

Extraction and chemical characteristics of nitro-humic acids from coals and composts

(Pengekstrakan dan sifat kimia asid nitro-humik daripada arang batu dan kompos)

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Key words: nitro-humic acids, humic acids, coal, compost, chemical characteristics

Abstract

Yield of humic acids (HA) extracted from Mukah coals and different types of compost using potassium hydroxide (KOH) extraction method was low even under optimized extraction environment. However, when the coals were initially subjected to nitric acids (HNO₃) oxidation followed by KOH extraction, nitro-humic acids (NHA) yield were 5–6 times higher than the HA equivalent. The amount of NHA extracted from composts was higher than the HA equivalent, although the increase was moderate. Mukah sub-bituminous coal produced the highest NHA (71.50–88.12%) yield using 3 M HNO₃ at 50 °C while the Kapit bituminous coal required higher temperature i.e. 90 °C to obtain high NHA yield of slightly more than 60%. Mukah lignite yielded best at about 70% NHA using 1 M HNO₃ at 25 °C. The chemical characteristics of NHA were different from those of HA extracted from the same materials. NHA has lower C but higher O, H, N, total acidity, CEC, carboxylic and phenolic groups. Fourier Transform Infrared Spectroscopy (FTIR) spectra indicated that HNO₃ oxidation had incorporated nitro (-NO₂) group into NHA at 1,540 cm⁻¹ and nitroso (-NO) group at 1,364 cm⁻¹ adsorption bands respectively. The HNO₃ used in the oxidation process could be recycled without affecting the performance of the oxidation process of coals by adjusting its acidity to its desired strength after each oxidation event.

Introduction

Previous study of yield recovery of humic acids (HA) extracted from coals and compost (Asing et al. 2005) using strong alkali was disappointingly low at about 10%. However, oxidation of coals with various oxidation agents is well known to produce high yield of nitro-humic acids (NHA) (Hayashi and Nagai 1961; Hansen and Schnitzer 1967; Won 1968; Green and Manahan 1979; Patti et al. 1992; Sim et al. 2006). The oxidation process degrades the complex coal molecule and humus

substances in the compost into smaller alkali soluble humic substances. This procedure also mimics the long natural oxidation process of coals into HA rich oxidized coal called 'Leonardite'. In principle, alkali-insoluble high rank coals can be rendered soluble by oxidation which increases acidic groups in the coal molecule (Lawson and Stewart 1989).

NHA has similar chemical structure to HA but with additional nitro (-NO₂) and nitroso (-NO) groups introduced into the NHA molecule during the nitration process

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(Green and Manahan 1979). Traditionally, HA is used as soil amendment and chelating agent in fertilizer formulation. Recent studies indicated that NHA could also be used to improve soil structure, retain plant nutrients, stimulate soil microorganism activity and improve buffering capacity of the soil (Patti et al. 1992). Mazumdar et al. (1988) reported that application of NHA with conventional nitrogen fertilizers such as urea and ammonium sulphate significantly increased paddy and wheat yield by 5–20%. Won (1968) reported that nitro-humates protected soils against fissures development and increased apatite water soluble P. Ammonium nitro-humate when added as a binder to coal briquette produced lower emissions of smoke and sulphur (Yildirim and Ozbayoglu 2004). NHA-based filter mixture was effective in removing heavy metals (Terajima et al. 1976) and oil in water (Terajima et al. 1977).

Malaysia does not produce HA in commercial quantity. A local trade source indicated that Malaysia imported at least 20,000 litres/year of K-humate and 30,000 t/year in 2005 of HA mostly from China, Australia and the USA (Behn Meyer Berhad, pers. comm. 2007).

The presence of humic acids and its derivative products is becoming increasingly evident in the fertilizer market. It is now common to see such label on compound fertilizers as having 10% HA additive and liquid fertilizers containing HA. There is very little international trade on NHA. Japan had been producing 70,000 t of NHA products yearly using Australian and Russian low rank coals over the last 20 years (Kline and Wilson 1994). This study attempted to define the extraction processes of producing NHA from coals and composts with a view to produce NHA in commercial quantity from local low quality coals and ligno-cellulose materials.

Materials and methods

Sampling and sample preparation

Coals of different ranks were selected to evaluate the HA and NHA yield. Four types of sub-bituminous Mukah coals at different locations, namely one bituminous coal each from 'Kapit Coal Field' and coal stock pile of 'TNB Kapar Power Station' and three lignite coals from 'Mukah Plantation' were used in the study. In addition, seven types of compost consisting of three different kinds of oil palm empty fruit bunch (EFB compost 1, EFB compost 3, EFB compost 5), chrysanthemum compost, composted fermentation waste, composted chicken dung and sugar cane biomass compost were also tested for HA and NHA yield. A commercial HA product, Leonardite and a humified peat material were used in HA and NHA extraction for comparison purpose. All samples were dried at 105 °C for 24 h before grinding to pass 100 meshes.

Extraction and purification of HA and NHA

All 10 g samples were mixed with 50 ml of 0.25 M KOH in an orbiter shaker for 24 h to extract humic acids (HA). The solid residue in the solution was separated by centrifuging and filtering. The recovered solid was further subjected to two more successive KOH treatments. The combined supernatants from the three extractions were acidified with 6 M hydrochloric acid (HCl) to pH 1.0 to precipitate HA in the solution. The HA was allowed to coagulate for 24 h before centrifuging to recover HA. The recovered HA was further subjected to two repeated 0.25 M KOH solutions and precipitations by acidification processes to produce relatively pure HA. Any impurities still present in the HA was subsequently removed by adding a solution of 0.5% hydrochloric-hydrofluoric acids (HCl- HF). The purified HA was washed with distilled water until no trace of Cl⁻ was detected chiefly to remove KOH from the HA. The HA was dried at 105 °C and stored in a desiccator.

Effect of nitric acid concentration and oxidation temperature on NHA yield

For NHA extraction, 10 g samples were treated with of 100 ml of 1 M, 3 M, 6 M, 9 M HNO₃ at three temperatures i.e. 25, 50 and 90 °C respectively for 50 min. Heating was accompanied by continuous stirring to prevent foaming. The oxidized material was recovered and dried in oven for 24 h at 105 °C. NHA was then extracted from the 'oxidized material' using 0.25 M KOH following the HA extraction procedure as outlined above. All extractions were carried out in three replicates. Data were analysed using the Analysis of Variance (ANOVA) and means separation was performed using the tukey's test. Statistical analyses were carried out using SAS Version 9.1 package (SAS Inst. Inc., Cary, N.C.).

Chemical and FTIR spectra analysis of NHA and HA

Elemental composition (C, H, N, S, O) of HA and NHA were analysed using a Varian ICP-OES CHNS analyser. Per, cent Oxygen (O) was calculated by subtracting the sum of C, H, N, and S from 100%. Cation Exchange Capacity (CEC) was determined using an acid washing method (Harada and Inoko 1980). Total acidity and carboxylic groups (COOH) of HA and NHA were determined by titration using barium hydroxide [Ba(OH)₂] and calcium acetate [CaCH₃(COO)₂] following the procedure of Schnitzer (1982). The phenolic (OH) content was calculated by the difference between total acidity and carboxylic groups. Ash content was recovered by heating the sample to 700 °C for 3 h. The FTIR spectra of pelleted samples were recorded over a spectral range of 4,000 to 400 cm⁻¹ on a Perkin Elmer Spectrum RX1 FTIR system.

Recycle of spent nitric acids

The nitric acids used in the oxidation process were recovered by filtering. The molarity of the used HNO₃ was adjusted to about 3 M by adding concentrated HNO₃.

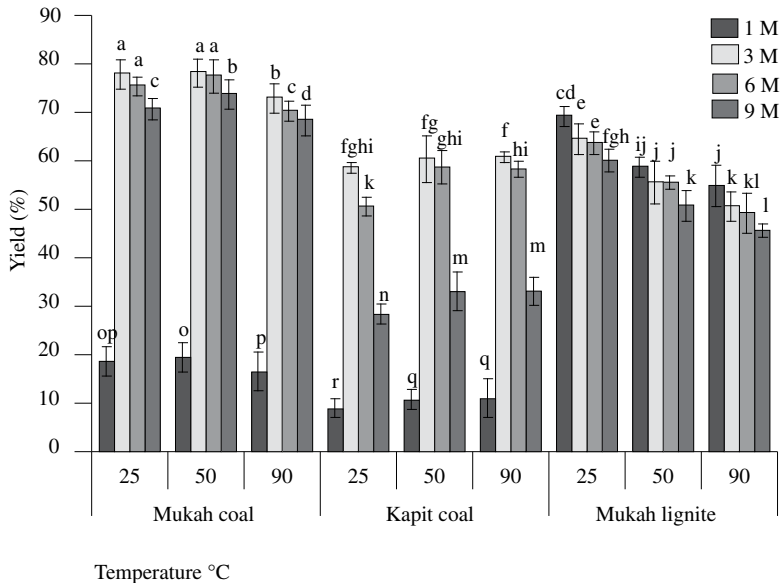
The amount of concentrated HNO₃ needed was determined by titration using KOH.

Results and discussion

Effect of acid strength and oxidation temperature on NHA yield

The strength of HNO₃ and oxidizing temperature greatly influenced the amount of NHA extracted from coals (*Figure 1*). Mukah sub-bituminous coal yielded the highest ($p > 0.05$) amount at 78.42% (3 M, 50 °C), 78.12% (3 M, 25 °C), 77.70% (6 M, 50 °C) and 75.65% (6 M, 25 °C) NHA by weight. Overall, the highest NHA yield obtained from coals when the molarity of HNO₃ was 3 M and the oxidation temperature at 50 °C. Kapit bituminous coal yielded increasing quantity of NHA at higher temperature under a given acid strength. The optimal oxidation condition for Kapit coal was at 50 °C using 3 M HNO₃ which yielded slightly over 60% NHA. The opposite happened to Mukah lignite. At increasing temperature for a given acid strength, decreasing amount of NHA was extracted. This showed that the higher the coal rank, the stronger the oxidation condition was required to obtain higher NHA yield.

During oxidation, the coal molecule apart from being degraded, gained additional acidic groups rendering it soluble under alkali condition. Under increasingly stronger oxidation condition at higher acid strength and temperature, the lower rank coal such as the Mukah lignite may break up into simpler compounds, thus producing lower amount of NHA. By oxidizing coals, Hansen and Schnitzer (1967) obtained high yield of NHA relative to humic acids. Among the degraded products were a variety of aliphatic di-carboxylic acids, benzene carboxylic acids, hydroxybenzoic acids and nitro compounds. When Stevenson (1982) subjected humus substances to oxidation, the humus substances were degraded to CO₂, H₂O and acetic acids. Oxidation of low rank coals using HNO₃ to obtained high NHA



^{a-t}Common letter within the same attribute are not significantly different ($p > 0.05$)

Figure 1. NHA recovery affected by acid strength and oxidation temperature

recovery (>80%) was consistent with results obtained by Patti et al. (1992) and Sim et al. (2006).

Yield comparison of alkali extracted HA and NHA

HA and NHA from different types of coals and humic substances were extracted using 0.25 M KOH. NHA was obtained by initial oxidation using 3 M HNO₃ at 50 °C before subjected to alkali extraction (Table 1). Recovery of NHA from Mukah sub-bituminous coals was high, 71.50–88.12% while HA yield remained at low level, 4.21–11.11%. Mukah lignites produced higher HA (8.51–21.63%) but lower NHA (43.20–60.60%) relative to Mukah sub-bituminous coals. The higher rank TNB and Kapit coals produced even lower HA at 1.5% and 10.62% respectively but recovered high amounts of NHA at 50.80% (TNB coal) and 61.19% (Kapit coal).

NHA yield relative to HA from composts was disappointingly low. NHA recovery from composts fell within a range of 4.98–22.77% while HA yield was

4.18–16.52%. HA content of EFB composts varied within a range of 7.08–16.52%. This is consistent with the 13.7% HA obtained from fermented EFB fibre treated with a lignocellulose degrading agent, *Trichoderma viride* (Umi Kalsom et al. 2003). Most composts yielded higher NHA content relative to HA. In contrast, humified peat with 31.55% HA and commercial Leonardite having HA at 58.48% yielded less NHA at 15.86% and 37.72% respectively. HA content in coals is related to their carbon ranking. The lower ranking Mukah lignites produced higher HA than the Mukah sub-bituminous coals, bituminous kapit and TNB coals. Lawson and Stewart (1989) reported that the yield of HA extracted from coal decreased as the coal rank increased.

Low C/N compost types (<12) made from chicken dung and fermentation waste had lower HA than those composts with higher C/N such as oil palm empty fruit bunches (EFB). The relatively low HA content is related to the synthesis of HA when biomass is subjected to humification processes during composting. The contemporary thesis of HA formation is that

Table 1. Humic acids and nitro-humic acids* recovery from various materials

Material	Humic acids (%)	Ash content (%)	Nitro-humic acids (%)	Ash content (%)
Mukah coal A	7.07	1.5	71.50	2.1
Mukah coal B	11.11	1.7	77.34	1.7
Mukah coal D	7.74	1.2	88.12	1.1
Mukah coal K	4.21	1.2	87.42	1.2
TNB coal	1.5	1.5	50.80	1.7
Kapit coal	10.62	1.8	61.19	1.7
Mukah lignite 1	21.63	1.8	55.67	2.1
Mukah lignite 2	8.51	1.9	43.20	2.0
Mukah lignite 3	19.70	1.8	60.60	1.8
EFB compost 1	9.32	2.8	11.84	3.3
EFB compost 3	7.08	1.9	11.56	2.0
EFB compost 5	16.52	2.2	22.77	3.3
Chrysanthemum compost	6.13	2.6	10.10	2.0
Fermentation waste compost	6.83	2.9	15.67	3.6
Composted chicken dung	6.36	2.2	6.32	3.6
Sugarcane biomass compost	4.18	2.2	4.98	3.0
Humified peat	31.55	2.4	15.86	3.1
Leonardite	58.48	1.9	37.72	2.3

* Prior oxidation using 3 M HNO₃ at 50 °C

vegetative cellular materials particularly lignin are degraded to structurally simpler compounds via bio-chemical processes and HA is subsequently synthesized from these compounds during humification processes (Orlov 1992). This is further supported by findings of Umi Kalsom et al. (2006) that elements of lignin, carbohydrates and long chain aliphatic structural groups were identified in HA extracted from fermented EFB fibre. Generally, composts yielded low quantity of HA and composting time is too short to allow extensive humification to produce high amount of HA. Low C/N ratio compost had too low lignin content to yield high HA. On the other hand, the higher C/N ratio EFB composts contained higher amount of lignin enabling it yielding more HA.

Coals are relatively large condensed molecules derived largely from vegetative materials containing lignin undergoing long term degradation, syntheses and consolidation processes. If the coalification (i.e. the transformation resulting from the high temperatures and pressures) processes

proceed to the bituminous stage, HA content will be lower because of extensive condensation of the coal molecule. Lower rank coals such as sub-bituminous and lignitic Mukah coals having higher acidity yielded higher HA than bituminous Kapit and TNB coals (Asing et al. 2005). Humified peat is a form of unconsolidated high moisture coal. It contained relatively high amount of HA. Australian Leonardite is a naturally occurring oxidized coal. Therefore, it contained the highest amount of HA. However, when the coals were subjected to oxidation by HNO₃, the complex coal molecules were degraded to smaller alkali soluble compounds (NHA). This explained the higher yield of NHA obtained from coals relative to HA.

Upon oxidation of humified peat and Leonardite, the materials were likely to be degraded into volatile components, water soluble organic acids, alkali soluble compounds and possibly fulvic acids. This accounted for the lower NHA yield relative to HA from these two sources. Dekker et al. (1990) obtained high yield

of humic products (85%) and fulvic acids by oxidizing reactive coals using a wet oxygen/air process. Therefore, it is unlikely that high amount of HA and NHA can be obtained from composts and peat while commercial quantity of NHA can potentially be extracted from Mukah sub-bituminous coals and lignites.

HA and NHA from coals with an ash content at about 2% were relatively free of mineral materials. HA and NHA derived from composts had slightly higher ash content at about 3%. This may be due to the presence of Al-Fe organo-metal complexes. Siva et al. (1998) detected moderate amount of Fe in humic and fulvic acids obtained from composted and clarified POME (palm oil mill effluent). Humic and fulvic acids from tropical mineral soil also contained relatively high amounts of Al and Fe (Norhayati and Verloo 1984). Ramalho et al. (1998) in a study of the metal complexing ability of NHA concluded that nitro-humic substances were more effective in complexing micronutrients, Zn (II), Cu (II) and Fe (III) than humic substances.

Chemical characteristics of HA and NHA

The elementary composition of NHA differed from HA derived from the same materials. The C content of NHA decreased while H, O and N increased relative to the HA (Table 2). The reduction of C and the increase in other elements were more marked in NHA obtained from composts and Leonardite than from the coals. Oxidation by HNO₃ of coals and composts had resulted in structurally simpler compounds with

higher saturation (higher H and lesser C) and more O containing functional groups. Similarly, Macphee et al. (2004) using TG-FTIR technique had determined that oxidized coal gave rise to O containing functional groups not present in the original coal. The higher N up to 6.6% in NHA was the result of nitration taking place during oxidation when additional NO and NO₂ groups were introduced into the NHA molecule (Figures 2–5). Patti et al. (1992) identified N being incorporated into the nitric acids oxidized brown coal molecule mainly as nitro group (–NO₂). The broad chemical changes brought by oxidation were also reflected in NHA acidity. Total acidity, carboxylic and phenolic groups of NHA were generally higher than the HA counterparts (Table 3). This is consistent with the higher O and H observed in elemental composition of NHA.

In general, higher total acidity (10–13.8 meq g⁻¹), COOH and phenolic OH groups were found in NHA obtained from coals than from compost and peat (6.6–8.2 meq g⁻¹). This is in line with the observed higher CEC of NHA (81.3–94.0 cmol (+) kg⁻¹) against the HA equivalents of 73.1 to 88.3 cmol (+) kg⁻¹. NHA derived from commercial Leonardite had the highest CEC at 127.5 cmol (+) kg⁻¹. This means that NHA has higher chemical activity (higher total acidity and CEC) than HA. Therefore, NHA would also be potentially more suitable for use as soil conditioner to enhance soil CEC and more effective as a micro nutrient complexing/chelating agent than HA.

Table 2. Elemental composition of humic acids and nitro-humic acids from various materials

Materials	C %		H %		N %		O %		S %	
	HA	NHA	HA	NHA	HA	NHA	HA	NHA	HA	NHA
Mukah coal A	55.8	52.7	3.9	4.2	1.1	3.8	35.0	38.9	0.3	0.4
Mukah coal B	52.1	47.2	3.8	4.3	1.1	4.1	42.7	44.0	0.3	0.4
Mukah lignite 1	50.3	44.3	4.0	5.9	2.1	3.2	43.3	46.3	0.3	0.3
EFB compost 3	50.3	43.9	4.3	6.9	2.3	4.8	42.8	43.9	0.3	0.5
Chrysanthemum compost	53.1	36.4	5.1	7.4	3.8	6.6	37.3	48.7	0.7	0.9
Leonardite	50.4	30.1	4.2	6.9	0.9	1.1	43.9	60.0	0.6	1.9

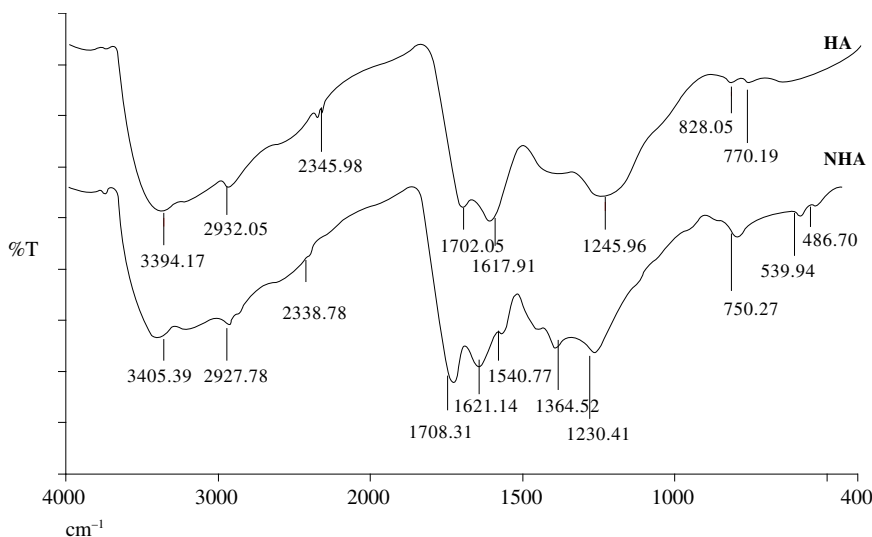


Figure 2. FTIR spectra of humic acids and nitro-humic acids derived from Mukah coal A

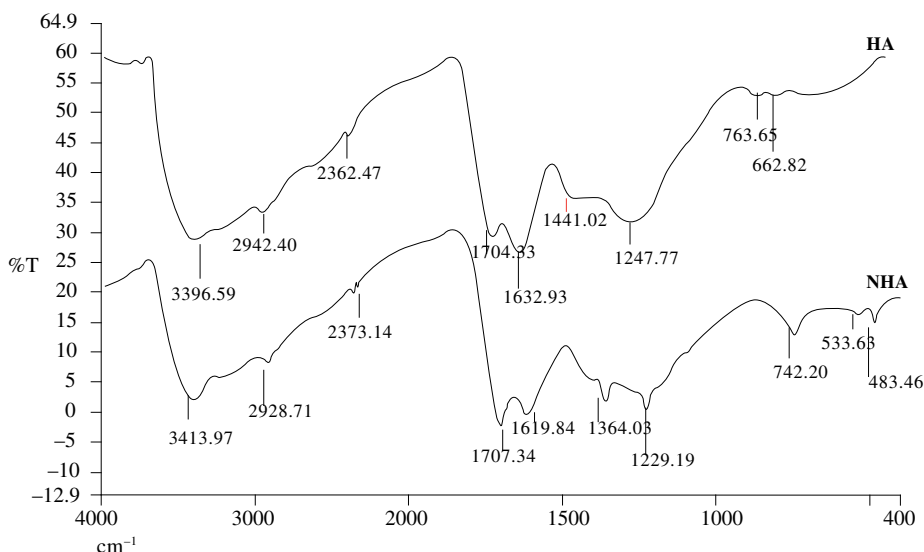


Figure 3. FTIR spectra of humic acids and nitro-humic acids derived from Mukah lignite 1

FTIR analysis of HA and NHA

FTIR spectra of HA and NHA derived from a Mukah coal A (Figure 2), Mukah lignite (Figure 3), chrysanthemum compost (Figure 4) and Leonardite (Figure 5) were obtained to study the structural changes brought about by HNO_3 oxidation. Adsorption bands that were common to HA and NHA were broad peaks between $3,385\text{--}3,409\text{ cm}^{-1}$ for hydrogen-bonded O-H

stretch, strong peaks at $2,918\text{--}2,942\text{ cm}^{-1}$ for aliphatic C-H stretch, weak $2,500\text{--}2,900\text{ cm}^{-1}$ for intra-molecular O-H stretch, strong clear peaks at $1,700\text{--}1,720\text{ cm}^{-1}$ for C=O stretch from ketone + ester + COOH, moderate $1,620\text{--}1,630\text{ cm}^{-1}$ peaks for aromatic C=C + H-bonded C=O and/or C=O of conjugated ketone and the broad and distinct bands at $1,220\text{--}1,250\text{ cm}^{-1}$ for C=O stretch of COOH. Broad bands around $1,411$

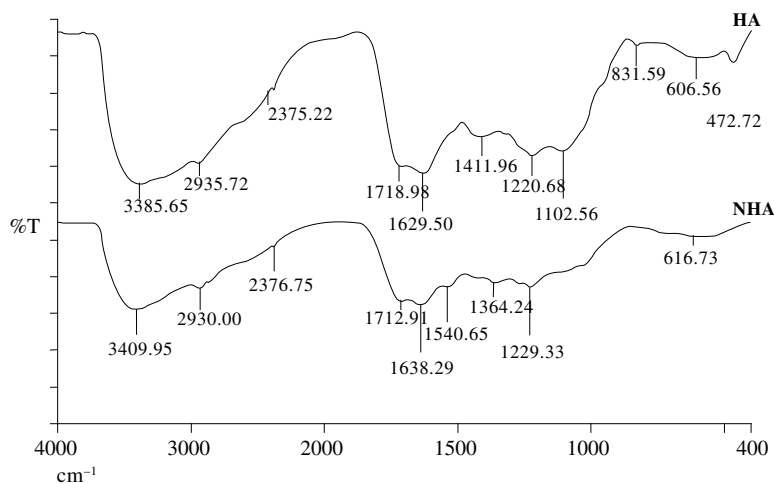


Figure 4. FTIR spectra of humic acids and nitro-humic acids derived from Chrysanthemum compost

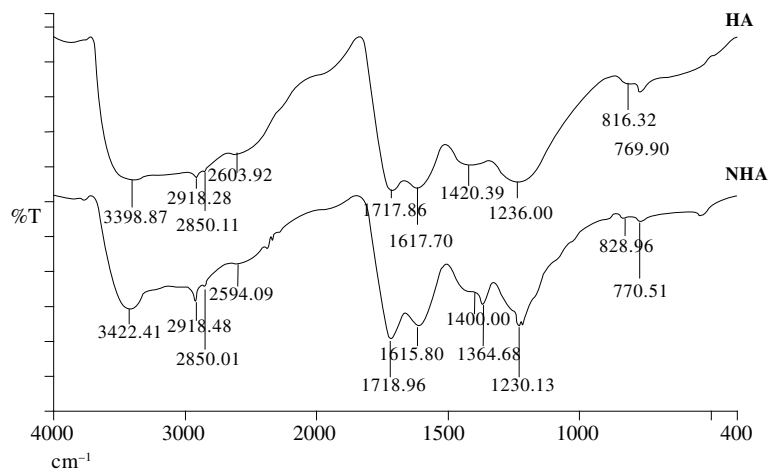


Figure 5. FTIR spectra of humic acids and nitro-humic acids derived from Leonardite

Table 3. Acidity of humic acid and nitro-humic acid from various materials

Materials	CEC (cmol (+) kg ⁻¹)		Total Acidity (meq g ⁻¹)		COOH (meq g ⁻¹)		Phenolic (meq g ⁻¹)	
	HA	NHA	HA	NHA	HA	NHA	HA	NHA
Mukah coal A	81.7	83.0	10.4	12.7	3.4	4.8	7.0	7.9
Mukah coal B	88.3	94.0	10.4	13.5	3.4	4.1	7.0	9.4
Mukah coal D	73.7	82.7	10.5	13.0	3.2	3.9	7.3	9.1
Mukah coal K	83.7	93.0	10.1	13.8	3.3	3.8	6.8	10.0
Kapit coal	86.3	88.0	10.2	10.8	3.3	3.7	6.9	7.1
Mukah lignite1	77.5	81.3	10.4	10.7	3.2	3.2	7.2	7.5
Mukah lignite3	81.0	88.8	9.9	11.4	3.2	3.0	6.7	8.4
EFB compost3	83.4	87.8	8.1	8.2	2.5	2.8	5.6	5.4
Chrysanthemum compost	80.0	88.0	6.1	6.6	2.7	2.7	3.5	3.9
Humified peat	75.7	80.0	7.2	7.2	2.6	2.9	4.6	4.3
Leonardite	124.9	127.5	10.3	10.5	4.6	4.7	5.7	5.8

Table 4. Effect of used and recycled nitric acids on NHA yield

Oxidation event	HNO ₃ molarity (M)	NHA yield (%)	Reconstituted HNO ₃ molarity (M)	NHA yield (%)
Initial	3.25		3.42	
1 st oxidation	2.77	73.68 ± 0.43	2.91	80.60 ± 0.54
2 nd oxidation	2.48	69.19 ± 0.22	2.96	72.67 ± 0.43
3 rd oxidation	2.43	66.31 ± 0.90	3.05	72.46 ± 0.56
4 th oxidation	2.30	54.19 ± 0.12	3.07	77.13 ± 0.98
5 th oxidation	2.28	51.03 ± 0.78	3.02	77.37 ± 0.47
6 th oxidation	2.19	50.41 ± 0.24	2.99	80.57 ± 0.65
7 th oxidation	1.95	25.52 ± 0.13	3.01	83.72 ± 0.19
8 th oxidation	1.94	23.13 ± 0.10	2.98	82.17 ± 0.92

cm⁻¹ appeared on HA spectra and were attributed to CH₂ or CH₃ stretching. The 1,102 cm⁻¹ peak attributed to C-O stretch of polysaccharides appeared on spectra of HA derived from chrysanthemum compost only. The polysaccharides of chrysanthemum were not completely destroyed during composting while the original polysaccharides present in the coal forming materials were eliminated during coalification processes.

NHA spectra from Mukah lignite and Leonardite exhibited moderate peak at 1,364 cm⁻¹ only while NHA spectra from Mukah coal and chrysanthemum compost showed moderate two peaks at 1,540 cm⁻¹ and 1,364 cm⁻¹. The 1,540 cm⁻¹ peak was attributed to nitro (-NO₂) stretch (Orlov 1992; Green and Manahan 1979) while the 1,364 cm⁻¹ peak was however ascribed to possibly tertiary aliphatic nitroso (NO) group (Patti et al.1992). Similar adsorption band at 1,544 cm⁻¹ was observed in NHA from coals (Sim et al. 2006). The FTIR spectra provided evidence that oxidation by HNO₃ introduced nitro (NO₂) and nitroso (NO) into the NHA molecule.

Recycling of nitric acids

As the Mukah sub-bituminous coals and lignites are potential sources for commercial production of NHA, the nitric acids used in the oxidation process needs to be recovered and recycled to save cost and prevent environment pollution. The recovered nitric acid was repeatedly used up to eight oxidation cycles to assess its effects on

NHA yield (Table 4). It is apparent that after each oxidation event, the molarity of HNO₃ decreased and it was accompanied by a reduction in NHA yield. After the third oxidation event, HNO₃ was no longer effective in producing satisfactory NHA yield (<60%). However, if the molarity of the used HNO₃ was adjusted to about 3 M after each oxidation event, NHA yield within a range of 72–84% did not appear to be affected. Therefore, the expensive HNO₃ can be recycled for use in producing NHA.

Conclusion

The optimal strength of HNO₃ and temperature of oxidation condition to generate high yield of NHA from coals differ depending on coal types. The higher the coal rank, the more vigorous oxidation condition is required to produce the desired NHA yield. NHA enhanced chemical activities relative to HA in terms of total acidity and CEC. In addition, the N content of NHA is about two times higher than that in the HA due to its incorporation of nitro (-NO₂) and nitroso (-NO) functional groups in the oxidized coals. This means that NHA can be a latent source of N supply to the plant when NHA is applied onto the soil. The HNO₃ used in the oxidation process can be recycled by adjusting its molarity to its desired strength for subsequent oxidation event without affecting NHA yield obviating the need to dispose off the spent HNO₃. The coals from Mukah can be a potential feed stock for commercial production of

NHA. Compost of various types and peat are unlikely to be potential rich sources of NHA.

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References

- Asing, J., Wong, N.C., Sim, S.F. and Lau, S. (2005). Potential sources of humic acids. *Proc. of Annual soil science conference of Malaysia 2005*, Pulau Pinang, p. 171–176. Kuala Lumpur: The Malaysia Society of Soil Science (MSSS)
- Dekker, J., Cronje, R., Louwrens, H.B. and Swart, R.S. (1990). Non-catalytic oxidation of water slurred coal with oxygen: A promising new route to osihumic and oxifluvic acids. *Proc. of the Seventh annual international coal conference*, Pittsburg, p. 703–708. University of Pittsburg, PA
- Green, J.B. and Manahan, S.E. (1979). Polarographic characterization of nitrohumic acids prepared by nitric acid oxidation of coal. *Anal. Chem.* 51(8): 1126–1129
- Hansen, E.H. and Schnitzer, M. (1967). The nitric acid oxidation of Danish illuvial organic matter. *Soil Sci. Soc. Am. Proc.* 31: 79–83
- Harada, Y. and Inoko, A. (1980). The measurement of the cation exchange capacity of compost for the estimation of the degree of maturity. *Soil Sci. Plant Nutr.* 26(1): 127–134
- Hayashi, T. and Nagai, T. (1961). On the components of soil humic acids (Part 8). The oxidative decomposition by alkaline potassium permanganate and nitric acid. *Soil Plant Food* 6: 170–175
- Kline, S.W. and Wilson, C.E. Jr. (1994). Proposal for experimentation with Arkansas lignite to identify organic soil supplements suitable to regional agricultural needs. (Preliminary draft)
- Lawson, G.J. and Stewart, D. (1989). Coal humic acids. Humic substances II. In: *Search of structure*, (Hayes, M.H.B., et al., eds.), p. 642–686. New York: John Wiley & Sons
- Macphee, J.M., Giroux, T.P., Charland, J.F. and Price, J.T. (2004). Detection of natural oxidation of coking coal by TG- FTIR- mechanistic implications. *Fuel* 83: 185–1860
- Mazumdar, B.K., Basu, S.K. and Kumar, S. (1988). Urea-coal acids combination fertilizer: some recent development. *Urja* 23: 383–390
- Norhayati, M. and Verloo, M. (1984). Characterization of organic matter in four soils of Malaysia. I. Extraction, fractionation and purification of humic substances. *J. Rubb. Res. Inst. Malaysia* 32(1): 30–39
- Orlov, D.S. (1992). Humic substances of soils and general theory of humification. In: *Russian translation series 111*, p. 8–49 and 153–214. USA and Canada: A.A. Balkema Publishers
- Patti, A.F., Verheyen, T.V., Douglas, L. and Wang, X. (1992). Nitrohumic acids from Victorian brown coal. *Sci. Tot. Env.* 113: 49–65
- Ramalho Merce, A.L., Lombardi, S.C., Mangrich, A.S., Levy, N.M. and Szpoganicz, B. (1998). Electrochemical and spectroscopic studies of the complexed species of models of nitrohumic acids derived from phthalic acids. *J. Braz. Chem. Soc.* 9(3): 231–242
- Schnitzer, M. (1982). Organic matter characterization. In: *Method of soil analysis Part 2, Chemical and microbiological properties*, (Page, A.L. et al., eds.), p. 581–594. Madison: American Society of Agronomy, Inc.
- Stevenson, F.J. (1982). Humus chemistry. In: *Degradation products and chemical structures*. p. 244–263. New York: John Wiley & Sons
- Sim, S.F., Lau, S., Wong, N.C. and Asing, J. (2006). Characteristics of coals derived humic acids from Mukah, Sarawak as soil conditioner. *J. Trop. Agric. and Fd. Sc.* 34(2): 333–342
- Siva, K.B., Aminuddin, H., Husni, M.H.A. and Manas, A.R. (1998). Analytical attributes of humic acids derived from tropical based resources. *Pertanika J. Trop. Agric. Sci.* 21(1): 53–58
- Terajima, K., Tomita, S., Matsuda, Y. and Abe, K. (1977). Nitrohumic acids-containing adsorbents and process for producing same. *United States Patent 4,013,585*
- Terajima, K., Tomita, S., Matsuda, Y., Abe, K., Higuchi, K., Iwashita, K., Nishiyama, N. and Kato, Y. (1976). Process for the production of adsorbents of nitrohumic acids series with an improved alkali-resistance. *United States Patent 3,994,830*
- Umi Kalsom, M.S., Emmy, A.K.R., Sashikala, M.P. and Norlea, A. (2003). Potential of *Trichoderma viride* in degradation of lignocellulose for humic acids production. *Trans. of the Malaysian Soc. of Plant Physiology* 12: 122–127
- Umi Kalsom, M.S., Nur, H., Norlea, A.A. and Ngaspan, S. (2006). Characterization of humic acids from humification of oil palm empty fruit bunch fibre using *Trichoderma*

- viride*. *J. Trop. Agric. and Fd. Sc.* 34(1): 165–172
- Won, T.K. (1968). Studies on the characteristics of humic acids and its utilization of humic acids (nitrohumates). *J. Korean Chem. Soc.* 13(1): 62–67
- Yildirim, M. and Ozbayoglu, G. (2004). Briquetting of Tuncbilek lignite fines using ammonium nitrohumate as a binder. *Trans. Ins. Min. Metall. C.* 113: 13–18

Abstrak

Pengekstrakan asid humik (HA) dengan kaedah agen alkali kalium hidroksida (KOH) daripada bahan arang batu Mukah dan pelbagai jenis kompos menghasilkan jumlah peratusan HA yang rendah walaupun dengan kaedah yang telah dioptimumkan. Namun, apabila proses pengoksidaan asid nitrik (HNO_3) terhadap arang batu dilakukan sebelum pengekstrakan KOH, hasil asid nitrohumik (NHA) yang diperoleh meningkat sebanyak 5–6 kali ganda berbanding dengan HA. Terdapat peningkatan yang sederhana bagi hasil ekstrak NHA berbanding dengan HA daripada sampel kompos. Arang batu sub-bitumen dari Mukah menghasilkan NHA (71.50–88.12%) yang paling tinggi berbanding dengan sampel lain dengan menggunakan 3 M HNO_3 pada suhu 50 °C. Sementara itu, arang batu bitumen dari Kapit memerlukan suhu yang lebih tinggi iaitu 90 °C bagi menghasilkan hasil NHA sehingga 60% manakala lignit dari Mukah dapat mencapai hasil 70% dengan 1 M HNO_3 pada 25 °C. Sifat kimia NHA didapati berbeza berbanding dengan HA. Kandungan C pada NHA lebih rendah manakala O, H, N, jumlah asiditi, CEC, kumpulan berfungsi karbosilik dan fenolik adalah lebih tinggi daripada HA. Spektra FTIR menunjukkan pengoksidaan dengan HNO_3 menghasilkan nilai penyerapan kumpulan berfungsi nitro ($-\text{NO}_2$) pada $1,540\text{ cm}^{-1}$ dan nitroso ($-\text{NO}$) pada $1,364\text{ cm}^{-1}$. Proses pengoksidaan dengan menggunakan kitaran semula HNO_3 dapat menghasilkan hasil NHA yang stabil dengan cara mengawal nilai molariti yang dikehendaki pada setiap kali proses pengoksidaan dibuat.