Structures Analysis of A Humic Acid of Peat Soil Which is Having Irreversible Drying Using Liquid Chromatography-Mass Spectroscopy (LC-MS)

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Abstract: There was a research that has been done about irreversible drying on peat soil using liquid method chromatography - spectroscopy mass. Peat soil was taken from Rimbo Panjang village 18 km from Pekanbaru city. The results of the analysis indicate that the peat soil has a pH of 3.5, it's irreversible drying. After it’s heated intensively at 35°C for 7 weeks. The heating will cause the formation of peat slabs and formed a pseudosand. The results of the analysis by LC-MS showed a change in the type of peat humic acid compounds with peat soils that have experienced irreversible drying.

Keywords: peat soil; irreversible drying; humic acid.

1. Introduction

Peat soil is derived from soil organic matter as the remains of plants and decaying plant tissue with a thickness of more than 50 cm. Peat soil is usually in the location of the stagnant water found in a relatively flat landscape. Cold and anaerobic conditions up to ten centimeters below the surface causing organic residues accumulate, to a depth of at least 30 cm and often up to several meters. Peat soil contains inorganic materials and organic materials (Hertkorn, et al, 2005).

Peat soil organic matter is separated into humificated and non humificated material. Non humificated compounds are in plants and other organisms, such as carbohydrates, proteins, amino acids, lipids, nucleic acids and lignin. These compounds are usually exposed to degradation and decomposition reactions. Sometimes it can be sequestered in soil organic components in anaerobic conditions. The humificated fraction that known as humus, now called as humic compounds. The term is derived from humic acid Berzelius in 1830. Humic acid is also called acid Ulmat. Humic compounds are defined as poly dispersed colloidal material that is amorphous, pH < 2, yellow to brown - black and has a relatively high molecular weight. Based on their solubility in acid and alkaline, humic compounds can be separated into several fractions (Muscolo, et. al, 2007).
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2. Related Works

Humic acid can be separated with a neutral salt solution into brown humic acid (dissolved in NaCl) and gray humic acid (insoluble in NaCl). Humic material is a very important component of the soil. Depending on the climate and culture techniques (Moore and Jukka, 2004). Together with the clay soil. Substances - humic substances are responsible for all activity in soil chemistry. Humic substances involved in the reaction complex and can affect plant growth. Humic compounds play an important role especially in the translocation or mobilization of Aluminum and Iron and very influential in the presence of soil nutrients are very important in soil fertility. In excessive amounts, peat humic acid can lower the pH of soil and disturb plant growth (Jeong, 2007).

Some experts stated that the decreased ability of peat due to peat experiencing severe dry due to continuous heating at high temperature (≥ 30°C) in a long period of time so that it will form a blanket (coating) retaining water. The nature of this is so-called irreversible drying. Dry on peat soil will form a plate peat. Peat plates when we squeeze it will form sand known as pseudosan (Gerzabek et.al, 2001)

This research aims to study the properties of non-reversible dry peat and changes in the chemical structure of humic acid peat soil under conditions of non-reversible dried by using Liquid Chromatography- Mass Spectroscopy. Non reversible dry peat associated with the ability to store, hold and release water. Peat that has experienced irreversible dry is non-productive for growing plants because the plates will form a very hard peat (Rieley et al, 1996 in Noor, 2009)

Irreversible drying mainly happening on tropical peat specially swamp peat. Irreversible drying decrease peat soil productivity. Decreased ability of peat to absorb water is the result of the formation of the blanket (coating) water retention caused by the blanket of organic particles (Qureshi, et.al, 2003).

3. Material & Methodology

3.1 Place and time
This research was conducted in Chemistry Education Laboratory, Education and Science Faculty Riau University, Pekanbaru, Electro Chemistry Laboratory and Organic Chemistry Laboratory, Andalas University, Padang,

3.2 Equipment and Materials
The materials used in this study are: peat soil, 0.1 N NaOH, 0.1 M HCl, aquades., tools used in this study are the octagon 250μm sieves, centrifuges, Electrical Oven, LC-MS.

3.3 Peat Soil Sampling
Peat soil was taken from the village of Rimbo Panjang, km 18 from the city of Pekanbaru, Indonesia. Method of soil sampling will determine the accuracy of the analysis results. Peat soil that had been treated as a composite taken at a depth of 20-30 cm. To avoid subjectivity in sampling, the soil sampling location points spread evenly to all areas within the plot. Further soil samples cleared of roots, trash, leaves, gravel and stone. Sampling of soil in each plot was collected in a container and stirred until uniform, then take
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500 grams and put in a plastic bag. Furthermore, the initial wind dried peat soil up to 50 % moisture content in the shade in the open air. Then stir until evenly distributed. Soil samples were then brought to the laboratory for further analysis.

3.4 Effect of temperature and duration of heating on the properties of Irreversible Drying of Peat
A total of 100 grams of peat was heated on temperature of 25°C, 30°C, 35°C, 40 °C, 45°C with a variation of the heating for 1 hour, 2 hours, 3 hours, 4 hours and 5 hours, 1 week in the oven (up to the plate to form). 200 ml of water was added, filtered using a separating funnel equipped with filter paper. Then calculate the volume of water collected and analyzed with a measuring cup. Filtrate was left to evaporate water until the soil dried and analyzed the formation of pseudo sand.

3.5 Peat Soil Humic Acid Analysis

a. Extraction of Peat Soil Humic Acid
Determination of humic acid uses extraction method that developed by Tan (1998), with the following steps:
5 g of soil sample was weighed as peat wind dried, 2 mm sieve, then put in a 25ml centrifuge tube and added 0.1 M NaOH shaken for 24 hours. Subsequently centrifuged for 15 minutes at 4500 rpm. Taken supernatant dark in color. The rest of the soil is washed with 25 ml of distilled water and then placed back in the supernatant and centrifuge again for 15 minutes to ensure that the material of non humic precipitate. Existing sludge dumped at the bottom of the centrifuge tube. Supernatant obtained coupled with 25 ml of 0.1 M HCl and centrifuged again for 15 minutes. Furthermore, the liquid is separated between the sediment. The precipitate formed is humic acid. Humic acid is washed with 10 ml and then filtered with a filter paper and wind dried.

b. Observation of Peat soil’s Irreversible Drying Characteristic with LC-MS
Isolates humic acid of dissolved with NaOH 0,1 N, mix it with sonicator, then it is filtered and then we analyze the filtrate that we got with LC-MS.

4. Results and Discussion

4.1. Effect of Heating Temperature and the time length of heating to Peat Soil’s Irreversible Drying Characteristic
A total of 100 grams of peat heated at various temperatures, namely, 25°C, 30°C, 35°C, 40°C, 45°C with a variation of the old heating for 1 hour, 2 hours, 3 hours, 4 hours and 5 hours, 1 week to 3 months in the oven with the aim to analyze the effect of heating on peat soil formation indicated by slabs of peat, clay and hard if we squeeze will loose sand forming false. Plate peat is formed when the water will not be able to bind water. It is shown that heating at a temperature of 25 0C and 30 0C is not formed peat even heating plates for 3 months. Heating at a temperature of 350 C for 7 weeks have formed peat plate. The longer the plate is heated, peat will be hard and the water levels will be smaller. Warming peat at a temperature of 400 C formed when peat plates heated for 6 weeks. And heating at a temperature of 450C, peat formed during the heating plate for 5 weeks. In this study, peat plate was formed at a temperature of 35 °C the higher the temperature the faster the heating plate is formed peat. This is in accordance with the opinion (Delapp et al., 2005) that the peat will be subject to intensive heating experiencing severe drought and decreases its ability to hold water. This condition is called dry non-return (irreversible drying). Peat which have experienced dry peat is not turning into a non-productive because of decreased ability to hold water. The higher the temperature the faster the plate peat is formed.
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4.2 Observation of Peat Soil’s Irreversible Drying Characteristic to Liquid Chromatography-Mass Spectroscopy (LC-MS)

Irreversible drying characteristic of peat soil can be observed through the humic acids which is contained in the peat soil. Observation of non-return properties of dried peat is observed through changes in humic acid compound which is extracted from peat soil that is compared with humic acid compound which is extracted from peat soil that has been heated to the optimum state of the research that is at a temperature of 35°C for 7 weeks. Humic acid is an organic compound that is present in large amounts in the peat soil. Humic acid is extracted from peat soil with extraction method. Furthermore, pure humic acids were analyzed by LC-MS.

The results of the analysis of humic acids that is extracted from peat soil by LC-MS can be seen in Figure 22. Chromatogram result of humic acid compound is shown in Figure 1, each peak in the chromatogram obtained with the MS data.

The results of the analysis of humic acids that is extracted from peat soil which was heated at 35°C for 7 weeks with LC-MS can be seen in Figure 2.

Chromatogram result of humic acid compound shown in Figure 1, each peak in the chromatogram obtained with the translated MS.

Figure 1. Spectra LC of the first peat soil humic acid compound

Based on the research by LC-MS on Figure 1 it can be seen that the peat soil in rimbo panjang have 7 types of humic acid compound that is in climax of 1.11; 4.86; 6.39; 10.82; 15.42; 23.43 and 25.64 minutes with each molecular weight is 1975.59; 1966.85; 1945.79; 1979.89; 1945.98; 1972.89 and 1975.78.

Figure 2. Spectra LC of peat soil humic acid compounds that have experienced irreversible drying
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As for the peat soil that has experienced a irreversible drying can be seen in Figure 2 there are 7 types of peat humic acid compounds contained in the climax of 1.1; 6.56; 9.56; 10.82; 21.04; 23.08; 25.13 minutes with each molecular weight is 1984.13; 1998.38; 1973.66; 1970.51; 1954.07, 1965.25 and 1949.06. There are differences in the type of humic acid compounds that is contained in the initial peat soil with peat soil that has undergone irreversible drying. It can be seen at the difference in retention time and molecular weight of each climax. The most dominant climax occurs at the same retention time is 10.82 minutes for the initial peat and peat soil that has been heated. A reduction in the molecular weight of humic acid compound from 1979.89. to 1970.51. Another dominant climax that occurred at a retention time of 23:08 minutes for the initial peat and 23.43 minutes for the peat soil that has undergone irreversible drying. A reduction in the molecular weight of humic acid compound from 1972.89 to 1970.51. There is also a change in the retention time for the start of peat humic acid compounds with peat humic acid compounds that have been heated, from 4.86 minutes to 9.63 minutes with a molecular weight of 1973.66 and 1966.85 and 15.42 minutes to 21.04 minutes with heavy molecule 1945,98 to 1954.07.

Heating causes the peat gets dehydration so that the soil becomes irreversible drying. The results of the research of LC-MS data processing in Figure 1 and Figure 2 shows that the continuous heating in peat soils causes chemical changes in the structure of humic acid, which is evident from the change in the retention time so that the peak of chromatogram is appeared and changes of the molecular weight of each peak. Changes in the chemical structure of humic acid is caused by;
1. Dehydration
2. OH-functional group of humic acid is oxidized to ketone and aldehyde groups
3. carboxylate groups are Increased due to the aldehyde functional group is oxidized to a carboxylic group.
4. Occurrence of the reaction partner, it is the second functional group of organic acids that are particularly polyfungsionil (presence of carboxyl and phenolic hydroxyl in one molecule) reacts couples.

According to Wilbraham and Matta, 1992 and Delapp et al., 2005, that peat which experiences intense heating will experience severe drought and reduced ability to hold water. This condition is called irreversible drying. Peat will be not productive anymore. The more the heat’s temperature then the peat’s slab formed faster which is eventually formed a pseudo sand, caused by the dehydration process of organic compounds that lead to a reaction between COOH functional groups.

Dehydration of organic compounds caused the both of functional groups of organic acids and carboxyl group and phenolic in a molecule that has functional characteristic will undergo couple reaction (Holden et al., 2006). Gerzabek et al., 2001; Wilbraham and matta, 1992 also explained that some carboxylic acid releases water in heating easily, heating will cause some of the alcohol group will be oxidized to ketones and aldehydes as well as carboxylic groups is increased because aldehyde group is oxidized to carboxylic acids.
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![Figure 3. Humic acid structure of peat soil](image)

![Figure 4. The Prediction of Humic acid structure of peat soil which is undergone irreversible drying.](image)

According to Willbraham and matta, 1992; Delapp et al., 2005; Holden et al., 2006). Gerzabek et al., 2001. If we relate it with the result of the research which have been done with LC-MS from figure 1 and figure 2. It can be predicted that there will be the change of humic acid structure in peat soil with peat soil which under gone irreversible drying. It is shown by Figure 3 and Figure 4.

5. Conclusion

1. Dry state of non-return (Irreversible Drying) on peat soil occurs as peat heated at high temperatures experienced in a long time. Peat soil heating at 35 ° C for 7 weeks to form slabs of peat which can not bind water and sand when squeezed will produce a pseudosand
2. By using LC-MS continued to be known chemical structure changes of peat humic acid and chemical structure of peat humic acids which have undergone no turning dry state (Irreversible Drying) due to heating at high temperature for a long time, so that the soil particles covered (coating) by humic acids are experiencing dehydration events, - OH functional groups of humic acid is oxidized to a ketone group, a carboxylic group increased due oxidized to aldehyde functional group and a carboxylic group reactions that couple second functional group of organic acids that are particularly polyfunction (presence carboxyl and phenolic hydroxyl of one molecule).

References

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