

Optimization of extraction method and characterization of humic acid derived from coals and composts

(Pengoptimuman kaedah pengekstrakan dan pencirian asid humik daripada arang batu dan kompos)

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Keywords: humic acid, coals and composts, extraction techniques, chemical characteristics

Abstract

Humic acid (HA), known as the black gold of agriculture, is increasingly becoming popular for use in agriculture. HA from sub-bituminous coals from Mukah, Sarawak, commercial HA product (leonardite), humified peat and various types of compost were extracted and their chemical characteristics compared. HA yield from various coals ranged from 1.5–11.1% while composts yielded HA from a low of 4.2% to 16.5%. Humified peat and commercial leonardite contained 31.6% and 58.5 % HA respectively. Functional group analyses of extracted HA from Mukah coals showed a narrow range of carboxylic group from 3.2–3.5 meq g⁻¹ while phenol-OH group was between 6.8–7.3 meq g⁻¹. Functional groups in HA from composts were, however, lower than those obtained from coals. The total acidity of HA from composts ranged from 5.6–9.5 meq g⁻¹, carboxylic group at 1.9–3.5 meq g⁻¹ and phenol-OH group, 3.5–6.2 meq g⁻¹. Fourier Transformed Infrared (FTIR) spectra of extracted HA from coals, leonardite and chrysanthemum compost had distinct clear absorption bands indicating the presence of major HA structural elemental groups such as H bonded OH (3400 cm⁻¹ peak), C=O of carbonyl (1710 cm⁻¹ peak) functional groups, aliphatic components CH₂ and CH₃ (2930, 1420 and 1370 cm⁻¹ peaks) and C=C of aromatic ring (1620 cm⁻¹).

Introduction

Humic acid (HA) is a complex organic molecule with high molecular weight ranging from approximately 5,000–100,000 Daltons. It is dark brown or black, soluble in alkaline solution and insoluble in acidic condition (Fulcrum Health Limited 2004). The role of HA in improving agricultural soils is well established, especially in soils with low organic matter (Pettit 2002).

Humic acid has long been used in enhancing crop productivity and soil fertility. It also plays an important role in human health and animal husbandry (ENVIROMATE TM 2002). Many reports on its medicinal values have also been published (Anon. 1999; ENVIROMATE TM 2002).

The market for humate is expanding. Humic acid products mainly as plant growth enhancers and as an ingredient in fertilizer

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products are widely distributed throughout the world. The largest markets are in Europe (Germany, UK, Switzerland, Spain and Italy), North America (USA, Canada) and also in Asia (Anon. 2004). Malaysia imports almost all its humic acid (HA) requirements in solid as well as in liquid forms. Most common high purity commercial HA are in the form of K, Na, and Ca humates while unprocessed HA of varying quality from naturally occurring low rank and oxidized coals are also found in the market.

Humic acid contains many functional chemical groups that help to physically modify and improve the chemical properties of the soil and biologically stimulate plant growth (Burdick 1965; Anon. 2003). These functional groups including the aromatic backbone and amines (R-NH₂) cause HA to be biologically active. The oxygen containing functional groups (carboxyl, phenol, hydroxyl and ketone) tend to increase the cation exchange capacity (CEC) of the soil. Traditionally, HA is extracted from lignite, brown coals and humified organic materials. Earlier work on extracting humic acids from peat with alkaline and sodium pyrophosphate solution had been attempted (Gracia et al. 1993).

The amount of extractable HA from humic substances and its chemical characteristics depend on several factors. These include the types of organic material from which HA is extracted, temperature, grain size, frequency of extraction, the extracting agent and its strength and drying procedure. Extracting HA under elevated temperature greatly enhanced HA recovery (Sasaki and Oyamada 1966; Asing et al. 2004).

Therefore, it is absolutely essential that when HA content is stated, it is to be accompanied by the method of determination. Much of the extraction techniques of commercial HA remain proprietary. Therefore, with the abundant availability of lignite, sub-bituminous coals and composted biomass in Malaysia, it may have commercial value if methods are

developed to extract HA from these local sources. The objectives of this study were to fine tune the method of extracting HA from low quality coals and composted biomass and to characterize their chemical properties.

Materials and methods

Sampling and sample preparation

Eight sub-bituminous coals were obtained from Mukah Coal Field, Sarawak (Coal A-E, G, H and K) while Tenaga National Berhad (TNB) coal was obtained from Kapar Power Station, Klang. Leonardite, a commercial HA product mined from naturally occurring highly oxidized coal in Australia and nine other types of composted ligno-cellular materials were also chosen for the present study. These included composts from chrysanthemum biomass, empty oil palm fruit bunches (EFB), chicken dung, sugarcane waste and fermented effluents from a sodium glutamate factory (Ajinomoto Berhad). In addition, humified peat was obtained from MARDI Peat Research Station at Sessang, Sarawak. Coal samples were washed and dried at 105 °C for 24 h before grinding into 100 mesh powder. The composts and peat material were also ground into powder before use and their moisture determined.

Extraction and purification

Studies on the effect of frequency of extractions, sample to extractant ratio, different extracting agents and their concentrations on HA recovery were carried out under ambient temperature. The extraction parameters are given below:

Frequency of extractions : 1, 2, 3 and 4 times with
0.25 M KOH
Sample to extractant ratio : 1:5, 1:10 and 1:20 with
0.25 M KOH
KOH concentration (M) : 0.1, 0.25 and 0.5
Extracting agents : 0.25 M KOH, 0.25 M
NaOH and 0.03 M Na₄P₂O₇
+ 0.175 M NaOH

The following HA extraction procedure was adopted from Asing et al. (2004). Coal samples weighing 10 g each were shaken up with 50 ml of 0.1, 0.25 and 0.5 M KOH respectively for 24 h in an orbital shaker. This was repeated for the 1:10 and 1:20 sample to extraction ratio. Residue in solution was separated by centrifuging at 10,000 rpm for 20 min before filtering. The residue was further subjected to two similar successive extractions. The combined supernatants from the three successive extractions were acidified to pH 1 by adding 6 M HCl to precipitate HA. The precipitate was allowed to coagulate for 24 h before centrifuging to recover the HA.

The recovered HA was again solubilized by adding the desired alkali to be followed by the acidification and coagulation procedure for purification purpose. Inorganic impurities in the recovered HA were removed by adding 20 ml of 0.5% hydrochloric-hydrofluoric acids (HCL-HF) solution. This was placed in an orbiter shaker for 24 h after which HA was separated by centrifuging and filtering. The recovered HA was washed repeatedly with distilled water until no trace of Cl^- was detected to remove soluble salts, chiefly KCl, from the HA. The yield of HA was calculated after drying the purified HA at 105 °C for 24 h. All determinations were carried out in triplicates.

Chemical analysis of coal samples

Elemental analysis Carbon (C), hydrogen (H), nitrogen (N), sulphur (S) were determined by using a CHNS analyser (CHNS-932 Model Lecco). Oxygen (O) was calculated by subtracting the sum of these elements from 100%.

Macro and micronutrients Boron (B), copper (Cu), zinc (Zn) and potassium (K) content in coals were brought into solution by a double acid digestion method (concentrated nitric and hydrochloric acids) and were subsequently analysed with an

inductively coupled plasma-optical emission spectrophotometer (Varian ICP-OES).

Cation exchange capacity

(CEC) CEC was determined by repeated washings with dilute HCl to be followed by barium acetate [$\text{Ba}(\text{OAc})_2$] saturation. Acid washing method has been used widely to measure the CEC of plant roots (Crooke 1964). The advantage of this method is to avoid dissolution and hydrolysis process. Basically, it involves the replacement of exchangeable cations by proton which was subsequently exchanged by Ba^{2+} . The amount of exchanged H^+ was titrated against sodium hydroxide (NaOH) to obtain CEC (Harada and Inoko 1980).

Ash content Samples and extracted HA were heated to 700 °C for 3 h. The ash (residue) was calculated on an oven dry basis.

Total acidity and functional groups

Total acidity and carboxylic groups (COOH) of extracted HA were determined by titration using barium hydroxide [$\text{Ba}(\text{OH})_2$] and calcium acetate [$\text{CaCH}_3(\text{COO})_2$] following the procedure of Schnitzer (1982). The phenol (OH) concentration was calculated by difference between total acidity and carboxylic groups.

Infrared spectroscopy Finely powdered mixture of KBr (300 mg) and HA sample (2 mg) was pressed at 10 tonnes pressure for 10 min to produce pellets. The Fourier Transformed Infrared (FTIR) spectra of pelleted samples were recorded on a Perkin Elmer Spectrum RX1 FTIR system on a spectral range of 4000 cm^{-1} to 400 cm^{-1} .

Results and discussion

Effect of extraction frequency on HA recovery

Frequency of extractions impacted HA recovery significantly (*Figure 1*). The first extraction produced low yield of HA from all the samples. The highest yield at about

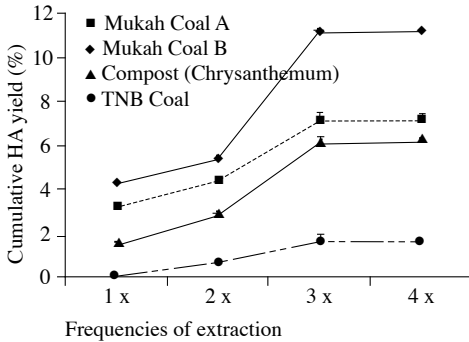


Figure 1. Effect of frequencies of extraction on HA recovery

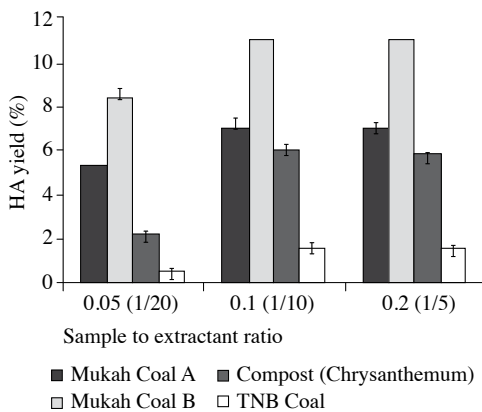


Figure 2. Effect of sample to KOH ratio on HA recovery (%)

4.0% was obtained for Mukah coal B and the least amount of HA was extracted from the high rank TNB coal during the first extraction.

With the second extraction, HA yield began to increase reaching a peak at the third extraction. The peak recovery of HA was 4.0, 6.9 and 1.6% from coal A, coal B and TNB coal respectively, while 4.7% was obtained from the compost sample. Further extraction of the residue did not benefit HA recovery.

The first extraction removed the more easily solubilized HA fraction while the second and third extractions attacked the more recalcitrant HA fractions. By the fourth extraction, the HA reservoir of the samples had been exhausted. The implication is that it requires longer time to extract HA more

effectively. Stevenson (1994) observed that the amount of humic substances extracted from soil with caustic alkali increased with the time of extraction. He attributed this to slow de-polymerization of high molecular weight complexes.

Effect of sample to KOH ratio on HA recovery

The effect of sample to extractant ratio on the HA yield is shown in Figure 2. There were little differences in HA recovery between the 1:5 and 1:10 extractant ratio. However, by widening the ratio to 1:20, the amount of HA recovered was reduced by between 22–66%. These indicated that the optimal sample to extractant solution ratio for extracting HA from humic substances is either 1:10 or 1:5. The 1:10 ratio was preferred because of easy handling during extraction. The International Humic Substances Society (IHSS) recommends the 1:10 sample to extractant ratio which gives the highest yield percentage in extracting HA from humic substances (Swift 1996).

Effect of extracting agents on HA recovery

Different alkaline solutions which selectively dissolve acidic groups were traditionally used to extract HA from humic substances (Gracia et al. 1993). Stevenson (1994) reviewed the roles and effectiveness of different extracting agents including NaOH and Na₄P₂O₇ in extracting humic substances. NaOH was more effective than Na₄P₂O₇ in extracting humic substances. Figure 3 indicates that HA recovery using 0.25 M KOH was 7.1, 11.1 and 6.1% for coal A, coal B and chrysanthemum compost respectively. They were considerable higher than HA extracted using either 0.25 M NaOH or mixture of 0.03 M Na₄P₂O₇ and 0.175 M NaOH. The HA recovery from TNB coal was very low for all the extracting agents because of inherent low HA content.

Nevertheless, even under the low HA environment, KOH consistently out yielded the other two extractants. KOH was a more efficient extractant than NaOH

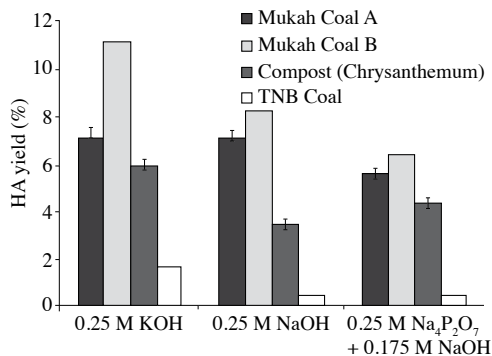


Figure 3. Effect of extracting agents on HA recovery (%)

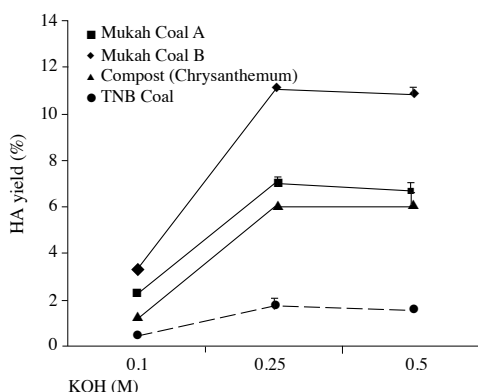


Figure 4. Effect of KOH strength on HA recovery (%)

due to the smaller size K^+ which allowed greater expansion and interactions of intra and intermolecular charges within the humic molecule (Rocha et al. 1998) to expose more acidic groups for attack by the alkali extractant. The mixed pyrophosphate and sodium hydroxide solution being a weaker alkali only removed the more easily soluble HA and thus producing the least HA yield.

NaOH due to its lower cost, has been widely used as a HA extractant. However, it has many limitations. Na humate has an undesirable high Na content with an average of about 7.5% (Anon. 2004). Adding Na to soil will adversely affect soil fertility because of its adverse effects on soil permeability and soil nutrient balance. KOH is the preferred choice as an extracting agent because it produces the highest HA yield

and contains high amount of K. In addition, there were also claims that KOH removed bioactive substances particularly the natural growth hormones and biostimulants from leonardite (Anon. 2004).

Effect of KOH concentration

The highest HA yield was obtained from all samples using 0.25 M KOH (Figure 4). The yield increase was three to four times higher than the yield obtained from 0.10 M KOH for coal A, B and chrysanthemum compost. Higher KOH at 0.50 M did not enhance HA recovery. This may be caused by enhanced disruption of intermolecular forces binding fulvic acids to humic acids, such as H-bonding or possibly ester-type linkages thereby altering the fulvic and humic acids ratio (Stevenson 1982). Therefore, upon acidification of the alkali extract, less humic acid was precipitated.

Although all three KOH concentrations produced low HA recovery from TNB high rank coal due to its intrinsic low acidic functional groups content (Table 5), 0.25 M KOH remained the most efficient. The yield of HA extracted from coal decreases as the coal rank increases (Helena Chemical Company 2003).

Chemical characteristics of coal

Generally, coal contains high amount of carbon (70–95%), 3–5% hydrogen, 2–22% oxygen and 1–2% of sulphur and nitrogen (Lawson and Stewart 1989). Coal with high C and low O content has low HA content. Coals from Mukah showed C content ranging from 54–63% and O from 30–39% (Table 1). The C content was far higher and O lower than those found in leonardite. Higher C in TNB coal is expected as TNB would require higher rank coal to maximize thermal output per unit from the fuel feed. As coal rank increased, the C content increased while H, N and O decreased. This is attributed to more intensive aromatization as coal rank increases (Francioso et al. 2003).

Table 1. Chemical analysis of coal samples

Coal	C	H	N	O	S	B	Cu	Zn	K	CEC (cmol (+) kg ⁻¹) sample	Ash content (%)
	(%)						(mg/kg)				
A	61.3	5.1	1.0	32.4	0.2	52.00	2.58	5.86	135.0	81.7	2.3
B	54.1	5.2	1.1	39.3	0.3	48.46	4.61	12.91	346.7	88.3	4.9
C	59.6	5.1	1.1	34.0	0.2	44.91	4.39	23.93	455.0	52.7	3.0
D	60.0	5.1	1.4	33.3	0.2	54.38	10.50	10.09	9871.3	73.7	11.4
E	56.8	4.9	1.2	36.9	0.2	54.70	4.89	2.00	8611.7	61.0	9.5
G	58.9	5.1	1.1	34.5	0.2	57.18	5.82	33.99	1078.3	87.0	5.3
H	58.2	5.3	1.1	35.2	0.2	46.68	5.70	33.72	1685.0	87.7	5.5
K	62.6	5.2	1.3	30.7	0.2	67.04	3.27	10.78	7115.0	83.7	2.7
TNB	68.3	4.8	1.2	25.4	0.3	19.21	7.70	10.30	1977.0	8.3	13.2
L	51.1	4.5	1.0	42.9	0.5	nd	nd	nd	nd	nd	12.8

L = Leonardite

nd = Not determined

Hydrogen with a range between 5.0–5.5% fell within values commonly observed for sub-bituminous coal as cited by Lawson and Stewart (1989). Nitrogen values had a narrow range of 1.0–1.4%. The persistence of N in relatively high rank coal such as those found in Mukah was probably due to its presence in stable heterocyclic compounds (Bonnett 1996; Knicker et al. 1996). The S content remained relatively stable at between 0.2–0.3%.

Cation exchange capacity (CEC) of coal is a measure of the acidic character of the coal as it contained high quantity of acidic functional groups such as carboxylic and hydroxyl acids (Lawson and Stewart 1989). Mukah coals had CEC ranging from 52.7–88.3 cmol (+) kg⁻¹ which was well within the range commonly found in coals. However, TNB coal had low CEC at 8.3 cmol (+) kg⁻¹ and this was attributed to its lower O content implying having lower level of reactive acidic functional groups. Mexican coals had CEC between 55–70 cmol (+) kg⁻¹ while coal deposits from North Dakota and Wyoming had higher CEC in the range of 100–140 cmol (+) kg⁻¹ (Ozdoba et al. 2002). These relative high reactivity coals may be suitable for use as soil conditioner in low activity soils and that their reactivity is likely to persist when

added to the soils as coal does not degrade easily.

The Mukah coals are relatively clean as reflected in the low ash content. The considerable B, Cu, Zn, K and high amount of ash at 13% generated from the TNB coal suggest that the ash may possibly be exploited as cheap source of trace elements and K for oil palm estates in the vicinity of the power station. The TNB power plant at Kapar generates huge amount of fly ash which is currently being contained in ponds.

Humic acid (HA) yield

The procedure developed in the previous sections for maximum yield of HA was deployed to extract HA from Mukah coals and composts. *Table 2* shows that HA content in Mukah coals (A–K) was generally less than 10% with the highest at 11.11% from coal B. TNB coal yielded a mere 1.50% HA while commercial leonardite produced 58.48% HA.

These findings are in agreement with those reported by Lawson and Stewart (1989) where small quantity of HA was extracted from sub-bituminous coals. Mexican and Russian lignite produced high amount of HA at 67.2% and 80.5% respectively (Levinsky 2002). On the other hand, coals from mine sites at Beysehir, Ermenek and Ilgin towns of Konya

Table 2. Mean yield (dry weight, %) of HA from Mukah coals, leonardite and humified peat

Samples	Purified HA yield (%)
A	7.07 ± 0.60
B	11.11 ± 0.09
C	7.81 ± 0.40
D	7.74 ± 0.55
E	10.11 ± 0.67
G	8.03 ± 0.43
H	8.55 ± 0.48
K	4.21 ± 0.12
TNB	1.50 ± 0.39
Leonardite	58.48 ± 0.95
Humified peat	31.55 ± 3.90

Table 3. Mean yield (dry weight, %) of HA from composts

Samples	HA (%)
EFB compost 1	9.32 ± 0.66
EFB compost 2	6.78 ± 0.57
EFB compost 3	7.08 ± 1.62
EFB compost 4	10.33 ± 2.17
EFB compost 5	16.52 ± 1.53
Chrysanthemum compost	6.13 ± 0.23
Ajinomoto compost	6.83 ± 0.77
Composted chicken dung	6.36 ± 0.64
Sugarcane waste compost	4.18 ± 0.29

Province, Turkey had lower HA content of between 30–42% (Kurbanli et al. 2003).

A majority of the composted biomass yielded less than 10% HA (Table 3). Generally, the yield of HA from composted EFB was higher than those obtained from other types of composted materials. Composts with low C/N ratio of less than 20 made from chrysanthemum biomass, Ajinomoto (a factory producing sodium glutamate) effluent, chicken dung and sugarcane waste produced low HA yield of between 4.18–6.83%. Lower C/N ratio would indicate more intense mineralization thus lower HA production.

The varying amount of HA obtained from different types of EFB compost is reflective of the degree of humification during composting. EFB contains relatively higher lignin content than other compost

types. Flaig (1988) hypothesized that lignin could probably be degraded into component units and then reassembled via bio-chemical processes into HA macromolecules. The HA yield from EFB composts was much higher than those from palm oil mill effluent (POME) at 1.82% (Siva et al. 1998).

Humified peat materials had by far the highest HA at 31.55% indicating advanced degree of humification. Oxidized surface peat generally produced higher HA than those from less decomposed subsurface peat material (Husni et al. 1996). The results indicated that highly carbonized coals and composts are unlikely to be rich sources of HA.

Comparison of elemental composition and ash content

Elemental composition and ash content of Mukah coal A, B, leonardite and chrysanthemum compost and their respective extracted HA are shown in Table 4. The C, H, N, O and S contents were within the range of values observed for diversified groups of coal HA (Lawson and Stewart 1989). Lower C and higher O occurred in leonardite as well as in the extracted HA than those found in coal A, coal B and chrysanthemum compost. During the transition from peat to coal, O is lost and the quantity of carboxyl groups is very much reduced with a corresponding increase in C.

The extracted HA had higher O and consequently higher O/C than its humic parent materials because the alkali selectively dissolved materials containing O bearing acidic groups from their source materials. Nitrogen was stable at about 1.0% for coals and leonardite and in their extracted HA as well. However, N and S were clearly higher in the chrysanthemum compost at 3.9% and 0.8% respectively. The N and S in the extracted HA were similar to the source materials. The amount of N and S as constituents in plant proteins and fats showed minimal changes having undergone composting process. Much of the original

Table 4. Elemental composition and ash content of Mukah coals, Leonardite and chrysanthemum compost and their respective extracted HA

	Coal A	Extracted HA	Coal B	Extracted HA	Leonardite	Extracted HA	Chrysanthemum compost	Extracted HA
Elemental content (%)								
C	61.3	55.8	54.1	52.1	51.1	50.4	54.4	53.1
H	5.1	3.9	5.2	3.8	4.5	4.2	5.6	5.1
N	1.0	1.1	1.1	1.1	1.0	0.9	3.9	3.8
O	32.4	38.9	39.3	42.7	42.9	43.9	35.3	37.3
S	0.2	0.3	0.3	0.3	0.5	0.6	0.8	0.7
Atomic ratio								
O/C	0.53	0.63	0.73	0.82	0.92	0.97	0.65	0.70
Ash (% dry basis)	2.3	1.5	4.5	1.7	12.8	1.9	25.9	2.6

Table 5. Total acidity, carboxylic and phenolic group content of HA (meq g⁻¹) from coals, Leonardite, peat and composts

Extracted HA	Total acidity	COOH	Phenolic	Acidity ratio
A	10.4	3.4	7.0	0.49
B	10.4	3.4	7.0	0.49
C	10.3	3.5	6.8	0.51
D	10.5	3.2	7.3	0.43
E	10.8	3.5	7.3	0.48
G	10.6	3.5	7.1	0.49
H	10.6	3.4	7.1	0.48
K	10.1	3.3	6.8	0.48
TNB	6.4	2.4	4.0	0.60
Leonardite HA	10.3	4.6	5.7	0.81
EFB compost 1	8.2	2.9	5.4	0.53
EFB compost 2	7.4	2.2	5.2	0.42
EFB compost 3	8.1	2.5	5.6	0.45
EFB compost 4	8.6	2.3	6.2	0.37
EFB compost 5	9.5	3.5	6.0	0.58
Ajinomoto compost	6.1	2.7	3.5	0.77
Chicken dung compost	6.8	3.0	3.9	0.77
Sugarcane waste compost	5.6	1.9	3.7	0.51
Chrysanthemum compost	6.4	2.1	4.3	0.49

N and S in the coals were removed during coalification processes thus accounting for the low N and S content in the coals.

The ash content reflects the degree of contamination by impurities, chiefly inorganic minerals in the original samples. High ash content in HA will indicate incomplete extraction and purification during HA preparation. High ash content in Leonardite (12.8%) and chrysanthemum

compost (25%) showed high degree of mineral contamination. Mukah coals with ash content less than 5.0% are relatively clean. However, the ash content of the humic acid extracted from the coals and Leonardite was low at less than 2.0%. The purification process carried out during HA extraction had effectively reduced the high ash content of chrysanthemum compost from 25.9% to 2.6%.

Acidic functional groups of extracted HA

Total acidity consisting of carboxylic acid and phenol groups has strong affinity for chelating metals such as Fe, Cu, Mn and Zn (Helena Chemical Company 2003). Humic acid from Mukah coals (A-K), leonardite and peat had a narrow range of total acidity (Table 5) of between 10.1 and 10.8 meq g⁻¹ but the ratio of COOH to OH groups differed greatly. Humic acid from Mukah coals had a COOH to OH ratio of 0.5 while the same acidic ratio of HA from humified peat and leonardite was considerable higher at 0.62–0.81.

Husni et al. (1996) reported even higher COOH to OH ratio at more than one in HA extracted from various tropical peat materials. The HA from high rank TNB coal had lower total acidity of 6.4 meq g⁻¹ but the COOH to OH ratio was 0.60 which contradicted findings by Francioso et al. (2003) that higher rank coal yielded HA with higher phenol-OH and less carboxyl group than those obtained from peat, brown coal and lignite.

Two categories of composts can be distinguished based on the total acidity and acidic functional groups of their HA. One category consisting of composts from Ajinomoto factory effluents, chicken dung, sugarcane waste and chrysanthemum biomass had total acidity of between 5.6–6.8 meq g⁻¹ in the HA while the second category from EFB composts had HA with

higher total acidity of between 7.4–9.5 meq g⁻¹.

There was also differences in distribution of COOH and OH in the HA from the compost materials. Humic acids from EFB and sugarcane waste compost had lower acidic ratio of less than 0.50 while HA from the Ajinomoto effluent and chicken dung composts had higher acidic ratio of 0.77. The implication is that compost derived from readily degradable material produces humic substances having more COOH than those containing higher content of lignin which is more resistant to degradation.

Fourier Transform Infrared (FTIR) analysis

The IR spectra of the HA extracted from coal A, B, leonardite and chrysanthemum compost (Figures 5 and 6) were obtained to detect structural differences among the HA. Interpretation of the spectra was based on MacCarthy and Rice (1985), Debska et al. (2002) and Dick et al. (2002).

The FTIR spectra of HA from the four materials were largely similar but differing in intensity (Table 6). The positions of the absorption bands of the four spectra fell within typical major absorption bands of HA which were at frequencies 3400–3300, 2940–2900, 1725–1700, 1630–1600, 1460–1440, 1400–1375 and 1260–1200 cm⁻¹. The first peak centred

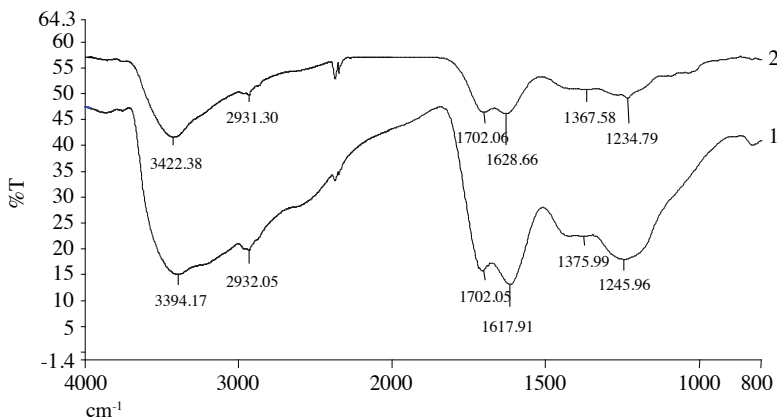


Figure 5. Infrared spectra of humic acid (HA) of: 1 = coal A; 2 = coal B

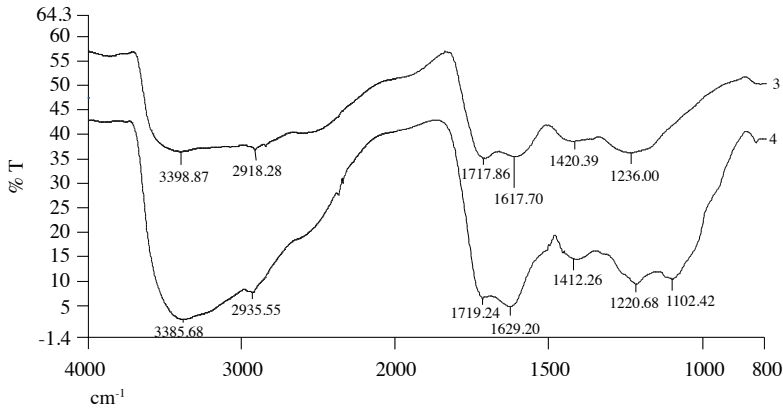


Figure 6. Infrared spectra of humic acid (HA) of: 3 = leonardite; 4 = chrysanthemum compost

in the vicinity of 3400 cm^{-1} region is attributed to phenol OH group bounded by intermolecular H bonds. The $2940\text{--}2900\text{ cm}^{-1}$ band usually has absorption maximum at 2926 cm^{-1} which is due to C–H stretching of alkane group (CH_2). All four spectra exhibited this peak in the near vicinity of this absorption maximum. The next major absorption band is between $1725\text{--}1700\text{ cm}^{-1}$. This band has been commonly ascribed to C=O stretching of mainly carboxyl group (COOH) with trace amount of ketones. Peak nearest to 1700 cm^{-1} indicates higher protonated carboxyl group.

Humic acid from Mukah coals contained carboxyl group mainly in the acidic form as the absorption band at 1702 cm^{-1} was close to 1700 cm^{-1} . Humic acids extracted from chrysanthemum compost and leonardite having an absorption band at about 1718 cm^{-1} contained carboxyl group mainly in the dissociated form as the absorption band was close to the upper carboxyl band at 1725 cm^{-1} .

Another classical absorption band for HA was between the $1630\text{--}1600\text{ cm}^{-1}$ region. This is primarily due to vibration of aromatic C=C with possibly minor component of H bonded conjugated ketone. The absorption maximum due to this group was at 1610 cm^{-1} . However due to the presence of water, the peaks shifted nearer

to 1625 cm^{-1} . All the spectra exhibited absorption peaks near the 1625 cm^{-1} region which is indicative of aromatic characteristics and incomplete removal of water in HA samples.

Humic acids from coal samples also had absorption peak at near 1370 cm^{-1} and this was attributed to symmetric deformation vibration of C–H bond of the methyl group (CH_3) in the aliphatic component of HA. However, the peaks shifted to higher frequency within the $1420\text{--}1410\text{ cm}^{-1}$ range from HA derived from leonardite and chrysanthemum compost. The later band is attributed to the asymmetric deformation vibration of methylene (CH_2) group. This supports the observation made near the 2930 cm^{-1} which indicates the presence of CH_2 in HA.

The weak band at the vicinity of 1230 cm^{-1} was due to the deformation vibration of C=O of the carbonyl group mainly the carboxyl (COOH) thus further emphasizing its significant presence in the extracted HA. The last peak was observed at 1102 cm^{-1} due to C–O stretching of polysaccharides and this peak appeared only in the spectra of HA from chrysanthemum compost. It is likely that during composting of the chrysanthemum biomass, not all the polysaccharides had been degraded while polysaccharides in coals and leonardite

Table 6. Absorption peaks and their intensity of FTIR spectra of extracted HA

Source material	Absorption maximum at cm^{-1}	Intensity	Interpretation
Mukah coal A	3394	Strong	Valence vibration of OH group bounded by intra-molecular H bonds
	2932	Moderate	C-H stretching of CH_2
	1702	Strong	C=O stretching mainly of COOH + ketones
	1617	Strong	Vibration of mainly aromatic C=C + H bonded conjugated ketone (C=O)
	1376	Weak	Symmetric deformation of C-H of C-CH_3
	1246	Strong	Deformation stretching of C=O chiefly of COOH
Mukah coal B	3422	Strong	Valence vibration of OH group bounded by intra-molecular H bonds
	2931	Moderate	C-H stretching of CH_2
	1702	Strong	C=O stretching mainly of COOH + ketones
	1629	Strong	Vibration of mainly aromatic C=C + H bonded conjugated ketone (C=O)
	1367	Weak	Symmetric deformation vibration of C-H of C-CH_3
	1235	Moderate	Deformation stretching of C=O chiefly of COOH
Leonardite	3399	Weak	Valence vibration of OH group bounded by intra-molecular H bonds
	2918	Weak	C-H stretching of CH_2
	1718	Moderate	C=O stretching mainly of COOH + H_2O + ketones
	1618	Moderate	Vibration of mainly aromatic C=C + H bonded conjugated ketone (C=O)
	1420	Weak	Asymmetric deformation vibration of C-H of CH_2
	1236	Moderate	Deformation stretching of C=O chiefly of COOH
Chrysanthemum compost	3386	Strong	Valence vibration of OH group bounded by intra-molecular H bonds
	2935	Moderate	C-H stretching of CH_2
	1719	Moderate	C=O stretching of COOH + H_2O + ketones
	1629	Strong	Vibration of mainly aromatic C=C + H bonded conjugated ketone (C=O)
	1412	Moderate	Asymmetric deformation vibration of C-H of CH_2
	1220	Strong	Deformation stretching of C=O chiefly of COOH
	1102	Moderate	C-O stretching of polysaccharides

had long being eliminated during the coalification process.

The FTIR spectra of the extracted HA contained all major characteristic absorption peaks of HA. These absorption peaks indicated the presence of the major structural elements of HA namely H bonded OH, C=C of aromatic ring, C=O of carbonyl group (both carboxyl and ketonic), CH_2 and CH_3 groups. These together with the elemental composition and acidity components of the extracted HA from

various source materials strongly indicates that the HA were authentic.

Conclusion

The highest HA recovery from coals and different types of compost were obtained by three successive extractions using 0.25 M KOH at 1:10 sample to extractant ratio. The Mukah coals had relatively high CEC with a range of 52.7–88.3 cmol (+) kg^{-1} and may possibly be used as a cheap source of soil conditioner. Humic acid

yield from the various coals ranged from 1.5–11.1% while composts yielded HA from 4.2–16.5%. Therefore, highly carbonized coal and composts are unlikely to be rich sources of HA.

Oxidized coal such as leonardite with HA content of about 58% is a rich source of commercial HA. Extracted HA from Mukah coals had narrow range of acidic functional groups with carboxylic group varied from 3.2–3.5 meq g⁻¹ while phenolic group ranged from 6.8–7.3 meq g⁻¹. Acidic functional groups in HA from composts were, however, lower than those obtained from coals. The HA from composts yielded 1.9–3.5 meq g⁻¹ of carboxylic group and 3.5–6.2 meq g⁻¹ of phenol group.

FTIR spectra of HA obtained from coals, leonardite and composts revealed that typical major structural elements of HA such as H bonded OH and C=O (both carboxyl and ketonic) functional groups, C=C in aromatic rings and aliphatic CH₂ and CH₃ groups were present indicating that the extracted HA were authentic.

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Abstrak

Asid humik (HA) yang juga dikenali sebagai emas hitam semakin kerap digunakan dalam pertanian. Jumlah pengekstrakan HA daripada sampel arang batu sub-bitumen dari Mukah, Sarawak, produk komersial HA (leonardit), tanah gambut dan pelbagai lagi bahan kompos telah diekstrak dan sifat kimianya dibandingkan. Hasil HA daripada pelbagai jenis arang batu ialah 1.5–11.1% manakala HA daripada kompos adalah rendah, 4.2–16.5%. Tanah gambut dan leonardit komersial masing-masing mengandungi 31.6% dan 58.5% HA. Analisis kumpulan berfungsi ekstrak HA daripada arang batu Mukah, menunjukkan kumpulan karboksil adalah pada julat 3.2–3.5 meq g⁻¹ manakala kumpulan fenol-OH berada antara 6.8–7.3 meq g⁻¹. Walau bagaimanapun, kumpulan berfungsi HA yang diekstrak daripada kompos adalah lebih rendah daripada HA arang batu. Jumlah asiditi HA daripada kompos ialah 5.6–9.5 meq g⁻¹, kumpulan karboksil 1.9–3.5 meq g⁻¹ dan kumpulan fenol-OH 3.5–6.2 meq g⁻¹. Spektrum FTIR bagi HA yang diekstrak daripada arang batu, leonardit dan kompos bunga kekwa mempunyai jalur serapan yang ketara untuk menunjukkan kewujudan kumpulan berfungsi seperti kumpulan fenolik –OH (ikatan H) (3400 cm⁻¹), C=O (karbonil) (1710 cm⁻¹), komponen alifatik CH₂ dan CH₃ (2930, 1420, 1370 cm⁻¹) dan cincin aromatik C=C (1620 cm⁻¹).