
1.3 Fly ash	9
1.4 Objective	10
2 Characterization	11
2.1 Methodology	11
2.1.1 pH.....	11
2.1.2 C/N ratio.....	11
2.1.3 Moisture content	11
2.1.4 Trace metals	12
2.1.5 BET surface area and pore volume.....	12
2.2 Results and discussion	14
2.2.1 SEM and elemental analysis of crushed CBPPFA	15
2.2.2 XRD pattern	18
3 Experiment design	19
3.1 PAHs analysis.....	20
3.2 Results and discussion	20
3.2.1 C/N ratio.....	21
3.2.2 Germination index (GI).....	23
3.2.3 Moisture content	24
3.2.4 pH.....	25
3.2.5 Electrical conductivity	25
3.2.6 Microorganism counting.....	26
3.2.7 PAH degradation.....	28
4 Conclusions and recommendations	29
References	30

List of Figures

Figure 2-1 SEM analysis of CBPP FA	16
Figure 2-2 (Pt1-Pt3) Elemental analysis of SEM	18
Figure 2-3 XRD pattern of FA.....	19
Figure 3-1 The C/N ratio of composted biosolids with and without FA	22
Figure 3-2 The germination index (GI) of composted biosolids with and without FA	23
Figure 3-3 The moisture content of composted biosolids with and without FA	24
Figure 3-4 The pH value of composted biosolids with and without FA.....	25
Figure 3-5 The electrical conductivity (EC) value of composted biosolids with and without FA	26
Figure 3-6 Free PAHs of compost with and without FA	28

List of Tables

Table 2-1 Characteristics of biosolids and CBPP FA.....	14
Table 3-1 Result of composting parameters	21
Table 3-2 Microbial counting	28

1 Introduction

1.1 Sludge

Sludge, the main by-product in any wastewater treatment process, contains solid wastes from municipal, agricultural, commercial, industrial, and surface water (Werther and Ogada, 1999). The sludge generated from wastewater treatment plants is always a serious environmental concern. Usually, after the dewatering process the remaining solids are compressed and disposed directly into the landfill. According to the official website of the City of St. John's (<http://www.stjohns.ca/living-st-johns/city-services/wastewater-treatment>), around 65 tons of solid waste are produced and end up in the landfill every day, occupying a large area of the landfill sites. Nearby communities complain about the unpleasant odour from this dewatered sludge.

There are three widely applied ways to manage and apply sludge: landfilling, incineration, and fertilizer or soil supplement (Chen et al., 2012; Werther and Ogada, 1999). In many developing countries, treated sludge is dumped directly into the sea (Werther and Ogada, 1999); and in China, sludge can also be used as a material in cement (Chen et al., 2012).

Landfilling is a popular way to manage sludge because it does not require the use of high-tech equipment and the cost is relatively low (Chen et al., 2012; Werther and Ogada, 1999). Sludge can be dumped directly (mono-disposal) or combined with other municipal solid wastes (co-disposal) (Werther and Ogada, 1999). However, landfilling leads to many environmental issues, such as occupying a large area in landfill sites, contaminating the soil and ground water, and emitting unpleasant odours (Chen et al., 2012; Werther and Ogada, 1999; Yoshida, 2013).

Incineration can reduce sludge volume dramatically, up to 90 percent of dewatered sludge (Werther and Ogada, 1999), by converting it to ash. Incineration can also help minimize the odour released from this sludge. The energy obtained from incineration can be reused for municipal power generation (Chen et al., 2012; Werther and Ogada, 1999; Yoshida, 2013). However, combustion can

also break down the organic contaminant and convert it to carbon dioxide, which is emitted into atmosphere, leading to a concern about releasing greenhouse gases. Incineration can also produce very toxic compounds, e.g., 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), polychlorinated dibenzo-*p*-dioxins (PCDD), and polychlorinated dibenzofurans (PCDF), which are all carcinogens (Schetter, 1989).

Sewage sludge, also called biosolids, is nutrient-rich organic waste which has the potential to be used as a good fertilizer or soil supplement after appropriate treatment (Chen et al., 2012; Werther and Ogada, 1999). For instance, about 6.2 million tons of biosolids in the form of dry sludge is generated in the USA every year, half of which is applied to the land to improve soil conditions (Fytili and Zabaniotou, 2008; US EPA, 2007); 9.0 million tons of dry sludge are produced annually in European Union (EU) countries, 45 percent of which is currently used in agricultural land (Fuentes et al., 2007). Canada produces about 660,000 metric tons of dry sludge annually. Although these biosolids contain organic matters and valuable nutrients such as nitrogen, phosphorus, iron, calcium, and magnesium, and various other macro and micronutrients essential for plant growth, due to the presence of trace levels of metals, pathogens, odours, and polyaromatic hydrocarbons (PAHs) its direct application to land is still being scrutinized (Smith, 2009).

1.2 Composting

In order to sanitize and stabilize biosolids and to minimize their detrimental health effects, composting is currently being practiced globally (Tandy et al., 2009). Based on previous research, sludge-based compost can improve soil properties physically, by enhancing the soil's ability to hold water, keeping soil particles together, and improving soil porosity. It can also help to return organic matter back into the biological cycle. Once artificial fertilizer is replaced by sludge-based compost, energy and resources can be saved dramatically (Werther and Ogada, 1999; Chen et al., 2012). Although biodegradation occurs during composting, traditional composting is usually not effective in immobilizing heavy metals and organic contaminants. Other emerging contaminants of concern include chlorinated organic compounds, paraffin, plasticizer di(2-ethylhexyl) phthalate, antibiotic-resistant microorganisms, and pharmaceuticals and endocrine-disrupting compounds present in sewage sludge (Smith, 2009).

Most PAHs are highly toxic and have mutagenic and carcinogenic properties; due to their high persistence characteristics, these compounds do not easily biodegrade or decay. Compost quality can be improved by increasing the aeration, immobilizing metals and PAHs, and absorbing moisture from biosolids by adding various bulking agents such as rice husks, straw, and sawdust during composting (Zorpas and Loizidou, 2008; Yanez et al., 2009). When biosolids are co-composted with activated carbon (AC) and biochar, the immobilization of metals and the reduction of organic contaminants and PAHs (Oleszczuk et al., 2012) significantly improve the compost quality; due to the high cost of activated carbon, however, the composting of biosolids is not economically feasible.

1.3 Fly ash

Fly ash (FA) is the main by-product generated by power plants (Ahmaruzzaman, 2009; Scheetz and Earle, 1998; Zacco et al., 2014). Zacco (2014) divided FA into three types: coal, heavy oil, and biomass. Coal FA is the main residue after coal is burned at 1200-1700°C; heavy oil FA is collected in oil-fired power plants using electrostatic precipitators or other particulate control devices from flue gas in power plants (Zacco et al., 2014); and biomass FA is obtained by scrubber equipment, which is used to produce power by incinerating and converting the biomass or municipal solid wastes in thermal power plants (Zacco et al., 2014). The properties of FA depend on the fuel source (Ahmaruzzaman, 2009; Scheetz and Earle, 1998; Zacco et al., 2014). Because of its physical properties and chemical content, FA is being used as an additive in cement and concrete (Wang, 2015; Scheetz and Earle, 1998), an adsorbent (Mofarrah et al., 2013, 2014), soil stabilizer (Mofarrah et al., 2012), colour ingredient in ornamental concrete (Mofarrah and Husain, 2013a, 2013b), and an adsorbent to remove chromium from industrial waste (Mofarrah et al., 2014), naphthalene and methylene blue (MB) from wastewater treatment plants (Mofarrah et al., 2012, 2013), and natural organic matters from water supply systems (Husain and Ahmad, 2014).

Based on Ahmaruzzaman's research (2009), FA is a good absorbent in cleaning flue gas and wastewater. It efficiently removes NO_x, mercury, and organic particles in flue gas. FA can help

eliminate both inorganic compounds (boron, fluoride, and phosphate) and organic matters (phenolic compounds) from wastewater (Ahmaruzzaman, 2009; Wang and Wu, 2006).

FA is an important fertilizer or soil amendment (Ferreira, 2003; Scheetz and Earle, 1998; Zacco et al., 2014). It is rich in phosphorous (P) and potassium (K), both essential for plant growth (Ferreira, 2003). Ferreira (2003) also noted that the length of plants grown in soil with FA was twice that of those grown without FA; this indicated that FA has the potential to improve soil quality. Ferreira's research studies also concluded that plants enriched with P and K were larger than those treated with only one nutrient (either P or K). In addition to providing nutrients, FA can also be an effective "liming agent" in agriculture (Ferreira, 2003; Zacco et al., 2014). Usually FA dissolved in water results in a high pH value; this characteristic enables it to reduce soil acidity in some cases (Ferreira, 2003).

1.4 Objective

The main objective of this study is to investigate the potential application of locally available carbon-enriched ash from the Corner Brook Pulp and Paper Limited (CBPP) in improving the quality of biosolids generated by the Riverhead Wastewater Treatment Facility (RHWTF), which serves the City of St. John's, Mount Pearl, and Paradise. CBPP currently generates an estimated 10,000 tons of ash every year, which is landfilled (Western Star, 2010). This ash contains a high level of carbon. Since fly ash has a high carbon content, its addition could also increase the carbon to nitrogen (C/N) ratio of biosolids. A C/N ratio in RHWTF of only 8:1 (Wang, 2015) is considered to be low; for a good compost, the ratio should be about 25:1 (Hackett et al., 1999). Biosolids also contain heavy metals, PAHs, and organic contaminants (OCs), which are harmful to human health and the ecosystem. Composting with the addition of fly ash helps stabilize the organic matter in the biosolids (Oleszczuk, 2008), and the heat generated during the thermophilic phase also kills pathogens. The organic content of sludge is converted into stabilized humic substances through mineralization and, hence, the volume of the sludge is significantly reduced (Gouxue et al., 2001). Considering these characteristics, the co-composting of biosolids with locally available ash with a high carbon content from CBPP not only increases the C/N ratio to an acceptable level but it also improves the quality of compost by immobilizing metals and reducing OCs and PAHs. In this way, the quality of the biosolids compost is improved

significantly. These composted biosolids, once applied to the soil, can accelerate plant growth, improve soil moisture retention, increase organic matter in the soil, and control erosion of the topsoil (Liang et al., 2003). These benefits are relevant for the province, where soil has little organic matter and, due to its geological characteristics, a thin top layer. The high-quality compost thus produced can be commercialized and used to improve soil fertility and develop greenbelts, landscaping, and golf courses.

2 Characterization

2.1 Methodology

2.1.1 pH

The pH of FA from CBPP was measured by following ASTM D1512-15b. Four grams of the FA sample was added to 50 ml boiling deionized water, kept boiling on a hot plate for four minutes, and then cooled to the ambient temperature. A VWR 3000 pH meter was used to analyze the pH value at the contact surface of water and FA slurry. The test was done in triplicate, and the average value is the pH of the sample.

Two grams of the RHWTF biosolids was boiled in hot deionized water on a hotplate for five minutes, then the pH was measured by a VWR 3000 pH meter.

2.1.2 C/N ratio

The C/N ratio, an important parameter in a successful composting process, generally needs to be 25:1. This ratio is determined by weighing 2 milligrams \pm 0.1 milligrams of sludge and FA in a tin capsule, and the total C, H, and N measured by a PE 2400 CHN analyzer.

2.1.3 Moisture content

The moisture content was determined by following ASTM D1512-05 (2012). A crucible was burned in a muffle furnace at 650°C for one hour to remove the organic matters, cooled in a desiccator, and weighed and the weight was recorded; 2 ± 0.1 grams of FA and the biosolids sample respectively were weighed in the crucible and placed in a conventional oven at $110 \pm 5^\circ\text{C}$ overnight. The crucible and samples are weighed together until there are no weight changes. All

samples were analyzed in triplicate and the average was calculated as the sample moisture content. The moisture content can be calculated as

$$M\% = \frac{w_{raw} - w_{dry}}{w_{raw}} \times 100\%$$

where:

M%: moisture content in W/W%;

w_{raw} : the weight of raw sample; and

w_{dry} : the weight of the sample after drying.

2.1.4 Trace metals

The trace metals in the FA and biosolids samples were analyzed by the modified EPA method 3050 by inductively coupled plasma mass spectrometry (ICP-MS). A 100 ± 10 milligrams sample was weighed placed in a 15 ml Teflon vial (Savillex) with a screw cap, and the vial weight recorded. Then 3 milliliters of 8N nitric acid (HNO_3) was added to the vial and heated on a hot plate at 70°C for two days. The vial cap was tightly closed to reflux the acid and generate pressure to speed up digestion. The samples were then dried and cooled; 1 ml of HNO_3 and 1 ml of hydrogen peroxide (H_2O_2) were added to the system and heated at 70°C for two days to remove organic matters. The samples were then dried and cooled. An additional 2 ml 8N HNO_3 and 1 ml hydrofluoric acid (HF) were added to the samples and heated at 70°C for two days. After drying and cooling, 3 ml of aqua regia ($V_{\text{HCl}}: V_{\text{HNO}_3} = 3:1$) was added to the sample and heated at 70°C for one day. The sample was dried, cooled, and dissolved in 2% HNO_3 . All the solution was transferred to a 50 ml conical centrifuge tube and deionized water was added to 45 grams. The solution was then filtered by a $0.45 \mu\text{m}$ syringe filter. Finally, 0.5 gram of the solution was transferred to an 11 ml tube and deionized water was added to 10 grams. The solution was analyzed by an Elan DRC II ICP-MS analyzer.

2.1.5 BET surface area and pore volume

The BET surface area and porosity of the FA sample was measured by N_2 adsorption at 77K using an automated adsorption apparatus Tristar II Plus micrometric analyzer. The surface area (m^2/g) was measured from the adsorption isotherm by the Brunauer, Emmett and Teller (BET)

equation (Equations 3-6 to 3-10), using a relative pressure range of 0.05-0.35, considering that the area of the N₂ molecule is 0.162 nm² at 77K (Rodriguez-Reinoso, 1997). The total pore volume, V_T, was obtained from the N₂ adsorption isotherm at p/p₀ = 0.99.

$$\frac{1}{v\left(\frac{P_o}{P}-1\right)} = \frac{1}{v_m c} + \left(\frac{c-1}{v_m c}\right)\left(\frac{p}{p_o}\right) \quad (2-1)$$

$$v_m = \frac{1}{S + I} \quad (2-2)$$

$$c = 1 + \frac{S}{I} \quad (2-3)$$

$$SA_{BET} = \frac{(v_m NA_{(N)})}{v} \quad (2-4)$$

$$S_{BET} = \frac{SA_{BET}}{a} \quad (2-5)$$

where, v = volume of adsorbed N₂ gas at standard temperature and pressure (STP), P and P₀ are the equilibrium and saturation pressures of the adsorbate, V_m = volume of gas (STP) required to form one monolayer, c = BET constant related to energy of adsorption, N = Avogadro's number (6.02E+23), A(N) = cross section of N₂ (0.162 nm²), SABET = total BET surface area (m²), SBET = specific BET surface area (m²/g), a = mass of adsorbent (g). The BET surface was calculated from the BET equation by plotting 1 / v [(P₀ / P) - 1] on the y-axis and P/P₀ on the x-axis in the range of 0.05 < P/P₀ < 0.35. The slope (S) and the y-intercept (I) of the plot were used to calculate V_m and the BET constant c.

One important index of the capability of physical absorption is the specific surface area. A higher surface area indicates a better adsorption capability. A nitrogen (N₂) adsorption isotherm curve is one of the most commonly used methods for surface area analysis. Industrially, an iodine test is the general method to determine the surface area of AC. A methylene blue test is utilized to analyze the mesopore volume of the AC. In this study, a TriStar II Plus micrometric analyzer was utilized to analyze the surface area and the pore distribution of the FA sample. The sample

was first heated at 120°C for 2 hours for degassing. Then 500 milligrams of the sample was weighed and analyzed under different pressure levels.

2.2 Results and discussion

The pH, C/N ratio, moisture content, and conductivity of the sludge and FA were measured and reported in Table 2-1.

The pH of the biosolids and the FA are 8.7 and 12 respectively; both are alkaline. The biosolids from RHWTF show a high moisture content, while the FA is very low, which can reach the ideal mixture moisture content of 55-60%. The specific surface area of 249.4 m²/g of the FA sample indicates a relatively high surface area. Commercial ACs normally have specific surface area of 800-1200 m²/g, while coal and oil fly ash have that of 2 m²/g. The high surface area of FA enables it to act as an adsorbent, absorbent, and moisture controller. However, the absorption of moisture can cause decomposition of the FA, and the addition of bulk agents, such as saw dust and chips are required to keep the system aerated. The high C/N ratio of FA indicates that composting is a good source of carbon.

The ICP-MS result shows that both samples are dominated by Al, Ca, Fe, Mg, and P. The concentrations of hazardous metals are relatively low in the CBPP FA than that in the biosolids.

Table 2-1 Characteristics of biosolids and CBPP FA

CBPP FA		RHWWT Sludge		
pH	12	pH	8.7	
Density	0.45 g/cm ³	Density		
PAHs	Not detected	PAHs	Not detected	
Moisture content	0.89 %	Moisture content	73%	
Surface area	249.4 m ² /g	Surface area	NA	
C/N ratio	572.95	C/N ratio	7.18	
Metal content in solid (Unit: mg/Kg)				
Mg	511.65	Mg	6493	5975
Al	947.025	Al	20294	18723
Fe	784.202	Fe	18000	16038
P	114.332	P	7546	6476.91
S	<LD	S	<LD	<LD
Cl	11634	Cl	22960	34256
Zn	11.724	Zn	933.278	824.002
Cu	7.280	Cu	674.172	591.868
Pb	2.252	Pb	88.295	82.129
As	<LD	As	2.947	2.39
V	15.460	V	39.108	35.81
Cr	4.725	Cr	44.158	39.584
Ni	15.962	Ni	23.862	20.698
Ca	2656.356	Ca	10234	4121

2.2.1 SEM and elemental analysis of crushed CBPP FA

The SEM analysis of the FA indicated a wood fiber structure with pores evenly distributed on the particle surface (Figure 2-1). The porous structure also matches the high micropore volume from the BET result. Free metal oxides found in untreated FA mainly contain CaO, MgO, and Al₂O₃. Micro- to meso-pore structures can be found on the 100 nm scale SEM photo.

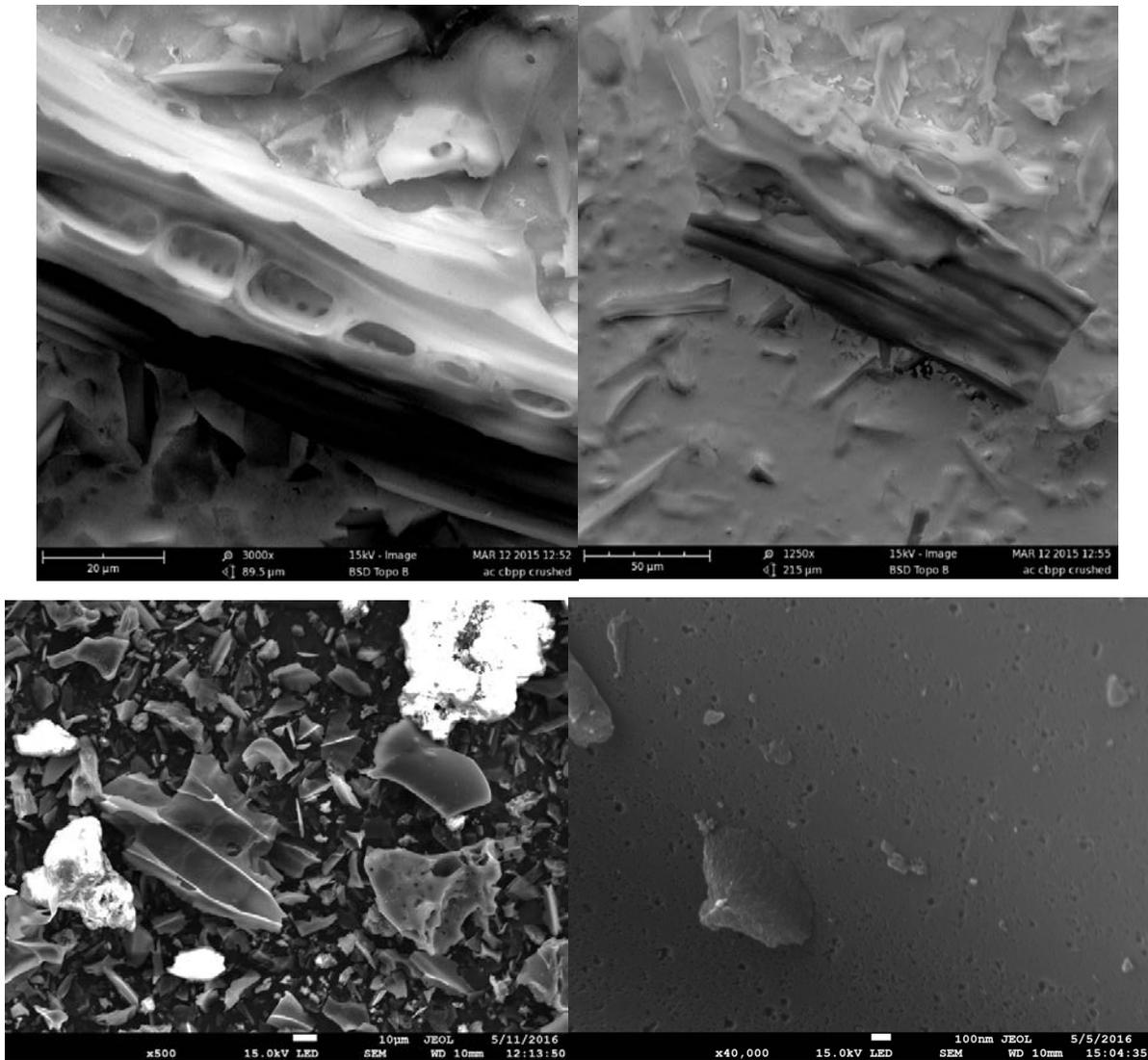
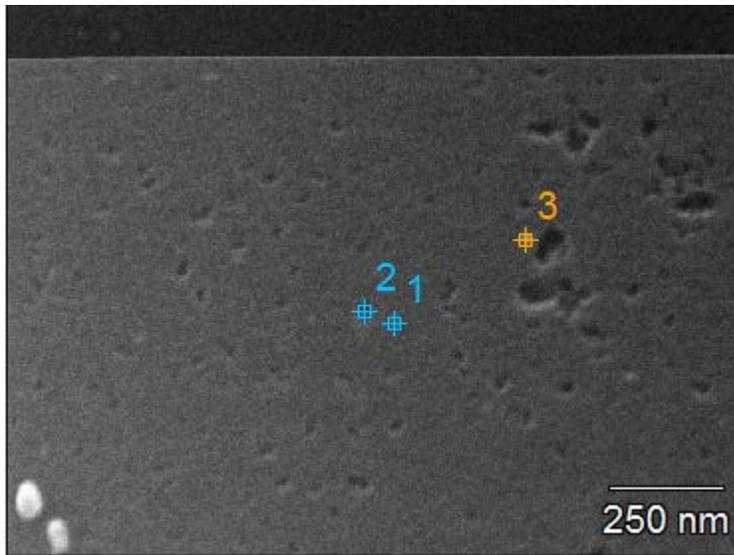
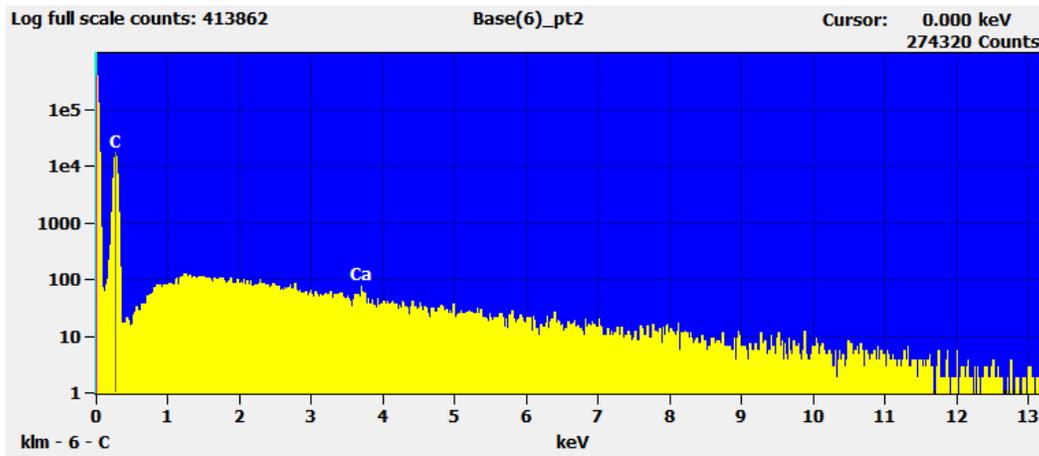


Figure 2-1 SEM analysis of CBPP FA

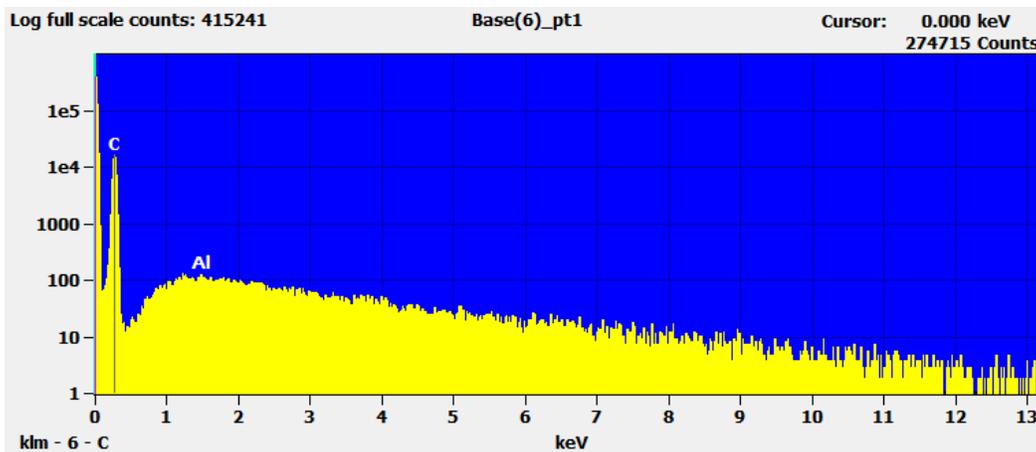
The point elemental analysis in Figure 2-1 indicates that FA is the carbon-dominated material and Ca and Al the major metal components. This also matches the ICP-MS result.



Pt1



Pt2



Pt3

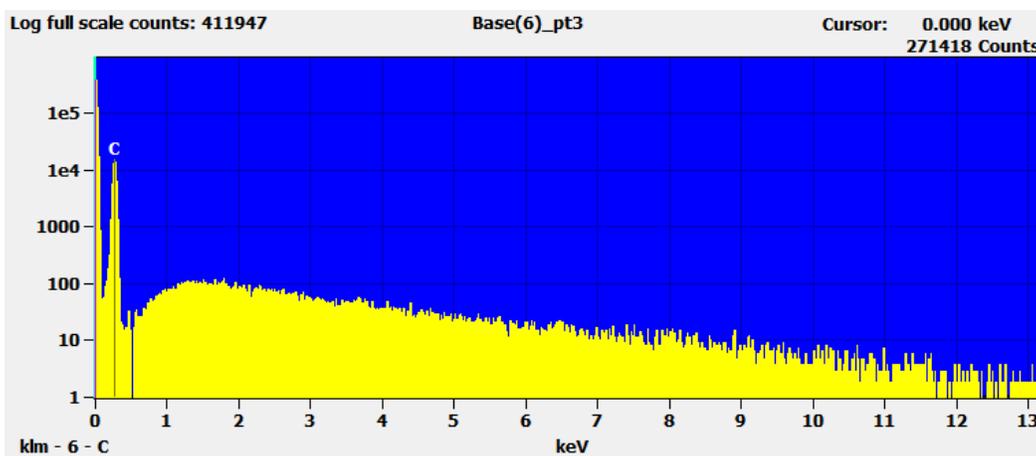


Figure 2-2 (Pt1-Pt3) Elemental Analysis of SEM

2.2.2 XRD pattern

The XRD pattern of the CBPP FA is shown in Figure 2-3. Generally, at $2\theta = 26^\circ$, the specific peak belongs to carbon. Horn illustrated the model to find out the carbon composition. The XRD pattern of FA shows the highly amorphous carbon content and low graphite carbon. This indicates the monolayer adsorption and the possibility of further modification to increase the surface area.

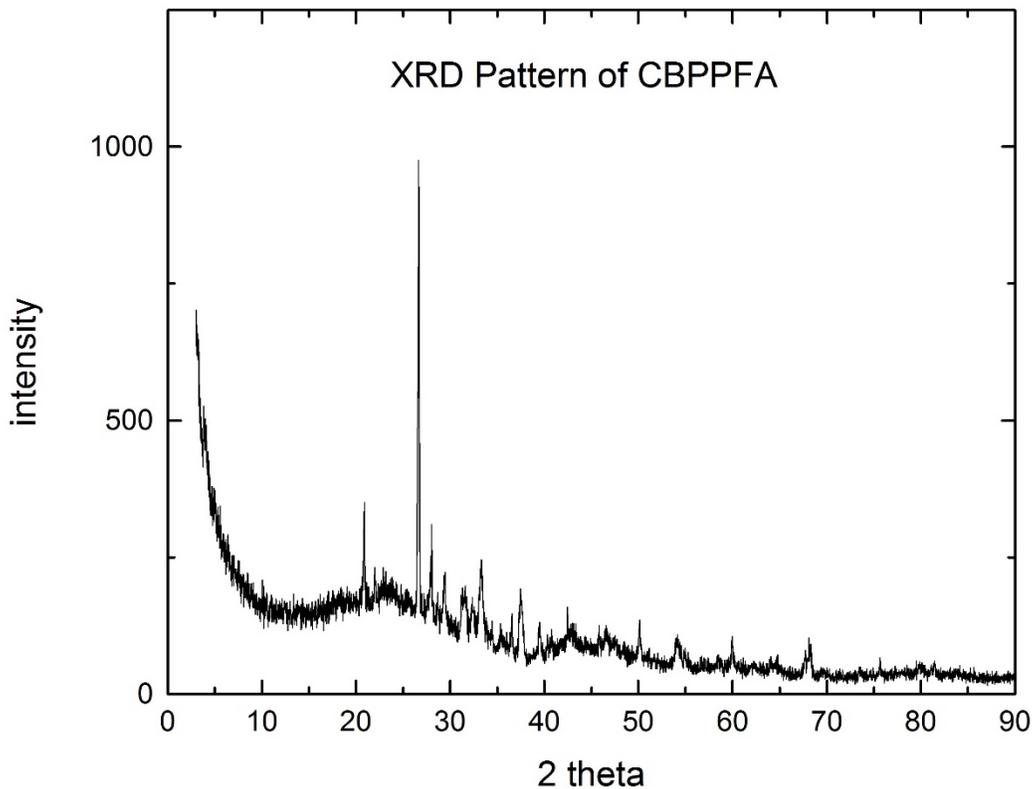


Figure 2-3 XRD pattern of FA

3 Experiment design

Two parallel experiments were conducted under the same conditions; however, the CBPP FA was added to only one reactor. The results of these two reactors can be compared to determine the capability of wood ash as a stabilizer. Seven kilograms of digested wastewater sludge and 2 kilograms of fish waste processed in a food processor were added to both reactors. An additional 500 grams of the CBPP FA was added to one reactor. The samples were turned twice a day to maintain air flow. Approximately 30 grams of samples were taken on days 1, 3, 6, 7, 9, 12, 15, 18, 21, 24, 27, and 30.

3.1 PAHs analysis

Originally, no PAH was detected in the sludge, FA, or fish waste. Crude oil was spiked as the PAH source in a 20 g/kg oil to solid weight ratio. Fish waste was added as the nitrogen source to balance the initial C/N ratio to 25:1.

PAHs were extracted by solvent extraction technology, followed by GC-MS analysis (Kriipsalu et al., 2008). A 3 ± 0.1 grams compost sample was weighed in a 15 ml conical glass centrifuge tube and 12 ml of extraction solvent (acetone: cyclohexane; v: v= 1: 1) added to it, anhydrous sodium sulfate (Na_2SO_4) can be added to the tube for free of flow purpose, then the tube was placed on a mechanical shaker for 16 hours at 200 rpm. The tube was centrifuged at 3000 rpm for 15 minutes to separate the solvent and the compost. All the solvent was transferred to another 30 ml tube, 6 ml 4% sodium chloride (NaCl) solution was added to it, and vortexed for one minute to ensure optimal mixing. The tube was allowed to settle for several minutes to separate the organic phase and the water, and then used a glass pipette to draw all of the organic phase and dried under air blow, 250 μl of hexane was added to dissolve the extract. The extract was then ready for cleanup, a process using silica gel chromatography: silica gel (SiO_2) and Na_2SO_4 were heated at 450 °C in a muffle furnace for 4 hours to activate the SiO_2 and to remove volatile Na_2SO_4 organic matters. Two grams of activated silica gel was weighed in a glass wool filled 6-milliliter syringe, then a thin layer of 2 millimeters of copper was added and an additional 2 millimeters of Na_2SO_4 was covered on the top of copper powder. After 6 ml hexane conditioning of the column, sample was added to the column and the first fraction eluted by 6 ml hexane, followed by 6 ml hexane: dichloromethane (DCM) (1:1, v:v) eluting target compounds and 2 ml DCM for medium to high polarity compounds. The hexane and DCM fraction was then air-concentrated to 2 ml for GC-MS analysis.

3.2 Results and discussion

The stability and maturity of a compost are generally determined by the C/N ratio C/N and the GI. In addition to these two parameters, the pH and moisture or water content of a final compost product are also tested. Compost samples were taken every three days over a 30-day period to determine the C/N ratio, GI, moisture content, and pH. The results are shown in Table 3-1.

Table 3-1 Result of composting parameters

Time (days)	Moisture content (%) - W	Moisture content (%) - W/O	GI (%) - W	GI (%) - W/O	pH - W	pH - W/O	EC - W	EC - W/O	C/N ratio - W/O	C/N ratio - W
1	68.45	71.30	21.35	21.37	7.52	7.24	10.16	10.03	10.70	14.02
3	69.95	71.10	23.45	28.01	7.66	7.54	10.09	9.48	10.63	14.78
6	68.98	70.48	21.14	26.00	8.20	7.95	9.8	8.98	10.55	14.56
9	68.79	69.39	24.30	23.20	8.16	8.02	9.505	8.47	10.48	14.27
12	69.80	71.58	28.89	25.07	8.29	8.13	8.5	8.25	10.26	14.18
15	70.57	72.15	26.59	27.26	8.50	8.22	8.16	8.41	10.17	14.12
18	70.20	70.85	29.22	30.79	8.47	7.96	8.29	8.57	10.20	13.95
21	70.19	69.92	31.42	32.92	8.79	7.84	9.905	8.62	10.07	13.74
24	72.37	72.75	28.08	32.94	8.82	8.01	9.18	8.71	9.67	13.85
27	71.65	71.56	33.20	35.33	8.45	7.84	9.28	8.14	9.57	13.64
30	70.54	70.59	29.26	38.22	8.68	8.12	8.84	7.86	9.76	13.72

3.2.1 C/N ratio

Carbon and nitrogen are important nutrients; microbes use carbon for energy and growth, and nitrogen for protein and reproduction. Biosolids mixed with fly ash in a ratio of 14:1 have been composted for 30 days, and the biosolids only is treated under the same conditions for comparison. Table 3-1 shows the C/N ratio change with two types of compost, biosolids and biosolids with fly ash, over a 30-day composting process and that the addition of fly ash can significantly increase the C/N ratio. However, the C/N ratio change for the two types of compost for this time period has similar trends and slope, which indicates that fly ash may not accelerate composting. The C/N ratio of biosolids with fly ash decreased from 14.0 to 13.7, while that of biosolids only dropped from 10.7 to 9.8. Both types of compost have a slight C/N ratio change, indicating that composting is quite slow in both.

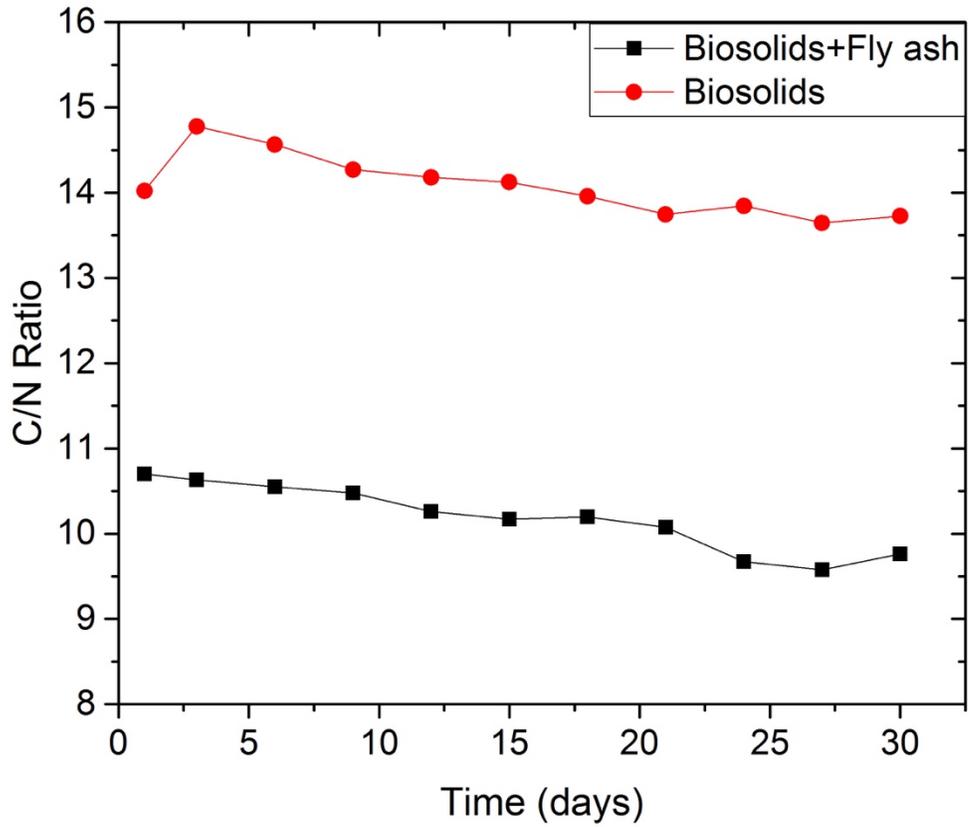


Figure 3-1 The C/N ratio of composted biosolids with and without FA

3.2.2 Germination index (GI)

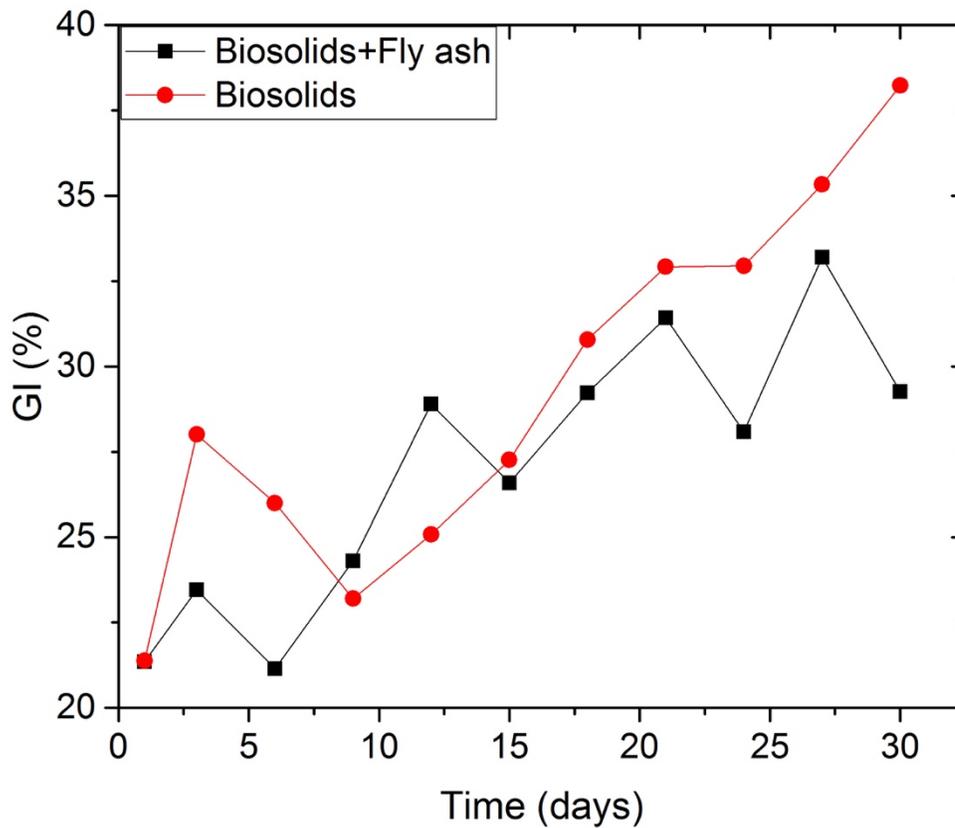


Figure 3-2 The germination index (GI) of composted biosolids with and without FA

GI is usually used for evaluating compost maturity, especially when compost products are applied to soil supplements or used as fertilizers. Figure 3-2 displays seeds sprouting in biosolids with fly ash and in sole biosolids. Within a 30-day period, the highest GI in biosolids with fly ash is 33.2%; in sole biosolids it is 38.2%. A compost with a GI value of more than 80% indicates a phytotoxic-free and mature compost (Zucconi et al., 1981). The result reveals that both types of compost are not mature enough. An extended composting time is necessary. Compared with biosolids without FA, the addition of FA hinders seed germination. Therefore, a further study is necessary to investigate phytotoxic compounds in FA.

3.2.3 Moisture content

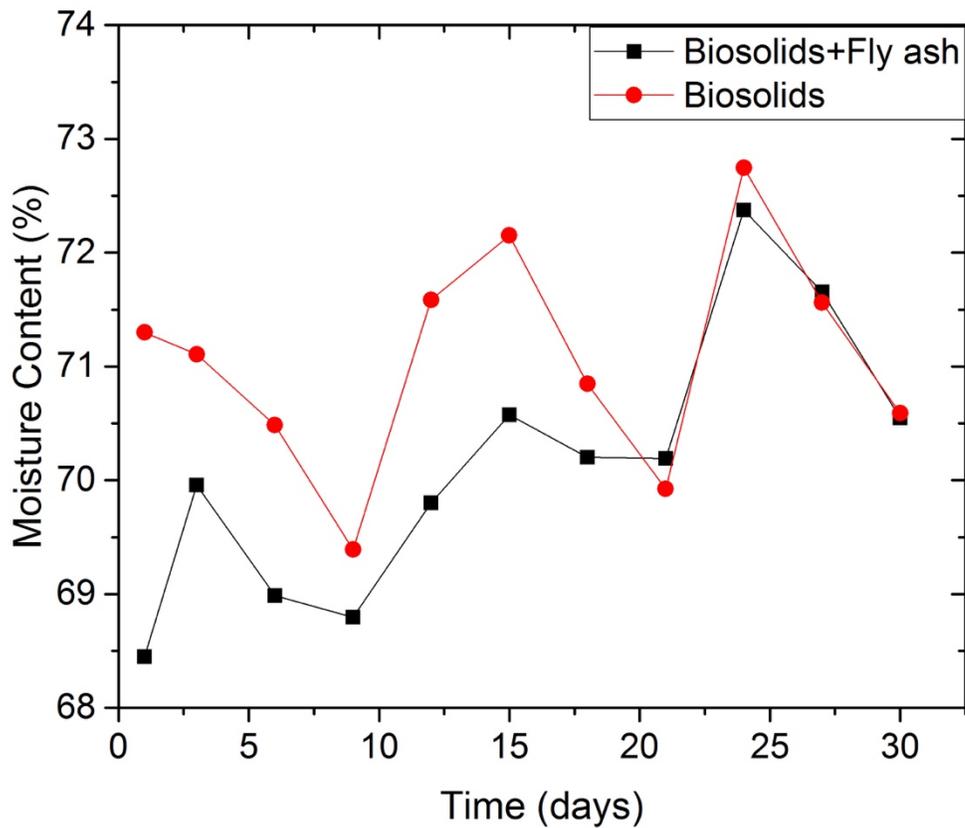


Figure 3-3 The moisture content of composted biosolids with and without FA

Moisture is essential for microbe growth: the ideal level is 40%-60%. Figure 3-3 shows the change of moisture in two types of compost during the composting process. A fluctuation of moisture is observed in both materials. The moisture content of biosolids with and without FA fluctuates between 68.5% and 72.4%, and 69.4% and 72.7%, respectively. This illustrates that both have a moisture content slightly higher than 60%, which could be why the degradation process is slowed down.

3.2.4 pH

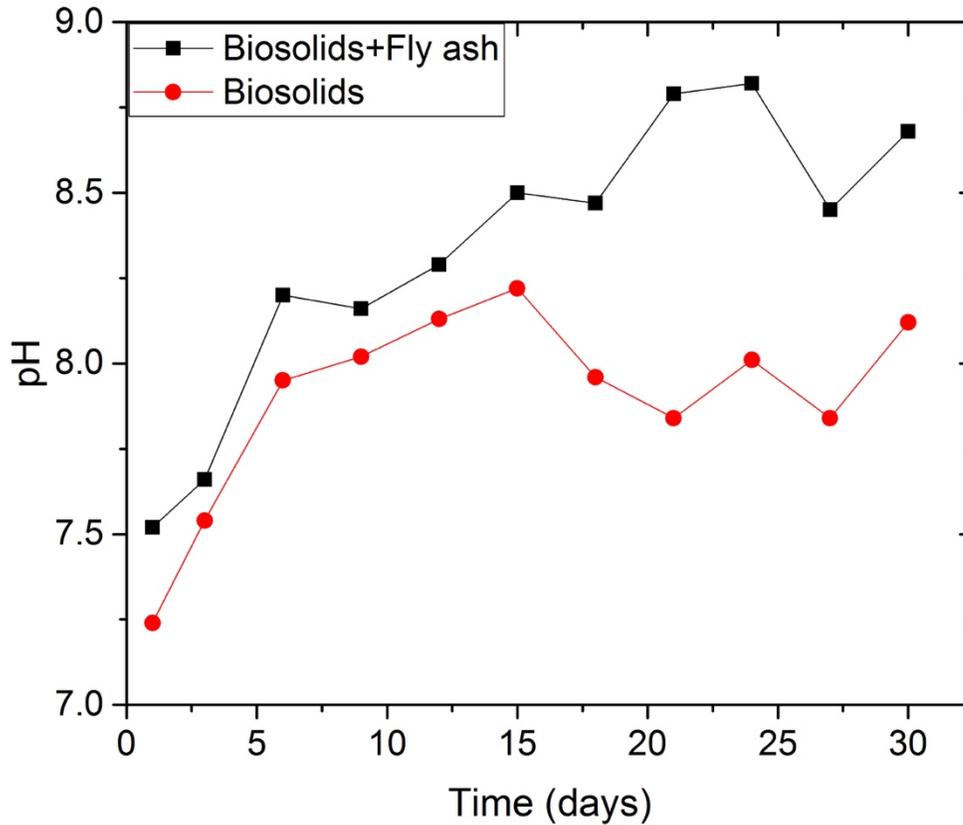


Figure 3-4 The pH value of composted biosolids with and without FA

The pH value indicates the alkalinity or acidity of the compost. During the microbial decomposition of organic compounds, ammonium (NH_4^+) is usually generated, and leads to a pH increase to above 8. As biodegradation continues, NH_4^+ is emitted from the medium as NH_3 ; meanwhile, some produced organic acid neutralizes the compost, which further decreases the pH. The pH of the compost will stabilize (Wichuk, 2010). Figure 3-4 demonstrates the change of pH in two types of compost over 30 days. The pH of both biosolids with fly ash and sole biosolids gradually increases to above 8 at the end of the 30-day period. This implies that both materials are possibly in the process of ammonium generation, and not mature yet. This is in good agreement with the results of other parameters.

3.2.5 Electrical conductivity

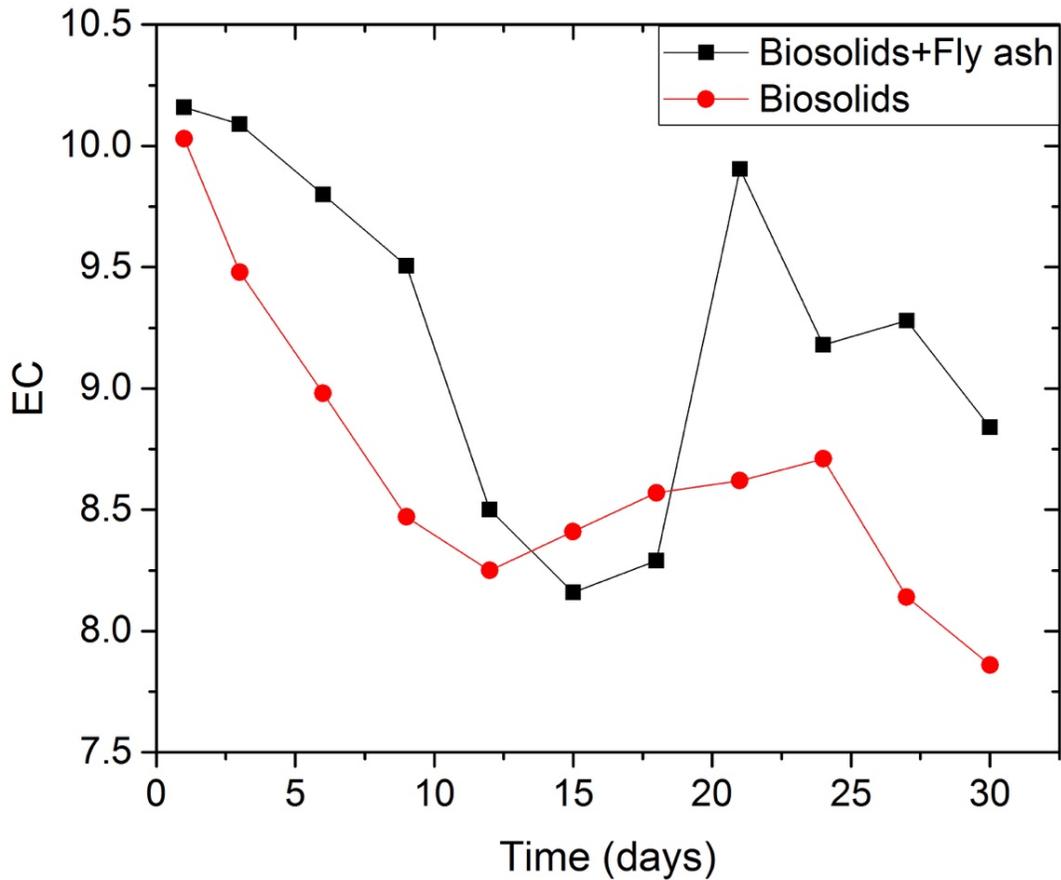


Figure 3-5 The electrical conductivity (EC) value of composted biosolids with and without FA

EC is determined at different sampling points to estimate the salinity and soluble nutrients in the compost. This value indicates whether the compost can be applied as a growth medium or an organic fertilizer. High levels of salt in compost can reduce crop yields as it hinders the root from extracting water from the soil-compost solution. In general, the majority of crops can grow in a compost with an EC below 10 mmhos/cm. Once the EC is above 10, the compost is better utilized as an organic fertilizer. As shown in Figure 3-5, the EC values of the two types of compost fluctuate between 7.9 and 10.2 mmhos/cm, which denotes that both can potentially be applied as a growth medium.

3.2.6 Microorganism counting

Microbial activity, another important indicator of compost maturity, is represented by plate counting.

Microorganism colonies were counted by the spread plate counting method. The culture medium for total thermophilic and mesophilic bacteria was 10% strength tryptic soy broth agar. A 10 grams sample was weighed in a 250 ml Erlenmeyer flask with the addition of 90 ml of a 0.85% (w/w) sterile NaCl solution. The flask was sealed and mixed on a mechanical shaker at 200 rpm for 30 minutes at room temperature. The supernatant was diluted into ten serial concentrations ranging from 10^{-2} to 10^{-10} . Four dilution factors were selected that could best characterize the microorganisms of the samples. Then 100 μL diluted solution was spread in a petri dish with the medium, and placed in a 30°C incubator for three days. The results are shown in Table 3-2. The microorganism of the sample with FA begins with higher starter, then slightly decreased in the first three days. It reaches a peak at the sixth day, and begins to decrease, at last reaches another peak at 21st day. This could be due to the unstable conditions of composting in first week, and with the increase of temperature and aeration, thermophilic bacteria began growing, then decrease after the peak. The sample without FA shows a more stable trend than the one with FA; this could be because, without FA, there is not enough carbon for bacteria growth, thus causing the slower maturity of the composting process.

Table 3-2 Microbial counting

Days	Sample with FA	Sample without FA
1	21×10^6	51×10^5
3	18×10^7	52×10^7
6	132×10^8	18×10^8
9	84×10^7	46×10^6
12	84×10^6	17×10^7
15	177×10^6	70×10^6
18	21×10^7	28×10^7
21	11×10^8	5×10^8

3.2.7 PAH degradation

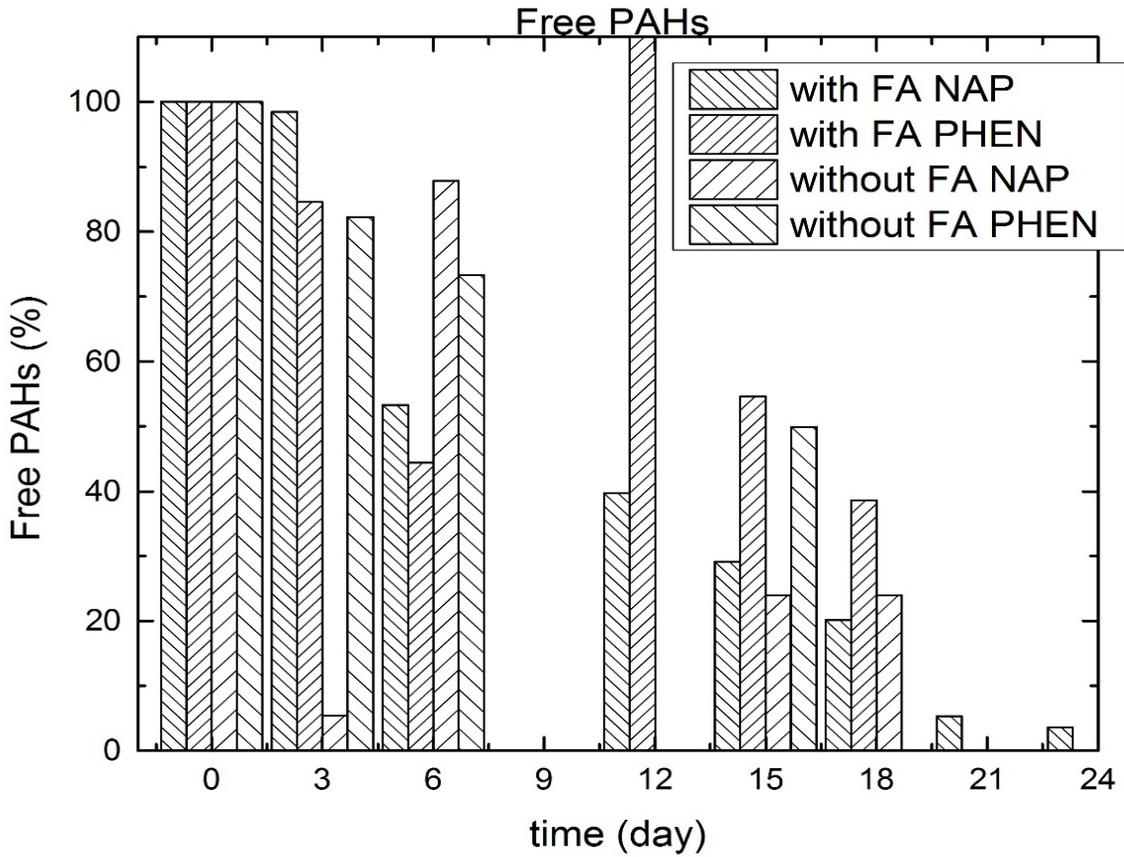


Figure 3-6 Free PAHs of compost with and without FA

Free PAHs in the compost system is one indicator of biodegradation. As shown in Figure 3-6, the concentration of extractable naphthalene (NAP) from both compost samples decreases during composting. The one with FA shows a better performance of NAP than the one without FA; this could be because the addition of high surface area FA can eventually improve PAH adsorption. Oleszczuk (2012) illustrated that AC can effectively adsorb PAHs with 5-6 rings; however, for 2-4 rings PAHs are barely effective. In this study, the better performance of compost with FA could have been due to better microbial activity.

4 Conclusions and recommendations

The following main conclusions are drawn from this research:

- 1) FA from CBPP shows good potential as a carbon source in composting;
- 2) The C/N ratio of municipal sludge is too low; an additional carbon source is required;
- 3) Utilizing municipal sludge and FA as raw materials for composting will be very slow to be matured or even cannot be matured;
- 4) FA-aided composting has the potential to reduce PAHs due to higher microbial activity and physical adsorption; and
- 5) Municipal sludge alone cannot be the raw material for composting because of the low C/N ratio.

The following recommendations are made from this study:

- 1) A high nutrient nitrogen source, such as fish waste, is recommended as the raw material to be added in a composting process;
- 2) More research is needed on the optimization of composting raw materials and related ratios;
- 3) Activated carbon maybe applied as one amendment for stabilizing persistent organic pollutants; and
- 4) The application of CBPP FA can be broadened to other fields, such as adsorbents or other media.

References

- Ahmaruzzaman, M. 2010. A review on the utilization of fly ash. *Progress in Energy and Combustion Science*, 36(3), 327-363.
- Chen, H., Yan, S.H., Ye, Z.L., Meng, H.J., & Zhu, Y.G. 2012. Utilization of urban sewage sludge: Chinese perspective. *Environment Science and Pollution Research*, 19(5), 1454-1463.
- Elaango, D., Thinakaran, N., Panneerselvam, P., & Sivanesan, S. 2009. Thermophilic composting of municipal solid waste. *Applied Energy*, 86, 663-668.
- Fernandez J.M., Plaza, C., Garcia-Gil, J.C., & Polo, A. 2009. Biochemical properties and barley yield in a semiarid Mediterranean soil amended with two kinds of sewage sludge. *Appl Soil Ecol*, 42:18-24.
- Ferreira, C., Ribeiro, A., & Ottosen, L. 2003. Possible applications for municipal solid waste fly ash. *Journal of Hazardous Materials*, 96(2-3), 201-216.
- Fuentes, M.J., Font, R., Gomez-Rico, M.F., & Molto, J. 2007. Multivariant statistical analysis of PCDD/FS in sewage sludges from different areas of the Valencian Community (Spain). *Chemosphere* 67, 1423-1433.
- Fytili, D., & Zabaniotou, A. 2008. Utilization of sewage sludge in EU application of old and new methods – A review. *Renew. Sust. Energ. Rev.* 12, 116-140.
- Gouxue, L., Zhang, F., Sun, Y., Wong, J.W., & Fang, M. 2001. Chemical evaluation of sewage sludge composting as a mature indicator for composting process. *Water Air Soil Poll.* 132.
- Hackett, G.A.R., Easton, C.A., & Duff, S.J.B. 1999. Composting of pulp and paper mill fly ash with wastewater treatment sludge. *Bioresour. Technol.* 70, 217-224.
- Husain T., & Ahmad, M. 2014. Low cost adsorbent to reduce disinfection by-products from drinking water in small communities. Proceedings of the 2014 International Conference on Environmental Engineering and Computer Application (ICEECA 2014), Hong Kong, 25–26 December 2014, CRC Press, pp. 99-104.
- Kriipalu, M., Marques, M., Hogland, W., & Nammari, D.R. 2008. Fate of polycyclic aromatic hydrocarbons during composting of oily sludge. *Environ Technol*, 29, 43-53.

- Liang, C., Das, K., & McClendon, C. 2003. The influence of temperature and moisture contents regimes on the aerobic microbial activity of a biosolids composting blend. *Bioresour. Technol.* 86, 131-137.
- Mofarrah, A., Husain, T., & Chen, B. 2013. Optimizing Cr (VI) Adsorption on Activated Carbon Produced from Heavy Oil Fly Ash. *Journal of Material Cycles and Waste Management*, DOI:10.1007/s10163-013-0197-7.
- Mofarrah, A., Husain, T., & Danish, E.Y. 2012. Investigation of the Potential Use of Heavy Oil Fly Ash as Stabilized Fill Material for Construction. *Journal of Materials in Civil Engineering, ASCE*, 24(6):684-690. [http://dx.doi.org/10.1061/\(ASCE\)MT.1943-5533.0000442](http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000442).
- Mofarrah, A., Husain, T., & Bottaro, C. 2014. Characterization of Activated Carbon Obtained from Saudi Arabian Fly Ash. *International Journal of Environmental Science and Technology (IJEST)*, 11(1): 159-168, DOI:10.1007/s13762-013-0370-5.
- Mofarrah, A., & Husain, T. 2013. Evaluation of Environmental Pollution and Possible Management Options of Heavy Oil Fly Ash. *Journal of Material Cycles and Waste Management*, 15(1), 73–81. DOI 10.1007/s10163-012-0090-9.
- Mofarrah, A., & Husain, T. 2013. Use of Fly Ash as a Color Ingredient in Ornamental Concrete. *International Journal of Concrete Structures and Materials*, 7(2):111-117, DOI 10.1007/s40069-013-0042-3.
- Oleszczuk, P., Hale, S.E., Lehmann, J., & Cornelissen, G. 2012. Activated carbon and biochar amendments decrease pore-water concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge. *Bioresour. Technol.* 111, 84-91.
- Oleszczuk, P. 2008. Phytotoxicity of municipal sewage sludge composts related to physico-chemical properties, PAHs and heavy metals. *Ecotox. and Environm. Safety* 69, 496-505.
- Scheetz, B.E., & Earle, R. 1998. Utilization of fly ash. *Current Opinion in Solid State and Materials Science*, 3(5), 510-520.
- Schetter, G. 1989. Assessment of PCDD and PCDF emissions from refuse incineration plants. *Chemosphere*, 19, 589-596.
- Sciubba, L., Cavani, L., Marzadori, C., & Ciavatta, C. 2013. Effect of biosolids from municipal sewage sludge composted with rice husk on soil functionality. *Biology and fertility of soils*, 49(5), 597-608.

- Smith, S.R. 2009. Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling. *Phil. Trans. R. Soc. A* 367, 4005-4041.
- Tandy, S., Healey, J.R., Nason, M.A., Williamson, J.C., & Jones, D.L. 2009. Heavy metal fractionation during the co-composting of biosolids, deinking paper fibre and green waste. *Bioresour. Technol.* 100, 4220-4226.
- The Western Star. 2010. Research project to examine reusing ash from Corner Brook Pulp and Paper, July 10, 2010.
- US EPA, 2007. Region 8 – Biosolids. <<http://www.epa.gov/region08/water/biosolids/index.html>> (verified February 2010).
- Wang, S., & Wu, H. 2006. Environmental-benign utilisation of fly ash as low-cost adsorbents. *Journal of Hazardous Materials*, 136(3), 482-501.
- Wang, Y. 2015. Use of blue-green algae to improve the chemical quality of municipal solid waste compost. M.Eng. Memorial University.
- Werther, J., & Ogada, T. 1999. Sewage sludge combustion. *Progress in Energy and Combustion Science*, 25(1), 55-116.
- Wichuk, K.M., & McCartney, D. 2010. Compost stability and maturity evaluation - a literature review. *Canadian Journal of Civil Engineering*, 37(11), 1505-1523.
- Yanez, R., Alonso, J.L., & Díaz, M.J. 2009. Influence of bulking agent on sewage sludge composting process. *Bioresour. Technol.* 100, 5827-5833.
- Yoshida, H., Christensen, T.H., & Scheutz, C. 2013. Life cycle assessment of sewage sludge management: A review. *Waste Management & Research*, 31(11), 1083-1101.
- Zacco, A., Borgese, L., Gianoncelli, A., Rudolf, P.W.J., Depero, L.E., & Bontempi, E. 2014. Review of fly ash inertisation treatments and recycling. *Environmental Chemistry Letters*, 12(1), 153-175.
- Zorpas, A.A., & Loizidou, M. 2008. Sawdust and natural zeolite as a bulking agent for improving quality of a composting product from anaerobically stabilized sewage sludge. *Bioresour. Technol.* 99, 7545-7552.
- Zucconi, F., Pera, A., Forte, M., & Bertoldi, M. 1981. Evaluating toxicity of immature compost. *BioCycle* 22, 54-57. ISSN:0276-5055.