



Faculty of Resource Science and Technology

**EXTRACTION AND CHARACTERIZATION OF COAL
DERIVED HUMIC ACIDS AS SOIL CONDITIONER**

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**EXTRACTION AND CHARACTERIZATION OF COAL DERIVED HUMIC ACIDS
AS SOIL CONDITIONER**

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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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ABSTRACT

Humic acids (HA) were extracted from young Mukah coal using alkaline extraction (NaOH and KOH solution). The humic acids precipitates were separated by centrifugation from its acidified solution. Samples were characterized by the yield, moisture content, ash content, total acidity, -COOH group, -OH group, nitrogen content and E_4/E_6 ratio. The functional groups were identified by FTIR spectroscopy. The properties of the coal-derived humic acids were compared with the properties of humic acids extracted from the nitrated sample which produce through regenerated process.

Keywords: Humic acids, alkaline extraction, nitrated coal, FTIR spectroscopy, regenerated process

ABSTRAK

Asid humik telah diekstrak daripada arang batu dari Mukah menggunakan kaedah pengestrakan beralkali (larutan NaOH dan KOH). Asid humik telah dipisahkan melalui teknik pengemparan ke atas larutan berasid. Sampel telah dicirikan berdasar kepada hasil pengestrakan, kandungan lembapan, kandungan abu, jumlah keasidan, kumpulan -COOH, kumpulan -OH, kandungan nitrogen dan nisbah E_4/E_6 . Kehadiran kumpulan berfungsi telah ditentukan melalui teknik spektroskopi infra-merah Transformasi-Fourier (FTIR). Sifat asid humik ekstrakan beralkali telah dibandingkan dengan sifat asid humik yang disediakan daripada sampel ternitrat dimana ia telah dihasilkan melalui proses pembentukan semula.

Kata kunci : *Asid humik, pengestrakan beralkali, arang ternitrat, spektroskopi infra-merah Transformasi-Fourier, proses pembentukan semula*

1.0 INTRODUCTION

Humic substances are the degradation products of plants and animals residue as well as through the decomposition of primary and high polymer organic compounds. Humic substances are naturally occurring, biogenic heterogeneous organic substances that can be characterized as being yellow to black in colour, of high molecular weight and refractory (Husni *et al.*, 1996). They are formed during humification of organic matter by soil micro organisms, which can be operationally separated into three fractions: humic acids, fulvic acids and humin (Stevenson, 1994).

Humic acids consist of the fraction of humic substances that is precipitated from aqueous solution when the pH is less than 2 (Aiken *et al.*, 1985). Fulvic acids consist of the fraction of humic substances that is soluble under all pH conditions. Humin is the fraction of humic substances that is not soluble in water at any pH value.

Humic acids comprised of highly reactive polymeric compound of varying molecular weight, containing C, H, O and N, and its reactivity is influenced by the nature and amount of oxygen-containing functional groups (Stevenson and Goh, 1972). They have important influences in agronomic and environmental fields. Their roles include the following (Hayes and Swift, 1978):

1. The formation and maintenance of good soil structure;
2. The improvement of water entry and retention by soil;
3. The retention of plant nutrients by cation-exchanges processes;

4. The slow release, from the transformation and mineralization of substrate, of nitrogen, sulphur, phosphorus, and some trace element;
5. The transport of metals into plant roots, and the possible stimulatory effects on plant growth (Flaig, 1990).
6. The immobilization of some anthropogenic chemical added to soil to influence crop growth;
7. The enhancement of the buffering capacities of soils.

Humic acids can be extracted from peat, composts or soils. Low-grade coal was discovered as a source of humic acids for crop production due to its high humic acids content. Low-grade coal recorded 40-85% of humic substances as compared to black peat, 10-40%; sapropel peat, 10-20%; brown coal, 10-30%; compost, 2-5%; soil and sludge, 1-5%. Coals are complex heterogeneous solids that vary widely in their properties and in their suitability for possible applications (van Krevelen, 1993). Coal humic acids are defined as dark-coloured substances derived from coals, which are soluble in aqueous alkali but insoluble in acids (Lawson & Stewart, 1989).

They could function as soil conditioner to promote the aggregation of soil particles for holding micronutrients for plant growth (Lawson & Stewart, 1989). Mbagwu and Piccolo, 1997 reported an increase of soil cation exchange capacity, pH, and organic matter on two Nigerian low fertile tropical soils after incorporation of coal derived humic acids. These improvements were reflected in higher crop productivity.

Coal resources in Malaysia to date are estimated at 1,050 million tones. Over the total amount, coal resources are mainly found in Sarawak and Sabah with 69% and 29%, respectively, most of which are low grade and sub-bitumous coal (Thaddeus, 2000). The potential of these coal deposits in agriculture is largely unexplored.

The aim of this study was to extract and characterise humic acids from coal. The coal sample was also regenerated with nitric acids oxidation prior to extraction. The extracted humic acids were subjected to chemical and spectroscopic analysis as well.

2.0 LITERATURE REVIEW

2.1 Introduction to humic acids

Humic substances are complex mixture of organic heterogeneous structures with a wide range of molecular sizes. They have the ability to form complexes with a variety of polyvalent metals (Nagao *et al*, 2004). Humic substances are categorized into humic acids, fulvic acids and humin based on the solubility in acid base. Each fraction of humic substances is regarded as being made up of a series of molecules of different sizes; hardly have precisely the same structural configuration or array of reactive functional groups (Stevenson, 1985).

Humic acids share some compositional and structural features with fulvic acids but there are also some significant differences. The molecular weight of humic acids is greater than fulvic acids. They are also less highly charged, less polar, and more aromatic (Hayes *et al.*, 1989). Humic acids are dominated by a relatively small number of structural moieties (benzene rings, aliphatic segments, hexose and pentose unit, amino acids), functional groups (carboxyl, hydroxyl, amine), and linkages (ester, amide, ether) (MacCarthy, 2001).

2.2 Importance of humic acids

Humic acids are important in agriculture application. They assist the release of micronutrients from soils to plant, enhance microbial growth, reduce soil erosion and stimulate plant growth. In addition, humic acids increase the availability of phosphate and contribute to mineralization and immobilization of nitrogen in soils (Beames, 1986). Manufacturers

worldwide are promoting the use of humic acids products in agriculture. These products are gaining acceptance in the agriculture community. Government of the United Arab Emirates (UAE) and Turkey have included these products as part of their import specifications (Fataftah *et al.*, 2001).

2.3 Studies of humic acids structures

There have been many investigations of humic acids by chemical and thermal degradative method (Hayes *et al.*, 1989) as well as by chemical derivatization (Leenheer & Noyes, 1989). The studies have provided much information about the composition of humic substances (e.g. functional group contents), as well as identifying aromatic and aliphatic component among the degradation products (MacCarthy, 2001). Humic acids have been found to be negatively charged polymers containing various functionalities attached to an aliphatic-aromatic backbone structure (Carlsen *et al.*, 2000). As the result of both hydrophilic and hydrophobic moieties, different intramolecular and intermolecular interactions can be expected in aqueous system of humic substances, depending on solution conditions (Pokorna *et al.*, 2001). In aqueous solutions humic substances show a tendency to self-assemble and they accumulate at interfaces and solubilize organic compound (Guetzloff & Rice, 1994).

2.4 Extraction of humic acids

Humic acids can be easily extracted with alkaline solution (such as NaOH and KOH) (Pang *et al.*, 1989). The extraction using alkaline solution comprises the ionization of the acid groups and solvation of the conjugated in aqueous medium (Rocha *et al.*, 1998). The

consequent dissociation, molecular expansion, solvent penetration resulted in transformation of humic acids from solid to the solution phase (Clapp *et al.*, 1993). The solubility of humic substances (and the molecular size distribution of the soluble component) depends on pH, ionic strength and nature of the electrolyte ions (Town & Powell, 1992).

Extraction with different extractant reagents may result in varying degree of extraction efficiency. For example, extraction with KOH was known to produce greater yield of humic acids compared to NaOH. The counter ions Na^+ and K^+ are responsible for the interaction and solvation of the negative charges dissociated from the humic macromolecule. The Na^+ and K^+ have different ionic radius whereby the ionic radius of K^+ is smaller in relation to Na^+ (Table 1) (Kielland, 1937). The difference consequently lead to a greater efficiency in expansion of the macromolecule, the counterbalance and the capacity of interaction of the intra and intermolecular charges of humic acids with K^+ (Rocha *et al.*, 1998).

Table 1: Thermodynamic properties of Na^+ and K^+ in aqueous solution

Ion	Ionic radius hydrated (10^{-9}m)
K^+	300
Na^+	450

The penetration of K^+ to humic macromolecule is greater than Na^+ , consequent the efficiency in systems which displaces or removes divalent and polyvalent cations and allows negative charges on the macromolecular matrix to repel each other and improve the ionization of the acid groups and solvation of the conjugated bases in aqueous medium. On the other hand,

Na^+ that has bigger ionic radius has less efficiency of solvent reaction to humic acid extraction because the penetration to the humic macromolecule difficult (Rocha *et al.*, 1998).

KOH is usually used in manufacture of humic acids for agriculture application due to the extraction efficiency. In addition, potassium is one of the elements that are important for plant growth. High concentrations of sodium (Na) can be detrimental to soil and plant growth.

2.5 Oxidation process

The amount of humic acids in coal was increased by oxidizing the sample via regeneration process (Piccolo *et al.*, 1997). Regeneration process can be achieved by employing oxidizing agent such as nitric acid (HNO_3) or by exposing the coal sample to the atmosphere oxygen at the earth surface for a long period (Lawson & Stewart, 1989). The oxidation agent makes humic acids attacked readily during extraction (Bailey *et al.*, 1954). As a result of the nitric acid oxidation, the humic acids extracted may comprise additional nitrogen content. The presences of extra nitrogen will produce a greater molecular weight of humic acids (Butler & Ladd, 1969) and increase the potential values of humic acids as fertilizers (Lawson & Stewart, 1989). The humic acids prepared with oxidative approach are commonly referred to as nitrohumic acids (Chambury *et al.*, 1945).

2.6 Spectroscopic characteristic of humic acids

Fourier-Transform Infrared Spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy (UV/Vis) are commonly used to characterise humic acids. By using FTIR, humic acids is analysed in the solid state as transparent KBr pellets. The humic acid-KBr pellet is scanned between range 4000 cm^{-1} and 400 cm^{-1} . The typical absorption bands that are usually observed in an IR spectrum are summarized in Table 2.

Table 2: Infrared Absorption Bands of Functional Groups in Humic Matter (Stevenson, 1994)

Wavelength (cm^{-1})	Proposed assignment
3400-3300	O-H and N-H stretch
2940-2900	Aliphatic C-H stretch
1725-1720	C=O stretch of COOH groups
1650-1630	C=O stretch (amide) aromatic C=C H-bonded C=O double bond conjugated with carbonyl and COO- vibrations
1650-1613	COO- symmetrical stretch
1280-1230	C-O stretch aromatic C-O phenolic C-OH

The spectrum is often categorized in two regions, *group frequency region* ($4000\text{-}1300\text{ cm}^{-1}$) and *fingerprint region* ($1300\text{-}650\text{ cm}^{-1}$). In the group frequency region, the principle absorption bands may be assigned to vibration units that consist of only two atoms to a

molecule. In the fingerprint region, single bond stretching and bending vibration of polyatomic systems are major features (Orlov, 1985).

Molecules with similar structure may demonstrate same absorption bands in the region of 4000-1300 cm^{-1} however, the absorption bands produce by both structure will be different in the fingerprint region. The method of FTIR is capable of distinguishing humic matter of different fractions (Orlov, 1985).

UV/Vis spectra of extracted humic acids are usually recorded in the range of 200-800 nm (Rocha *et al.*, 1998). The spectra are often difficult to interpret because they are featureless and similar. The absorbance decreases when moving toward longer wavelength. This is due to the overlapping absorbance of numerous different chromophores caused by very complicated structures of humic acids (Stevenson, 1982; MacCarthy & Rice, 1985). However, ratio of absorbance at 465 nm and 665 nm, which is referred to as E_4/E_6 , is widely used to characterise humic materials (Carlsen *et al.*, 2000). The E_4/E_6 ratio serves as an index of humification (Burba *et al.*, 1995). The absorbance ratio E_4/E_6 of humic substances is a traditional parameter to estimate their humification degree and/or their molecular size (Chen *et al.*, 1977; Bloom & Leenheer, 1989). The E_4/E_6 ratio has traditionally been employed to indicate differences in the molecular sizes of humic substances, and it is generally accepted as being inversely related to molecular weight (Garcia *et al.*, 1993).

The E_4/E_6 ratio is mainly correlated to the average molecular weight and size and to a lesser degree to the oxygen content of the humic material (Chen *et al.*, 1977). The E_4/E_6 ratios also related to the decomposition level and presence of aromaticity inside the humic acids (Rocha

et al., 1998). A higher E_4/E_6 ratio indicates a low average molecular weight, size and aromatic group as well as high oxygen content (Carlsen *et al.*, 2000; Novak *et al.*, 2001). The low ratio indicates high degree of condensation of aromatic constituents. The E_4/E_6 coefficient of humic acids is usually less than 5, while for fulvic acids it ranges from 6.0 to 8.5 (Novak *et al.*, 2001).

3.0 MATERIALS AND METHODS

3.1 Samples

Coal samples from Mukah were used for extraction and characterization.

3.2 Extraction of coal-derived humic acids

3.2.1 Extraction of humic acids using NaOH

Coal sample was pulverized, washed through 50 μm sieve and dried at 105 °C overnight. Approximately 1.00 g of coal sample was added to 10 ml of NaOH with different molarity (0.1, 0.5, 1.0 M) and heated at 70 °C for 2 hours. The supernatant was filtered through 50 μm sieve and the coal residue was washed with distilled water until the supernatant is clear. The coal residue was dried at 105 °C and weighted. The supernatant was acidified with concentrated H_2SO_4 to attain pH 1-2 and let stand overnight to precipitate humic acids. Humic acids were separated from fulvic acids by means of centrifugation at 6000 rpm for 15 minutes. The precipitated of humic acids were washed with distilled water and centrifuged. Humic acids were dried in oven at 60 °C, weighted and stored in desiccators for characterization. The extraction procedure was repeated with KOH at 0.1 M, 0.5 M and 1.0 M.

3.2.3 Extraction of nitrated humic acids

Coal sample was pulverized, washed through 50 μm sieve and dried at 105 $^{\circ}\text{C}$ overnight. Approximately 1.00 g of coal sample was added to 5 ml of HNO_3 at 10% and heated at 70 $^{\circ}\text{C}$ for 2 hours with continuous stirring. The supernatant was drained and the oxidized coal samples was dried in oven at 60 $^{\circ}\text{C}$ and stored in desiccators for extraction of humic acids. A 1.00 g of coal sample was added to 10 ml of 0.5 M KOH and heated at 70 $^{\circ}\text{C}$ for 2 hours. The supernatant was filtered through 50 μm sieve and the coal residue was washed with distilled water until the supernatant is clear. The coal residue was dried at 105 $^{\circ}\text{C}$ and weighted. The supernatant was acidified overnight with concentrated H_2SO_4 to attain pH 1-2 to precipitate humic acids. Humic acids were separated from fulvic acids by means of centrifugation at 6000 rpm for 15 minutes. The precipitated of humic acids were washed with distilled water and centrifuge. Humic acids were dried in oven at 60 $^{\circ}\text{C}$, weighted and stored in desiccators.

3.3 Characterization of coal-derived humic acids

3.3.1 Chemical characterization

3.3.1.1 Moisture Content

Moisture contents of the extracted humic acids were calculated from differences in weights before and after drying in oven at 105 $^{\circ}\text{C}$ overnight.

3.3.1.2 Ash content

The ash content of the extracted humic acids was obtained after ignition in furnace at 800 °C for 2 hours.

3.3.1.3 Total acidity

Approximately 50-100 mg of humic acids were dissolved in 20 ml of 0.2 N Ba(OH)₂ solution in a 125 mL ground-glass stoppered Erlenmeyer flask. A blank consisting of 20 mL of 0.2 M Ba(OH)₂ only was prepared simultaneously. The airs in each flask were displaced by N₂ and were shaken for 24 hours at room temperature. The suspension was then filtered and the residue was washed thoroughly with distilled water. The filtrate was titrated potentiometrically (glass-calomel electrodes) with standard 0.5 M HCl solution to pH 8.4 (Schnitzer, 1977). Three replicates of each samples was prepared for the analysis of total acidity.

The total acidity (meq g⁻¹) was calculated based on the following equation:

$$\text{Total acidity} = \frac{(V_b - V_s) \times N \times 10^{-3}}{\text{g of sample}}$$

Where V_b and V_s represented the volumes of standard acid used for the blank and sample, respectively, and N is the concentration of the acid (0.5 M HCl).