Article

Characterization of the Coal Derived Humic Acids from Mukah, Sarawak as Soil Conditioner

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Na Malásia encontram-se abundantes reservas de carvão em Sarawak e Sabah. A utilização dessas reservas, até agora, ocorre principalmente para produção de energia. O uso não-energético como condicionador de solo ainda é inexplorado. Assim, este estudo foca a caracterização de ácidos húmicos presentes no carvão de Mukah e a avaliação de suas propriedades como condicionador de solo. Os ácidos húmicos presentes em carvão regenerados foram também avaliados. Os resultados revelaram que diferentes extratores influenciam as propriedades dos ácidos húmicos. A extração com KOH 0,5 mol L^{-1} produziu carvões com baixo teor de cinzas e alto teor de grupos ácidos funcionais, que são importantes como condicionadores de solo. No entanto, o rendimento foi baixo. Amostras de carvão regenerado com ácidos nítricos aumentam o rendimento em 83,45% em média. A acidez dos grupos funcionais nitro-húmicos foi aumentada mantendo-se a quantidade de cinza em nível mínimo.

In Malaysia, abundant coal resources were found in Sarawak and Sabah. The utilization of coal resources, to date, is emphasized on the energy productions. The non-energy utilization as soil conditioner is unexplored. Therefore, this study attempted to characterize the coal humic acids extracted from Mukah coal and to evaluate its properties as soil conditioner. The coal humic acids from the regenerated sample were also assessed. The results revealed that different extractants and concentrations influenced the properties of humic acids. The extraction with KOH at 0.5 mol L^{-1} produced humic acids with low ash content and high acidic functional groups, which are substantial as soil conditioner. However, the yield was low. Regeneration of coal sample with 10% nitric acids improved the yield to an average of 83.45%. The acidic functional groups of nitrohumic acids were improved with the ash content remained at a low level.

Keywords: coal, humic acids, nitrohumic acids, regenerated

Introduction

Coal forms from the accumulation of vast quantities of plant remains. Formation of coal initially involves formation of peat in waterlogged environments. The peat later becomes overlain by sediments and subjected to moderate temperature and high tectonic pressure. Over geological periods of time, lignite, brown coal and bituminous coals of increasing maturity are formed.[1] Coal particularly low-grade coal, is known to be one of the resources rich in humic acids. The humic acids can be found in various environments such as soils, natural waters, rivers, lakes, sea sediment plants, peat and composts however, none of these resources are as abundant as low-grade coal. The low-grade coal recorded 40-85% of humic substances compare to black peat, 10-40%; sapropel peat, 10-20%; brown coal, 10-30%, compost, 2-5%, soil and sludge, 1-5%.

Humic acids were reported in numerous researches as an excellent natural and organic way to provide plants and soil with a concentrated dose of essential nutrients, vitamins and trace elements. Addition of humic substances extracted from an oxidized coal to soil was found to retard the onset of runoff process under rainfall.[2] Furthermore, an increase of soil cation exchange capacity, pH and organic matter was observed after incorporation of coal derived humic acids on two Nigerian nutrient poor tropical soils.[3] The impacts of these improvements were reflected in higher crop productivity. Nevertheless, the principal

properties and its potential application depend strongly on the origin and the isolation procedures. For example, similar formations of leonardite deposits have been discovered throughout the world, each with varying characteristics. Sources with little humic content, high ash content and lesser oxygen functional groups are not an ideal source for agricultural humic acids.

Coal resources in Malaysia to date are estimated at about 1,050 million tones. The known resources may be categorized into 231.85 million tones proven reserve; 171.38 million tones indicated reserve and 646.84 million tones inferred reserve. Of the total amount, coal resources are mainly found in Sarawak and Sabah with 69% and 29%, respectively.[4] The quality of the coal resources may range from lignite to anthracite; bituminuous to sub-bituminuous. To date, the utilization of coal resources is specifically for energy generation. An estimated 300,000 tonnes of coal from Merit-Pila Field was produced for Sejingkat Power Plant in Sarawak in 1999. The non-energy utilization of the coal resources as soil conditioner remains unexplored. Therefore, the objectives of this study are to extract and to characterize humic acids derived from the indigenous coal and to assess the suitability of the extracted humic acids as soil conditioner.

Experimental

Extraction of humic acids

Alkali extraction. Mukah coal sample was pulverized, washed and sieved through 50 μm sieve to eliminate the coal dust. The retained coal sample was oven-dried at 105 °C overnight. 10 g of the coal sample was added to 100 mL of NaOH (0.1 mol L^{-1}) and was heated to 70 °C for 2 h. The supernatant was filtered through 50 μm sieve and the coal residue was washed with distilled water until the washed water was clear. The coal residue was dried at 105 °C and weighed. The supernatant was acidified with concentrated H_2SO_4 to pH 1-2 and allowed to stand overnight. The precipitated humic acids were separated by centrifugation at 6,000 rpm for 10 min. The humic acids were washed with distilled water and centrifuged for twice. The gel-liked humic acids were oven-dried at 60 °C and stored in desiccators. The procedure of extraction was repeated with 0.5 mol L^{-1} and 1.0 mol L^{-1} of NaOH and 0.1 mol L^{-1}, 0.5 mol L^{-1} and 1.0 mol L^{-1} of KOH according to the International Humic Substances Society, 1983 with modifications.[5]

Nitration of coal. The coal sample was oxidized to produce regenerated coal prior to extraction in attempt to improve the yield of humic acids. The regenerated coal was obtained by nitrating the coal sample with nitric acids at 5%, 10% and 20% (1 g of coal with 5 mL of nitric acids) at 70 °C for 2 h with continuous stirring. The coal sample was dried in oven at 60 °C. The nitrated coal was subjected to the alkaline extraction and the resulting extracts were referred to as nitrohumic acids.

Yields. The yield of humic acids was calculated as the weight of extracted humic acids per unit weight of coal.

Characterization of humic acids

Moisture. The moisture content was determined by drying the samples at 105 °C overnight. The ash content was determined by combustion of samples at 800 °C for 2 h.[6]

Total acidity, carboxylic and phenolic content. The total acidity was measured using the barium hydroxide method and the carboxyl groups were determined by using calcium acetate. The phenolic content was calculated as the difference between the total acidity and the carboxyl groups.[7]

Total nitrogen content. The nitrogen content was analyzed with Kjeldahl digestion procedure.[8]

FTIR analysis. FTIR spectra of the samples were recorded on KBr pellets (2 mg humic acids and 100 mg KBr) using a Shidmadzu Series FTIR spectrophotometer. All of the spectra were self-deconvoluted to improve the apparent resolution.

UV-Vis analysis. Approximately 5.0 mg of humic acids samples were dissolved in 25 mL of 0.05 mol L^{-1} $NaHCO_3$ solutions with pH adjusted to 8-9 with 0.1 mol L^{-1} NaOH to assist solubility. Absorbances at 400 nm, 465 nm, 600 nm and 665 nm were recorded. The E_4/E_6 value was calculated based on the ratio of absorbance at 465 nm and 665 nm. Absorbance at 465 nm expresses presence of humic acids formed in initial humification stage and absorbance at 665 nm indicates presence of humic acids formed in well-humified organic matter.[9] The value of Δ log K coefficient, $\Delta \log K = \log A_{400} - \log A_{600}$, was calculated to categorize the degree of humification.[10]

Results and Discussion

Extraction of humic acids

Table 1 summarizes the extraction yield of humic acids with NaOH and KOH at varying concentrations. Generally, the yield of humic acids was increased with the

concentration of alkaline solution. The trend may be attributed to the increase in the solubility of humic acids with pH.[11] Yates and Von Wandruszka,[12] reported an increase in surface tension with concentration of Na^+, which indicated that humic solute was more anionic and therefore hydrophilic at higher molarity. The present results also revealed greater extraction efficiency with KOH. It has been well established that KOH is a more efficient extractant for humic acids. Garcia *et al.*,[13] compared the extraction efficiency with NaOH, KOH and $Na_4P_2O_7$, revealed the greatest yields with 0.25 mol L^{-1} KOH. The observation was likewise supported by Rocha *et al.*[14] The solubility of humic substances involves dissociation, molecular expansion and solvent penetration. KOH possess a greater efficiency, as the ionic radius of hydrated K^+ (300 x10^{-9} m) is smaller in relation to hydrated Na^+ (450 x 10^{-9} m). This allows a greater expansion, counterbalance and capacity of interaction of the intra and intermolecular charges present in the humic substances.[14] Generally, the maximum extraction yield was obtained at an average of 20% with KOH. Re-extraction of humic acids produced an average yield of < 2% from 0.5 and 1.0 mol L^{-1} of KOH which, did not reflect a significant improvement on the yield. The essential yield of humic acids is economically insufficient as the soil conditioner. In comparison to leornadite marketed elsewhere (contains average of 80% of humic acids), the humic acids extracted from the indigenous coal were far too little for economically sustainable exploitation. However, pretreatment of the coal samples with 10% of nitric acids (HNO_3) improved the yield tremendously to an average of 83.45%. Improvement as such was also reported in the study by Won,[15] as the yield of nitrohumic acids was 5 times (by weight) more than the original humic acids. The role of HNO_3 in regeneration process was to manipulate the solubility of humic acids by introducing acid groups from HNO_3 to enable them more readily attacked during extraction. Therefore, the yield of humic acids is governed by the concentration of HNO_3. The present study revealed

that application of 10% of HNO_3 has optimized the extraction yield.

Chemical characteristics of humic acids

Table 2 presents the chemical characteristics of humic acids extracted with NaOH and KOH at varying concentration. They were prepared from the Mukah coal containing 2.20% moisture and 0.78% ash. The moisture content in the humic acids was from the sample preparation. The ash content however may be due to the sample preparation or the origin of raw materials. The value exceeded the ash content of the raw material, indicating the contribution of residual Na_2SO_4/K_2SO_4 from preparation process. Nevertheless, increasing alkalinity of NaOH and KOH from 0.1 mol L^{-1} to 0.5 mol L^{-1} produced humic acids with decreasing ash content. This observation was also recorded in the study of Rosa *et al.*[16] The ash content was augmented in the extraction with 1.0 mol L^{-1} of KOH and NaOH. Levesque and Schnitzer[17] reported high ash content in humic acids produced with 0.1-0.15 mol L^{-1} NaOH. Reduction of the ash content from 25% to 5% was achieved when 0.4 mol L^{-1} NaOH was used. Considering the total acidity, humic acids extracted with KOH generally consisted more acidic functional groups (-COOH and phenolic OH) compared to NaOH. Under alkaline condition, auto-oxidation and chemical changes such as condensation between amino acids and aldehydes or quinones may take place. The occurrence of alkaline auto-oxidation processes is indicated by an increase in the C=O groups.[18] The results obtained demonstrated a greater C=O content in the KOH extracts, suggesting the promotion of alkaline auto-oxidation. The nitration process further improved the total acidity of humic acids thus enhanced its feature as soil conditioner. The oxidation process may degrade the core structure of humic acids into a variety of aliphatic dicarboxylic acids, benzenecarboxylic acids, hydroxybenzoic acids and nitro compounds such as nitrophenols, nitrobenzoic acids and dinitrosalicyclic acids.[19] The presence of these compounds was reflected in the results of carboxyl and phenolic content. In addition, the nitration process substitutes the nitro and nitroso groups to phenolic structures of humic acids which was observed by the increased of nitrogen content.[20,21]

FTIR

The FTIR spectra of the isolated humic acids exhibited similar absorption bands as reported elsewhere (Figures 1 and 2).[14,22,23] The important features of the spectra are:

Table 1. Yield of humic acids under different extraction conditions

Extraction conditions	Concentration (mol L^{-1})	Yield (%)
NaOH	0.1	3.61
	0.5	9.83
	1.0	13.67
KOH	0.1	3.43
	0.5	16.00
	1.0	20.00
Regenerated with 5% HNO_3, extracted with KOH	0.5	67.00
Regenerated with 10% HNO_3, extracted with KOH	0.5	83.45
Regenerated with 20% HNO_3, extracted with KOH	0.5	65.10

Table 2. Characteristics of humic acids with varying extractants and concentration

Extraction Condition	Moisture (%)	Ash (%)	Functional groups (m equiv. g^{-1})			Nitrogen (%)
			Total acidity	-COOH	-OH	
0.1 mol L^{-1} NaOH	4.44 ± 1.93	25.56 ± 1.93	6.36 ± 0.04	2.42 ± 0.03	3.95 ± 0.06	0.68 ± 0.04
0.5 mol L^{-1} NaOH	18.59 ± 2.37	14.10 ± 0.17	8.17 ± 0.05	2.10 ± 0.06	6.07 ± 0.10	0.68 ± 0.03
1.0 mol L^{-1} NaOH	29.04 ± 4.73	16.83 ± 0.80	7.93 ± 0.05	1.52 ± 0.03	6.41 ± 0.05	0.55 ± 0.04
0.1 mol L^{-1} KOH	11.68 ± 3.07	20.39 ± 0.34	7.17 ± 0.03	1.60 ± 0.04	5.57 ± 0.06	0.65 ± 0.04
0.5 mol L^{-1} KOH	8.09 ± 1.73	10.06 ± 0.92	11.49 ± 0.04	2.27 ± 0.05	9.22 ± 0.05	0.65 ± 0.03
1.0 mol L^{-1} KOH	9.89 ± 3.34	23.08 ± 7.81	8.36 ± 0.02	2.76 ± 0.03	5.60 ± 0.03	0.43 ± 0.05
HNO$_3$/0.5 mol L^{-1} KOH	5.42 ± 1.82	8.68 ± 1.77	11.28 ± 0.04	3.59 ± 0.05	7.69 ± 0.04	1.65 ± 0.05

i) a weak sharp band at 3690 cm^{-1} which is attributed to the valence vibration of water; *ii*) a broad band around 3400 cm^{-1} due to O-H stretching of phenol and alcohol; *iii*) a couple of weak bands between 2920 and 2850 cm^{-1} attributed to C-H aliphatic; *iv*) a well-defined band at 1706 cm^{-1} due to C=O stretching of ketonic and carboxylic groups; *v*) a strong peak at 1620 cm^{-1} assigned to aromatic C=C stretching, C=O of conjugated ketones and carboxylate ions; *vi*) a couple of peaks at 1430 cm^{-1} and 1334 cm^{-1} due to C-H stretching; *vii*) a group of low intensity bands between 1000 cm^{-1} and 1100 cm^{-1} attributed to Si-O stretching and C-O stretching of polysaccharides; *viii*) weak bands at 1040 cm^{-1} due to S=O due to treatment of humic acids with sulphuric acids
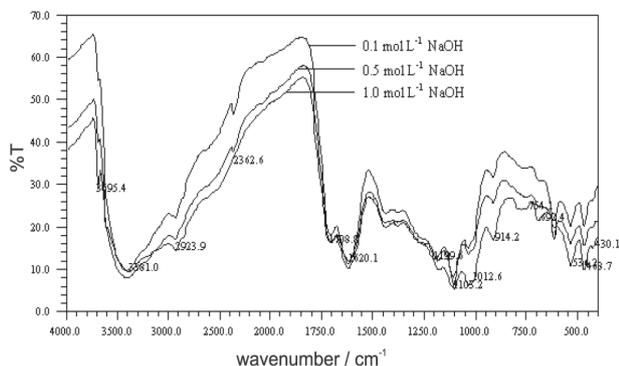
Figure 1. FTIR spectra of humic acids extracted with different concentration of NaOH.
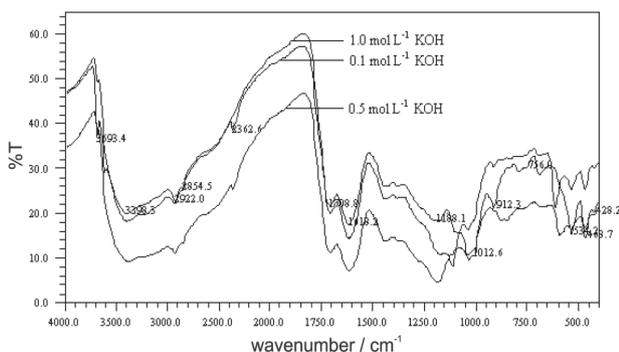
Figure 2. FTIR spectra of humic acids extracted with different concentration of KOH.

and *ix*) absorption bands at 470-480 cm^{-1} and 530-540 cm^{-1}, which are due to mineral components.[19]

The spectra show relatively more bands in the region of 400-700 cm^{-1}; and they are greater in intensity compared to those reported in the literature.[14,23] Humic acids may differ significantly with respect to their contents of inorganic constituents, which manifests in the region of 470-480 and 530-540 cm^{-1}. The variation may be due to the differences in the extraction and purification procedures. The purification with HF/HCl treatment, which aims at removing the ash content was not included in this study therefore the impurities due to mineral components are prominent. The humic acids prepared with NaOH and KOH demonstrated similar pattern on the IR spectra. The humic acids extracted with different molarity of NaOH exhibited closer similarity, suggesting an interrelated structure. The spectra of humic acids prepared with 0.1 mol L^{-1} and 1.0 mol L^{-1} of KOH showed a decrease in band intensities at 3400 cm^{-1}, 1700 cm^{-1} and 1620 cm^{-1}. The reduction in the intensity at 1700 cm^{-1} may be attributed to the substitution of carbonyl groups to salts, as the humic acids prepared with 0.1 mol L^{-1} and 1.0 mol L^{-1} KOH were higher in ash content. The absorption bands presented in the region of 1000 – 1100 cm^{-1} were rather shifted for humic acids extracted with KOH. In this region, absorption bands are assigned to the presence of mineral content. It is inappropriate to be used for characterization of atomic groups as minor silicates may induce strong absorption.

Several changes due to regeneration were observed on the IR spectra of humic acids prepared from the regenerated coal: *i*) an additional poorly-defined shoulder at 1544 cm^{-1} attributed to amide II (possibly nitrogroups in humic acids oxidized by nitric acids); *ii*) absence of a band at 1200 cm^{-1} with formation of a band at 1110 cm^{-1} and *iii*) increase in band intensity at 1040 cm^{-1} (Figure 3). The absence of band at 1200 cm^{-1} (carboxylic groups) with the increase of band at 1040 cm^{-1} (C-N bending) suggested that the nitration might occur at the expenses of the carboxylic groups. These observations were slightly
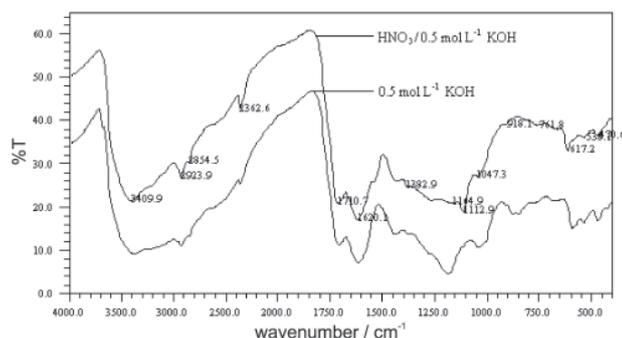
Figure 3. FTIR spectra of humic acids prepared from nitrated coal and untreated coal with 0.5 mol L^{-1} KOH.

deviated from the study of Dick *et al.*[23] A sharp absorption band at 1530 cm^{-1} due to NO$_2$ stretching which was reported as an indicative of the nitration process was not noticed in the present study.

UV-Vis

The E$_4$/E$_6$ coefficient is widely used in agricultural practices to express the degree of humification. A low ratio may be indicative of a relatively high degree of condensation of aromatic constituents; a high ratio infers the presence of relatively more aliphatic structures.[19] The E$_4$/E$_6$ ratio is expected to decrease with increasing molecular weight.

Table 3 shows the UV-Vis spectral properties of humic acids. The E$_4$/E$_6$ ratios progresses in an increasing trend, although variably, when alkaline media with higher molarity was applied. The results demonstrated that there was a possible structure fractionation with higher concentration of alkaline media leading to a smaller molecular weight. Levesque and Schnitzer[17] revealed partial fractionation in humic acids prepared with 1.0 mol L^{-1} NaOH as an increase in the E$_4$/E$_6$ ratio was observed. Rosa *et al.*,[16] investigated the parameters influencing on the humic substances extraction, inferred similar observation. In comparison to the extractant employed, the E$_4$/E$_6$ of humic acids yielded with KOH were relatively higher compared to those extracted with NaOH, indicative of more aliphatic structure. This observation was in contrast to the study of Rocha *et al.*[14] The nitration process on the other hand, produced humic acids with lower E$_4$/E$_6$ ratio demonstrating higher level of condensation. It was well recognized that the degradation products of oxidation process were enriched with aromatic compounds.[24] Piccolo *et al.*,[25] related the plant nitrate uptake and growth regulations with the structural features of humic acids, concluded that the most effective humic fraction were those with higher acidic

Table 3. UV-Visible spectral properties of humic acids

Preparation	Concentration (mol L^{-1})	E$_4$/E$_6$	Δ log K
NaOH	0.1	3.372	0.555
	0.5	3.765	0.572
	1.0	3.709	0.590
KOH	0.1	3.642	0.579
	0.5	3.530	0.566
	1.0	4.206	0.642
Regenerated with 10% HNO$_3$ extracted with KOH	0.5	3.334	0.660

functionality and smaller molecular size. The aliphatic and aromatic content of the extract did not appear to play a role.

Kumada,[10] correlated the values of Δ log K coefficient and the degree of humification. On the basis of Δ log K coefficient, humic acids were divided into 3 types: type A – humic acids of high degree of humification for which the values of Δ log K coefficient is up to 0.6; type B- those of corresponding values between 0.6-0.8 and type R$_p$ - Δ log K coefficient within the range of 0.8-1.1. No significant different was observed at 95% confidence level for Δ log K coefficient of humic acids with varying treatments. In agricultural perspective, fertilizer with higher humification degree is expected to have a better agronomic quality. Nevertheless, the differences of UV-Vis properties of humic acids were not significant enough to enable this parameter be used as an indicator of humification degree.

Conclusions

For agricultural purposes, there are several criteria that humic acids products shall comply. Sources with sufficient humic concentration are substantial of high economical value. Humic acids with higher acidic functional groups and lower ash content however are imperative for the effectiveness in influencing the biological activity of the plant system and soil properties. The study concluded that the extraction yield depended on the extractant and its concentration. KOH extraction produced a better yield compare to NaOH. The extraction with KOH at 0.5 mol L^{-1} generated humic acids with higher acidic functional groups and lower ash content. However, the yield was economically inadequate therefore constraining the application of coal humic acids as soil conditioner. The nitration process enhanced the features of humic acids as soil conditioner as the yield and the acidic functional groups were improved significantly with the ash content remained low. The IR spectra of humic acids extracted with KOH and NaOH were similar. The IR spectrum of

nitrohumic acids however revealed an additional poorly-defined shoulder at 1544 cm^{-1} and the disappearance of the band at 1200 cm^{-1} with increased band intensity at 1040 cm^{-1} as an indication of nitrogen incorporation. The UV-Visible spectral properties of humic acids did not demonstrate a significant different to enable this parameter dependable as indicator of humification degree.

Acknowledgments

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