



Effect of Blood Cockle Shell and Palm Kernel Shell Weight Ratio on the Acid Neutralizing Capacity of Calcined Products

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ABSTRACT

Heavy metals from mining sites can contribute to adverse health and environmental issues. Conventional liming practice depletes natural limestone deposits. Blood cockle shell (BCS) and palm kernel shell (PKS) calcination produced alkaline ash to immobilize heavy metals in soil. This study investigates the acid neutralizing capacity (ANC) of calcined BCS and PKS composites. BCS and PKS composites were prepared at various weight ratios (i.e. 1:0, 1:1, 1:5, 1:10, and 0:1) and were combusted for 1 hour at 400°C and 900°C, respectively. BCS and PKS composites were determined by its yield, pH, and ANC. The combustion characteristics for composites was conducted using thermogravimetric analysis (TGA). Elemental analysis was conducted using X-ray fluorescence (XRF) spectroscopy. Fourier transform infra-red (FTIR) was conducted for functional groups analysis. Ash content of composites increased when the portion of PKS feedstock is decreased. Increasing combustion temperature from 400°C to 900°C reduced the ash contents. The pH of raw and combusted composite (at 400°C) decreased as the portion of PKS feedstock is increased. Calcined composites at 900°C have slightly different pH value except for 0:1 sample. ANC value increased as PKS portion in composites reduced. Higher content of calcium oxide (CaO) in the composites increased the ANC value.

Keywords: Bioaccumulation, bivalve waste, heavy metals, pyrolysis, soil remediation

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INTRODUCTION

Widespread heavy metal contamination of soil is a global issue. Leachate from mine soil can contain hazardous levels of heavy metals (Ali et al., 2004). Prolonged exposure to heavy metals may contribute to anaemia and severe damage to the nervous system. The conventional remediation method for mine soil is liming with alkaline minerals such as

ground magnesium limestone (GML) or dolomite. Liming neutralizes the pH of acidic soil, and immobilizes toxic metals in the soil (Trakal et al., 2011). Consequently, large amounts of limestone are required for in-situ remediation of contaminated soil. Excessive quarrying may lead to depletion of natural limestone reserves.

Blood cockle shell (BCS) has a high calcium carbonate (CaCO_3) content, and can be a potential liming agent for soil remediation. Combustion increases the alkalinity of BCS as CaCO_3 is converted to calcium oxide (CaO). The increased alkalinity in the calcined BCS is essential for effective heavy metal immobilization in the mine soil. Palm oil milling industry generates an abundance of biomass, such as palm kernel shell (PKS) and empty fruit bunches (EFB). Palm oil milling production in Malaysia contributed around 4506 kilotonnes of PKS as waste produced. Burnt PKS may improve soil fertility by providing nutrients such as magnesium and potassium.

Calcination on BCS and PKS composite with various weight ratios generates a different percentage of CaO. The addition of PKS may aid in the combustion of BCS. Acid neutralizing capacity (ANC) determines the capability of materials to neutralize acidity and is significantly influenced by the CaO contents in the combustion of BCS and PKS composite. The aim of this study is to evaluate the effect of BCS and PKS calcination at various weight ratios on the chemical and physical characteristics of ash (i.e. yields, pH, elemental composition and ANC). The study hopes to determine the optimum BCS and PKS feedstock composition for producing ash with high ANC value for immobilizing heavy metals in soil.

METHOD

Preparation for BCS and PKS

Blood cockle shell was collected from Sabak Bernam, Selangor. The as-received BCS was boiled with deionized water for 2 hours and oven-dried for 72 hours. Dried BCS were crushed and pulverized to 75 μm in diameter. Palm kernel shell from Jengka, Pahang was sun-dried and oven-dried for 48 hours and 24 hours, respectively. Then, PKS was crushed and pulverized to 75 μm in diameter. Both BCS and PKS were kept in polyethylene zip lock bags.

Pyrolysis of BCS and PKS

Blood cockle shell and PKS were homogenized at various weight ratios (i.e. 1:0, 1:1, 1:5, 1:10, and 0:1). 10 g from each composite were placed in an uncovered crucible and combusted for 1 hour using muffled furnace under air condition at 400°C and 900°C, respectively. The ash samples from pyrolysis process was cooled in a desiccator.

TGA/DSC 1 Star System (Mettler Toledo, USA) instrument was used for TGA analysis. Composites sample (20 mg) was combusted to 900°C at 10°C/min of heating rate. Air flow rate was set at 50 mL/min for combustion process.

Ash samples from combustion and commercial liming products (i.e. ground magnesium limestone (GML) and dolomite) were homogenized prior to chemical characterization. Elemental compositions for ash samples were determined using X-ray fluorescence (XRF) spectroscopy (Epsilon3-XL PANalytical, Netherlands). FTIR spectra were recorded from KBr

disc containing 10% w/w of ash samples, using an FTIR spectrometer (Perkin Elmer Spectrum One, USA). 2 g of ash samples were mixed with 20 mL of 10 mM CaCl_2 , and the pH values were determined using a calibrated pH meter. The ANC values were determined based on the method described by Venegas et al. (2015). All analyses were conducted in duplicate and the average values were determined using MS Excel spreadsheet.

RESULTS AND DISCUSSION

Figure 1 shows the pH and weight percentage of ash for BCS and PKS composites. Increasing portion of PKS reduced the composites ash content weight percentage. In addition, composites that were combusted at 900°C produced lower ash content compared to those at 400°C. Composites with more PKS portion (i.e. 1:10) and combusted at 900°C produced only about 13% of ash. Compared to others weight ratio, the 1:10 composite contains more lignocellulosic component, and was mostly combusted. For comparison, 1:0 composites have higher ash content due to the high content of CaCO_3 in BCS feedstock.

Reduction in pH value can be traced once the PKS ratio is increased for raw and 400°C composites samples. Composites samples calcined at 900°C have slightly similar pH value except for 0:1 composite. This may due to the presence of calcium oxide (CaO), produced by the decomposition of CaCO_3 in the BCS-added composites. Combustion of PKS in the 0:1 composite has negligible amount of CaO (i.e., 0.8 and 1.8% at 400°C and 900°C, respectively).

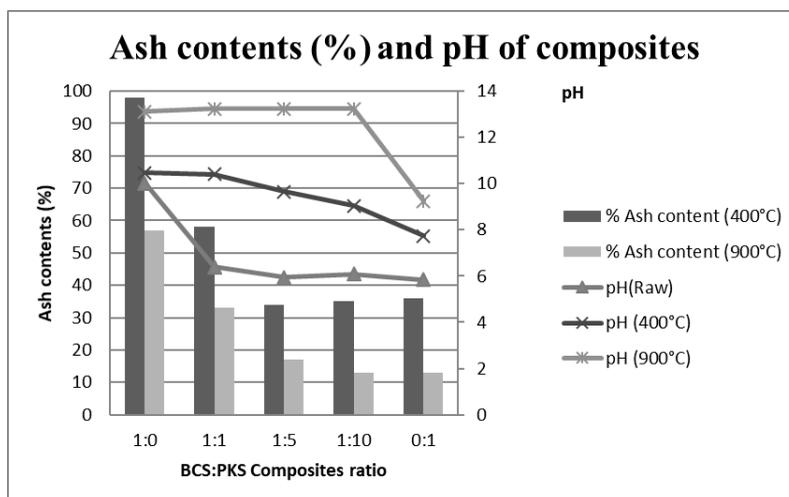


Figure 1. Ash content (%) and pH values of BCS: PKS composites (BCS:PKS feedstock ratio: 1:0, 1:1, 1:5, 1:10, and 0:1)

Figure 2 illustrates thermogram for BCS and PKS composites (1:0, 1:1, 1:5, 1:10 and 0:1). BCS samples (1:0) that contain primarily aragonite decomposed at 830.47°C (Mustakimah et al., 2012). High temperature was required for thermal decomposition of aragonite to calcite (Mustakimah et al., 2012). Decomposition of PKS (0:1) involved four stages: (1) the removal

of moisture (at temperature between 30.38°C to 114.79°C); (2) decomposition of hemicellulose (at temperature between 114.79°C to 192.94°C); (3) decomposition of cellulose (at 192.94°C up to 343.26°C); and lignin decomposition (at 346.34°C up to 531.46°C). Composite samples that contain a greater portion of PKS (i.e., 1:10) decomposed faster than those with the lower portion of PKS (i.e., 1:1 composite). Moisture removal from 1:10 composites samples occurred between 35.44°C and 113.37°C. Decomposition of hemicellulose and cellulose started rapidly at 113.37°C to 158.16°C, and 158.16°C to 543.78°C, respectively. The addition of PKS into BCS increased lignocellulosic material in the composite, and may have accelerated the decomposition process.

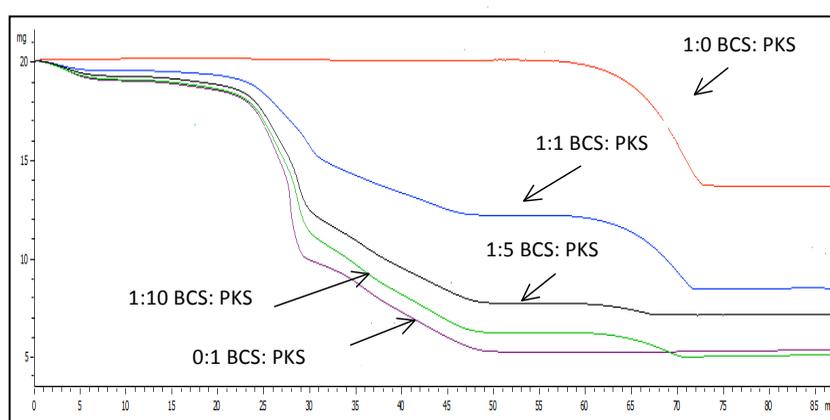


Figure 2. Thermograms for BCS and PKS composites (BCS:PKS feedstock ratio: 1:0, 1:1, 1:5, 1:10, and 0:1)

Table 1 shows FTIR wavenumber for 900°C BCS: PKS composites. FTIR wavenumber obtained is essential to distinguish present of calcium oxide from several ratios of 900°C BCS: PKS composite samples. Presence of medium bands at 3644 cm^{-1} and 3645 cm^{-1} for three composite samples (i.e., 1:0, 1:1 and 1:5) indicates that CaO is present (Zaki et al., 2006). 1:0 composites ratio has slightly more content of CaO as compared to 1:1 and 1:5 ratios. 1:10 composites have SiO- band due to presence of PKS that contain more silicate components.

Table 1
FTIR wavenumber for BCS: PKS composites (BCS:PKS feedstock ratio: 1:0, 1:1, 1:5, 1:10, and 0:1) produced at 900°C

Composites Ratio	Wavenumber (cm^{-1})			
	CaO ⁺ (medium band)	CaO ⁺ (medium broad band)	COO ⁻	SiO ⁻
1:0	3645	1458	-	-
1:1	3645	1412	876	-
1:5	3644	1416	876	-
1:10	-	1416	-	1036

Table 2
 Chemical composition of BCS and PKS composites (BCS:PKS feedstock ratio: 1:0, 1:1, 1:5, 1:10, and 0:1) produced at 400°C and 900°C

Elemental Composition [%]	1:0 BCS:PKS		1:1 BCS:PKS		1:5 BCS:PKS		1:10 BCS:PKS		0:1 BCS:PKS						
	Raw	400°C	900°C	Raw	400°C	900°C	Raw	400°C	900°C	Raw	400°C	900°C			
CaO	55.68	49.53	61.42	37.73	48.70	56.74	16.2	20.49	41.76	11.0	16.63	30.90	0.52	0.82	1.80
K ₂ O	0.14	0.09	0.17	0.68	0.85	0.60	1.23	1.63	1.85	1.41	2.89	2.76	1.54	3.04	5.42
MgO	4.08	3.80	3.52	4.37	3.05	5.56	3.59	3.44	3.24	3.36	3.53	4.24	3.85	3.78	4.35
Al ₂ O ₃	6.45	6.64	7.84	7.62	9.87	8.65	6.18	7.39	16.29	4.35	11.60	22.98	3.76	10.57	29.98
Fe ₂ O ₃	0.07	0.08	0.06	1.21	1.45	1.23	3.71	3.41	5.17	4.89	7.49	7.95	6.70	10.98	20.07
SiO ₂	0.95	0.88	0.78	4.52	8.47	6.20	7.30	12.86	25.45	8.19	22.65	35.56	7.26	22.43	55.23

Table 3 shows ANC values for BCS and PKS composites prepared at 400°C and 900°C. Raw samples for BCS and PKS composites have lower ANC value than BCS (1:0). As the samples undergo thermal degradation, high temperature altered the condition and chemical composition of feedstock materials. The calcined 1:0 composite (900°C) has the highest ANC value (746 meq kg⁻¹), followed by calcined 1:1 composite (900°C) (698 meq kg⁻¹). ANC value increased as the combustion temperature was increased to 900°C. In contrast, the value of ANC was reduced when the composition of PKS feedstock were increased in the composite samples. The pH values for both calcined composites of 1:0 (13.12) and 0:1 (9.24) were slightly lower than the 1:1 composite (13.23). Major chemical compounds that have contributed to the increase of the ANC value are CaO, MgO and SiO₂. As illustrated in Table 2, calcined BCS has about 61.42% of CaO, slightly higher than the 1:1 composite (56.74%). Surprisingly, the calcined 1:1 composite has about 0.60 % K₂O, 5.56% MgO and 6.20% SiO₂ compare to the 1:0 composites (900°C) (0.17% K₂O, 3.52% MgO and 0.78% SiO₂). Higher content of K₂O, MgO and SiO₂ in the calcined 1:1 composite (900°C) contributed to the shifting of the ANC value of samples (Paul et al., 2005).

Table 3
Acid neutralizing capacity value of various materials

Samples	Acid Neutralizing Capacity value (meq kg ⁻¹)		
	Raw	400°C	900°C
CaO (Bendosen, 99.0%)	845	-	-
CaCO ₃ (John Kollin, 99.80%)	399	-	-
CaCO ₃ (Merck, 98.50%)	358	-	-
Dolomite	348	-	-
GML	369	-	-
1:0 BCS: PKS	369	434	746
1:1 BCS: PKS	112	437	698
1:5 BCS: PKS	46	191	474
1:10 BCS: PKS	42	136	296
0:1 BCS: PKS	11	10	25

CONCLUSION

The calcined 1:0 composite has an outstanding ANC value of 746 meq kg⁻¹. Data obtained from this study revealed that chemical compositions of BCS and PKS composites were changed when different weight ratio of BCS and PKS feedstock were selected. High yield of ash from the combustion process, and increasing CaO content in the combusted composite samples) increased the ANC value. High ANC values for the combusted composite indicates that it is a suitable material for liming contaminated soil.

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