PRODUCTION OF ACTIVATED CARBON FROM OIL PALM EMPTY FRUIT BUNCHES FOR REMOVAL OF ZINC

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ABSTRACT

Activated carbons derived from oil palm empty fruit bunches (EFB) were investigated to find the suitability of its application for removal of heavy metal (Zinc) through adsorption process. The thermal activation at 500, 750 and 1000°C for 15, 30 and 45 minutes was used for the production of activated carbons. The statistical analysis and batch adsorption test were done to optimize the activation conditions for activated carbon production. The results indicated that activated carbon derived from 1000°C and 30 minutes has maximum adsorption capacity (1.63 mg/g) for the removal of zinc (98%) in the aqueous solutions. The characterization of ACs produced was measured to evaluate its high quality.

Keywords: Activated carbon, oil palm empty fruit bunches, adsorption, zinc

INTRODUCTION

Heavy metals are common in industrial applications such as in the manufactures of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel etc (Kvech and Tull, 2005). Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they are exposed to humans in agricultures, manufacturing, pharmaceutical, industrial, or residential settings (Lenntech, 1998). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs (International Occupational Safety and Health Information Centre, 1999). Therefore, the removal of heavy metals from wastewater is necessary before safely discharged. The main objective of water treatment is to produce high quality water that is safe for human consumption, has aesthetic appeal, conforms to state and federal standards and economical for production. One of the tools that help to achieve these goals is by using activated carbon (Kvech and Tull, 2005).

Various treatment technologies have been developed for the purification of water and wastewater contaminated by heavy metals. The most commonly used methods for removal of metal ions from industrial effluents include chemical precipitation, solvent extraction, oxidation reduction, dialysis/electro dialysis, electrolyte extraction, reverse osmosis, ion exchange, evaporation, cementation, dilution, adsorption, filtration etc. Among these, adsorption has evolved as the front line of defense especially those could not been removes by other techniques (Mohan and Singh, 2001). One of the methods of adsorption is by using activated carbon. A variety of activated carbon available commercially but a few of them is selective for heavy metals removal and very costly. Besides, a large quantity is required for treatment of large area. Thus, utilizing economically feasible method is the solution for the problems.

Activated carbon includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended inter-particulate surface area (Kvech and Tull, 2005). These qualities impart activated carbon with excellent adsorbent characteristics that make carbon very useful for a wide variety of processes including filtration, purification, deodorization, decolorization, purification, and separation. Activated carbons have been produced from a large number of carbonaceous raw materials such as coal, lignite, wood, coconut shell, and some agricultural waste products (Guo and Lua, 1998). The effectiveness of activated carbon as an adsorbent attributed to its unique properties, including large surface area, a high degree of surface reactivity, universal adsorption effect, and favorable pore size (Kvech and Tull, 2005).

Malaysia is the largest palm oil producer in the world. This industry creates almost 14 million tonnes oil palm empty fruit bunches (EFB) per year (Suhaimi and Ong, 2001). This wastes product can be use as renewable resources to reduce the environmental problems such as disposal and burning of biomass. EFB proposed as raw material for activated carbon production due to its high carbon content. Conversion of EFB to value-added product such as activated carbon would directly solve part of the environmental problems while utilizing abundant and cheap biomass. Therefore the activation conditions were optimized to produce high quality of activated carbon for the effective removal of zinc in aqueous solution.

MATERIALS AND METHODS

Sample collection and preparation for activated carbon

Oil palm empty fruit bunches (EFB) as the raw material for the production of activated carbon was collected from Oil Palm Industry, Dengkil, Malaysia. The raw material EFB was washed several times using tap water and finally with distilled water. The EFB sample dried at 105°C for 24 hour in oven to remove excess water content until constant weight. Then, the dried sample was grinded to size of ≤0.5 mm and stored at room temperature for further use.

Production of activated carbon by thermal activation using statistical approach

For thermal (heat) activation, the initial weigh of grinded EFB was measured and placed in crucible with covered and heated in a furnace at different temperatures and times according to the design of experiment for its optimization (Alam et al. 2007). Then, the samples (activated carbon produced) were crushed and sieved using sieve shaker to size fractions less than <150 µm. Two variables such as activation temperature and time with three levels were chosen for its optimization by full factorial design (FFD) for maximum removal of zinc. A total of 9 experiments by FFD were set for the production of activated carbons (Table 1). A statistical software, Minitab Release 14, was used for statistical optimization by developing the model equation, analysis of variance, p-test, t-test, regression coefficient etc.

Characterization of activated carbon

Bulk density determination

Activated carbon with known weight was wrapped in a plastic bag. The bag dropped into 400 ml of water in a 500 ml measurement cylinder. The difference in the level of water was measured. The weight of activated carbon divided by the volume of dazed water gave the density of activated carbon (Norazatul, 2005).

Determination of moisture content

Moisture content of EFB and activated carbon were measured using oven drying method (Tina, 1994).

Determination of ash content

The AC produced (2 g) was weighted and placed into a tare crucible. Crucibles containing the AC set in the furnace. The temperature brought to 575°C and the samples left in the furnace for 12 hour or overnight. The crucible was transferred to desiccator using safety tong. Finally, the crucible allowed cooling prior to weighing (Tina, 1994).

Surface structure

Scanning Electron Microscope (SEM) was used to observe surface pore structures of activated carbons with magnification of 3000 to 5000 times (Guo and Luo, 2000).

Adsorption study

The adsorption capacity of zinc by activated carbon produced from EFB was measured under the effect of contact time, concentration, adsorbent dose, pH and agitation rate. 50 mL of zinc (10 mg/L) in aqueous solution with different dosage of adsorbent was agitated in a rotary shaker at room temperature (30±2°C). The residual concentrations were measured using HACH spectrophotometer using the manual (HACH 2002). The pH was adjusted using reagent grade dilute sulfuric acid and sodium hydroxide.

The adsorption capacity, q_e were calculated from the difference between the initial concentration and equilibrium concentration, which can calculate from:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where q_e is adsorption capacity (mg/g), C_0 and C_e are initial and equilibrium concentration (mg/L) respectively, M is the adsorbent dosage (g) and V is the volume of solution (L).

Percentage removal of heavy metal (Zn) from initial solution concentration calculated from the following Equation. Adsorption capacity and percent removal were used to optimize the activation conditions:

$$\%\,\text{Removal} = \frac{(C_0 - C_e)}{C_0} \text{x}\, 100 \quad (2)$$

RESULTS AND DISCUSSION

Production of activated carbon from oil palm empty fruit bunches for adsorption of zinc

Activated carbons were produced with different thermal temperatures and times. The optimum thermal temperature and time was determined by using statistical approach. A full factorial design was conducted to produce 9 activated carbons in order to evaluation its high quality through adsorption and characterization (Table 1).

Table 1: Activated carbons produced by the experimental design (FFD)

Run	Activated carbon	Temperature (°C)		Time (minute)	
		Coded	Actual	Coded	Actual
1	AC-1	−1	500	−1	15
2	AC-2	−1	500	0	30
3	AC-3	−1	500	+1	45
4	AC-4	0	750	−1	15
5	AC-5	0	750	0	30
6	AC-6	0	750	+1	45
7	AC-7	+1	1000	−1	15
8	AC-8	+1	1000	0	30
9	AC-9	+1	1000	+1	45

Characterization of activated carbons

Table 2 shows the characteristic of activated carbons derived from EFB at different activation temperatures and times. The yield of activated carbons was calculated from the sample weight after activation to its initial weight. Table 2 shows the percent yield versus activation temperature for different activation times. The yield decreases as temperature and times increases. The differences in AC yields became less for increasing time since more volatiles might be released, leaving only small quantities of volatiles available for evolution at the end of activation times (Guo and Luo 1998). However, the effect of activation times showed insignificant on the yield. Thus, the lower the temperatures and times produced high product yield over raw material. Thus, this factor could not been evaluated as best activated carbon since it is know that the structural properties are the most important to measure the effectiveness of the adsorbent.

Table 2: Characterization of activated carbon produced by FFD with different temperatures and times

Temp. (°C)	Time (minute)	% Yield	Bulk Density (g/cm^3)	% Moisture	% Ash
500	15	26.47	0.1999	4.26	10.82
500	30	25.73	0.2001	4.25	10.79
500	45	25.19	0.2006	4.00	10.73
750	15	22.56	0.2058	3.76	12.91
750	30	22.50	0.2062	3.09	12.90
750	45	21.47	0.2083	3.16	13.01
1000	15	19.71	0.2145	2.15	12.93
1000	30	21.01	0.2203	2.09	10.66
1000	45	18.26	0.2211	2.11	13.67

Table 2 shows that the density increases as temperature and times decreases. Bulk density defined as the weight per unit volume of material. The test provided a gross measure of particle size and dispersion, which can affect material flow consistency and reflect packaging quantity. The size of activated carbons, which was less than 150 µm, provides greater surface area and faster rate of adsorption kinetics. The high density of activated carbons attributed to high carbon content in raw material EFB (Ahmedna, 2000).

Moisture contents measured from the loss of water over initial weight of raw materials. The moisture content decreased as temperature and times increased (Table 2). However, the effect of times showed insignificant loss in moisture at temperature of 1000°C. The higher temperature has lower moisture content as it was released during activation. Activated carbon at 1000°C and 30 minutes has lowest percent moisture, which was 2.1% compared to the raw material (72%).

Ash content is the measurement of the amount of mineral matter (e.g. Ca, Mg, Si, and Fe) in activated carbon. Thus, low ash content is preferable for activated carbon. Further chemical acid treatment is required for high ash content activated carbons. The ash content increased as temperature and times increases for 500°C and 750°C. The high ash content of the activated carbon would be explained by their high specific mineral content in EFB (Ahmedna 2000). As temperature increased, the volatile content of activated carbons decreased while ash content increased. This is expected because increased devolatilization during activation resulted in the char that was being predominantly carbon (Guo and Luo, 1998).

Surface structure

The results for scanning electron micrograph (SEM) of raw EFB and the derived powdered activated carbon for activation at 1000°C and 30 minutes under 4300 times magnification are shown in Figures 1(a-b). The surface of the raw material was dense and planar without any cracks and crevices (Guo and Luo, 1998). This surface pattern had poor and negligible adsorption capacity of the heavy metals. In contrast, the activated carbon observed in the SEM was found in clear pore structure developed. A system of advanced pore network was formed since there were no more lignocellulosic structures on the surface but many small cavities over the surface. Due to these well-developed pores, the activated carbon possessed high surface area and adsorptive capacity. The adsorption capacity of heavy metals depends on the molecular size of the contaminants and the pore size of activated carbons. The pore size distribution of different activated carbon shown in Table 3 indicated that the pores diameter is greater than 2 µm which shows that meso-pores developed in all of the activated carbons.

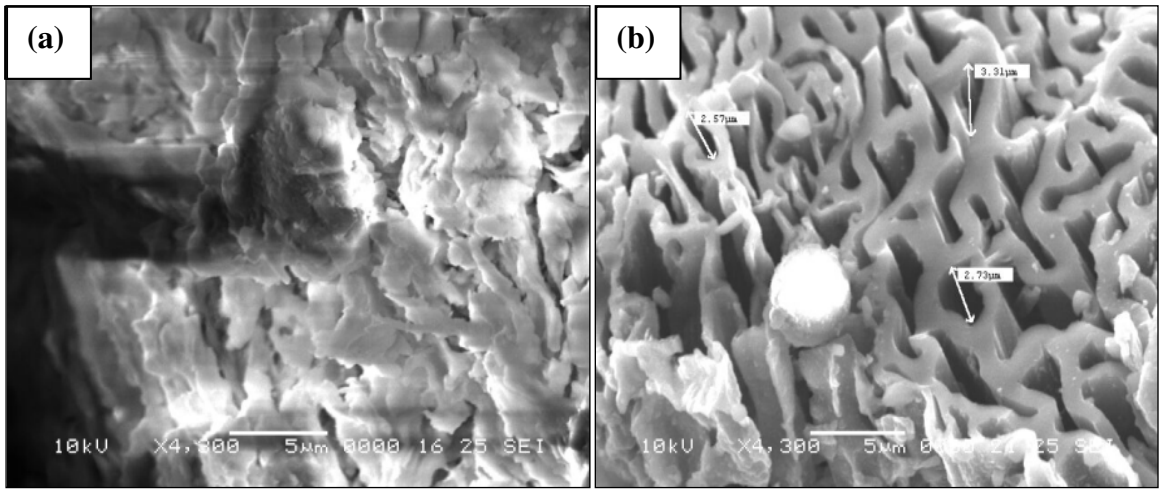


Fig. 1: SEM of (a) raw EFB; (b) activated carbon at 1000°C for 30 minutes activation

Table 3: Pore Size estimation from SEM

Activated Carbon	Pore size distribution (µm)
500 °C - 15 minutes	2.04 – 4.43
500°C - 30 minutes	2.21 – 16.40
500 °C - 45 minutes	4.43 – 7.43
750 °C - 15 minutes	3.12 – 7.26
750 °C - 30 minutes	3.36 – 7.18
750 °C - 45 minutes	5.37 – 10.8
1000°C - 15 minutes	2.26 – 5.50
1000 °C - 30 minutes	2.57 – 7.46
1000 °C - 45 minutes	1.86 – 8.51

Optimization of the activation temperature and time through the adsorption of zinc in aqueous solution

The activation temperature and time for the production of high quality of activated carbon were optimized based on percentage removal of zinc concentration. The adsorption tests were used to analyze the best activated carbon for heavy metal adsorption under different temperatures and times for activation. The adsorption tests were done at fixed parameters (contact times: 2 hour; initial zinc concentration: 10 mg/L; adsorbent dose: 6 g/l; pH 5.5; agitation 150 rpm).

Table 3 shows predicted values along with the experimental results for percentage removal of zinc. From the data, it was observed that the optimum percentage removal achieved for AC produced at 1000°C and 30 minutes of activation, which had the final concentration of 0.20 mg/l. The adsorption capacity was also highest compared to others which was 1.6333 mg/g.

Table 4: Experimental and theoretical values for percentage removal of zinc

Temperature (°C)	Time (hour)	Adsorption capacity	Experimental %removal	Theoretical %removal
500	15	1.1	67.0	66.5
500	30	1.2	72.9	74.5
500	45	1.3	80.0	79.3
750	15	1.4	82.0	81.6
750	30	1.5	88.0	88.2
750	45	1.5	90.7	91.4
1000	15	1.5	90.0	90.5
1000	30	1.63	98.0	98.5
1000	45	1.61	96.9	97.3

The statistical software Minitab Release 14 was used to generate the second-order regression equation correlating the adsorption capacity with independent variables, X_1 and X_2 as shown below:

$$Y = 3.67 + 0.136\ x^1 + 0.848\ x^2 - 0.000054\ x_1^2 - 0.00325\ x_2^2 + 0.000441\ x_1.x_2 \quad (3)$$

where Y is the dependent variable which is the adsorption capacity. The independent variables x1 and x2 are activation temperature (°C) and time (minutes); the quadratic independent variables, x11 and x22 for temperature and time and interaction independent variables, x12.

The t-value and p-value of the coefficients indicated the tests statistics and significant of each parameter. The larger the magnitude of t-test value and smaller p-values indicates the high significant of corresponding coefficient. Significant of coefficients reported to be directly proportional to t-value and inversely to p-value (Raihana, 2006). From the p-values, it is identified that activation temperature are highly significant in production of AC for high removal of zinc. The linear effect of activation temperature and time, quadratic effect of activation temperature and interaction effects between temperature and time were significant since the p-value less than 0.05.

Table 5: Coefficients of linear, quadratic and interaction effects for regression analysis

Predictor	Coefficient	Standard Error (SE) Coefficient	T-value	P-value
Constant	3.667	5.640	0.65	0.562
x1	0.13559	0.01469	9.23	0.003**
x2	0.8479	0.1547	5.48	0.012*
x11	-0.00005415	0.00000935	-5.79	0.010**
x22	-0.003248	0.002739	-1.19	0.321
x12	-0.00044103	0.00009000	-4.90	0.016*

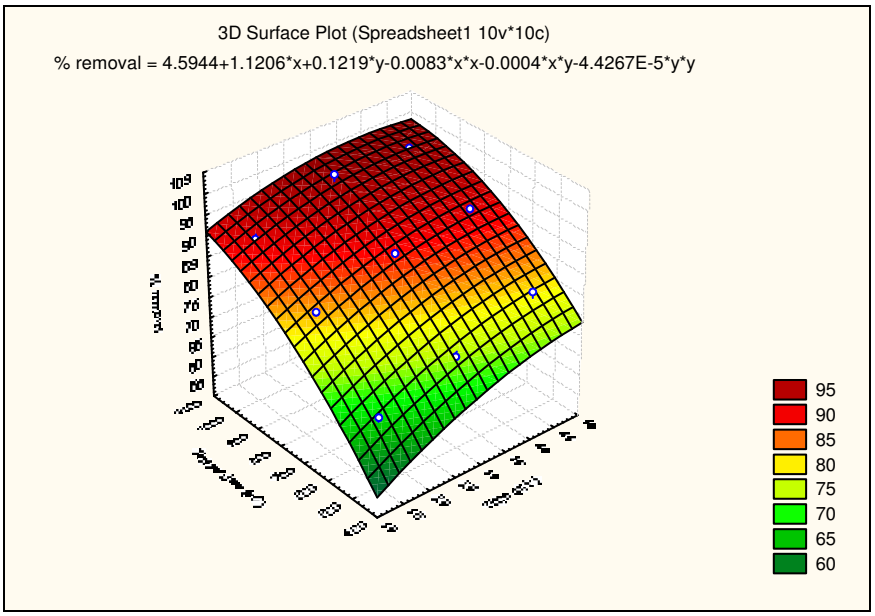
**p<0.01; *p<0.01

The model presented a high determination coefficient ($R^2 = 0.998$) explaining 99.8% of the variation in percentage removal can be explained by the independent variables; temperature and time. While the adjusted R^2 obtained is 99.4% of the variation in percentage removal. This adjusted R^2 value is necessary when comparing two or more regression models that predict the same dependent variable but have different numbers of explanatory variables (Raihana, 2006).

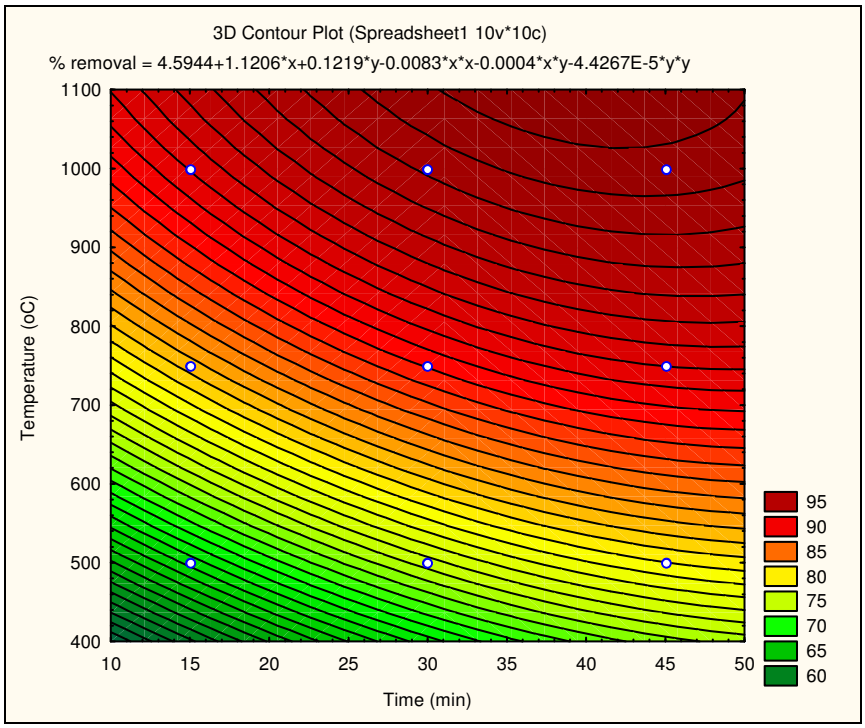
The 3D response surface and the 2D contour plots are graphical representation of the regression equation in order to determine the optimum values and the limit of each independent variable. Both plots presented in Figure 2a-b. The main goal of response surface is to hunt efficiently for optimum values of the variables such that the response maximized. Each contour curve represents an infinitive number of combinations of two-test variables. The maximum predicted value indicated by surface confined in the smallest ellipse in the contour diagram. Elliptical contours obtained when there is a perfect interaction between independent variables. The surface plot in Figure 2a indicated that as the temperature and time increased, the percentage removal increased. However, it been reported that high temperature may cause shrinkage of activated carbon at post softening and swelling temperatures, resulting in narrowing or closing pores (Guo and Lua, 1998). Thus, increasing temperature higher than 1000°C may not necessarily increase the adsorption capacity as well as would not be practical for large scale production.

CONCLUSIONS

The results obtained in this study indicated that oil palm empty fruit bunches (EFB) as an effective and inexpensive raw material for the production of activated carbon for the removal of zinc from wastewater. The activated carbon produced was at optimum activation temperature of 1000°C and time of 30 minutes. The SEM showed the presence of pores with estimated pores size between 2.57 to 7.46 µm. Based on the characterization study, activated carbon produced at 1000°C and activation time 30 minutes has yield of 21%; bulk density of 0.22 g/cm^3; moisture content of 2.1% and ash content of 10.7%. The AC produced with optimum conditions were able to remove about 98% removal of zinc in aqueous solution with the adsorption capacity of 1.63 mg/g.



(a)



(b)

Fig. 2: Removal of zinc by activated carbon at temperature of 500-1000°C and time of 15-45 minutes(a) Surface plot (b) Contour plot; of Percentage Removal of Zinc in response to activation temperatures and times

ACKNOWLEDGMENT

The authors are grateful to the Ministry of Higher Education, Malaysia for financial support by approving the Fundamental Research Grant Scheme (FRGS).

REFERENCES

Ahmedna, M., Marshall, W.E., Rao, R.M., Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. Bioresource Technology, Vol. 71, pp. 113-123, 2002.

Alam, M.Z., Muyibi, S.A., Mariatul, F.M., Radziah, W., Activated carbons derived from oil palm empty-fruit bunches: Application to environmental problems. Journal of Environmental Science, Vol. 30, pp. 315-321, 2007.

Guo, J., Lua, A.C., Characterization of chars pyrolyzed from oil palm stone for the preparation of activated carbons. Journal of Analytical and Applied Pyrolysis, Vol. 46, pp. 113-125, 1998.

Hach Company. Water Analysis Book. Hach Company, Colorado, 2002.

Hamdan M., Country Report Biomass -Potentials, Research and Development and Application in Malaysia. Retrieved August 8, 2006, from: http://www.sirim.com.my, 2006.

International Occupational Safety and Health Information Centre (1996). Heavy Metal Toxicity. Retrieved August 2, 2006 from: http://www.lef.org/protocols/prtcl-156.shtml#comm

Kvech, S., Tull, E., Activated Carbon. Retrieved August 10, 2006, from: http://ewr.cee.vt.edu/environmental/teach/wtprimer/carbon/sketcarb.html

Lenntech, H. B.V. Heavy Metals. Retrieved August 8, 2006, from: http://www.lenntech.com/heavy-metals.htm

Mohan, D., Singh, K.P., Single-and multi component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Research, Vol. 36, No. 9, pp. 2304-2311, 2001.

MPOB. Malaysian Palm Oil Board: Review of the Malaysian Oil Palm Industry, Malaysia, 2000.

Norazatul, H., Production, Characterization and Utilization of Activated carbon and Pyroligneous Acid from Oil Palm Shell. Bachelor's Thesis, Department of Process and Food Engineering, University Putra Malaysia, 2005.

Raihana, S., Chromium removal from polluted water using activated carbon and carbon nanofibers. Bachelor's Thesis, Department of Biotechnology Engineering, International Islamic University Malaysia, 2006.

Suhaimi, M., Ong, H.K., Composting Empty Fruit Bunches. Retrieved August 4, 2006, from: http://www.agnet.org/library/article/eb505a.html#0

Tina, E., Laboratory Analytical Procedure: Standard Method for Ash in Biomass, UPM, Malaysia, 1994.