

Humic Acid as Detoxification Substance for Heavy Metal Removal in Laterite Barren Soil

Muhammad Ukasyah Irfan Mat Rahimi¹, Zaidi Embong^{1*},

¹Faculty of Applied Sciences and Technology (FAST),
Universiti Tun Hussein Onn Malaysia (UTHM), Pagoh Campus, Km 1,
Jalan Panchor, Pagoh, Muar, 84600, Muar, Johor, MALAYSIA

*Corresponding Author Designation

DOI: <https://doi.org/10.30880/ekst.2022.02.02.038>

Received 02 January 2022; Accepted 02 March 2022; Available online 23 November 2022

Abstract: Laterite barren soil is usually unsuitable for plant growth because it lacks of nutrient content and it contain unnecessary metal ion. Humic acids and their functional acidic groups are the key factors responsible for metal cation binding for their state and concentration in soils in order to obtain a fertile soil. The objectives of this study are to measure the heavy metal concentration in laterite barren soil from Pagoh Education Hub, Johor using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX). In addition, the functional group for humic acid liquid will be characterised using Fourier Transform Infra-Red (FTIR). Next, Laser Raman is also used to determine the laterite barren soil and humic acid molecular structure. Hence, the heavy metal concentration and molecular structure of the laterite barren soil between pre and post are compared in order to prove the efficiency of humic acids chemical treatment. Humic acid is applied to the laterite barren soil for 3 days within 14 day. The weight percentage of main in element in the soil samples like oxygen (O), silicon (Si), iron (Fe) and aluminum (Al) were obtained through SEM-EDX. Majority of the main elements shows significant changes at the end of the process which can benefits the plant through the nutrient uptake. Surface morphology shows that the fibre is completely disappear from the soil after 2 weeks of detoxification. Next, FTIR was used identify the functional group of humic acid which is the main key of the cation binding in the soil. Laser Raman was also used to obtain the molecular structure of laterite barren soil which prove the presence of humic acid substance between pre and post detoxification process. Also, humic acid's molecular structure which made up the specific properties remediate the soil is obtain through Laser Raman analysis. On the whole, based on the data obtained, humic acid is one of the effective ways to remediate the laterite barren soil.

Keywords: Humic Acid, Laterite Barren Soil, Soil Remediation, Heavy Metal Concentration, Fertile Soil

1. Introduction

Malaysia is one of the countries that depends on agriculture sector to boost the economy sector and rice is a staple food for Malaysian. The increasing of population of the country had increase the demand of rice. In order to fulfil the market demand, the farmer use pesticides, fertilizers, along with advance tractor technology to boost the rice growth rate. This situation indirectly had effect the environment with heavy metal [1]. Heavy metals have harmful effects on soil microorganisms, resulting in changes in the diversity, population size, and overall activity of soil microbial communities [2].

However, some area around Peninsular Malaysia are covered by laterite barren soil. Laterite is a soil and rock type rich in iron and aluminium because of the high iron oxide content, nearly all laterites are rusty-red in colour. Lateritic soils are important soils that are found in tropical and subtropical climates. Lateritic soils are distinguished by their distinct hue, low fertility, high clay content, and decreased cation exchange capacity. Furthermore, lateritic soils contain a high concentration of iron and aluminium oxides. Iron oxides, which exist mostly in amorphous and crystalline inorganic forms, are a prominent component in several soils [3].

Next, barren soil is characterised by sparse soil, sand, or rocks. Poor soil management can lead the soil to become completely barren which harmful and dangerous to plant and even human. The continuous use of pesticides, herbicides and fertilisers contributes significantly to contaminated, unproductive, and barren soils. Barren soil also can give an adverse effect for the plant growth. When soil is unsuited for plant life, none will thrive when planted on it. Desertification has increased. Drought and aridity occur when the soil is unable to support plant life. As a result, the desertification process is greatly accelerated, and previously fruitful areas become arid. Barren soil also can lead to flood disaster because the soil's ability to retain water is diminished. More floods occur as a result of the land's inability to soak up and hold water [4].

Humic acids and their functional acidic groups are the key factors responsible for metal cation binding in soils. [5]. Furthermore, humic acid alters soil nutrient concentration, increasing not only total nitrogen, total phosphorus, and total potassium content, but also alkali nitrogen, accessible phosphorus, and available potassium content, allowing the plant to absorb more nutrients [6].

The objectives of this study are to measure the heavy metal concentration in laterite barren soil from Pagoh Education Hub, Johor using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX). In addition, the functional group for humic acid liquid will be characterised using Fourier Transform Infra-Red (FTIR). Next, Laser Raman is also used to determine the laterite barren soil and humic acid molecular structure. Hence, the heavy metal concentration and molecular structure of the laterite barren soil between pre and post are compared in order to prove the efficiency of humic acids chemical treatment.

2. Materials and Methods

In this work, the sample is taken within the perimeter of the Pagoh Education Hub. Humic acid was prepared by crushing humic acid in granular form into homogenised powder. The powder was mixed with distilled water, 1.0034g of humic acid and 500ml of distilled water. Then, the humic acid was applied to the laterite barren soil within 3 days in 14 days duration.

After the detoxification process is complete, the soil samples are dried at 110°C in box furnace up to 24 hours. Next, all of the soil samples and humic acid were crushed using mortar and pestle in order to obtain a fine powder down to to a particle size of < 200 microns. The soil samples powder form is used in SEM-EDX analysis. Further step is taken for Laser Raman analysis which the soil and humic

acid powder went through the pelletizing process with the diameter of 1cm and 2g of both samples. The pelletizing process take place by giving a 3 tones force to the powder for 1 minutes.

The Scanning Electron Microscopy (SEM) analysis was used in order to investigate the surface morphology of the pre-detoxification and post detoxification soil sample for the first and second week. While the element concentration in the soil samples are obtained through the Energy Dispersive X-ray (EDX) Spectroscopy. Next, the Fourier-Transformed Infrared (FTIR) Spectroscopy was used to identify the functional group that existed in the humic acid. Lastly, the molecular structure of soil sample and humic acid are also obtained by using Laser Raman Spectroscopy.

3. Results and Discussion

Scanning Electron Microscopy and Energy Dispersive X-Ray (SEM-EDX) EM30AX model is used to examine and analysis the surface morphology and the elemental compound of the pre and post detoxification of laterite soil. Figure 1 shows the surface morphology of the three samples, for pre detoxification and first and second week of detoxification.

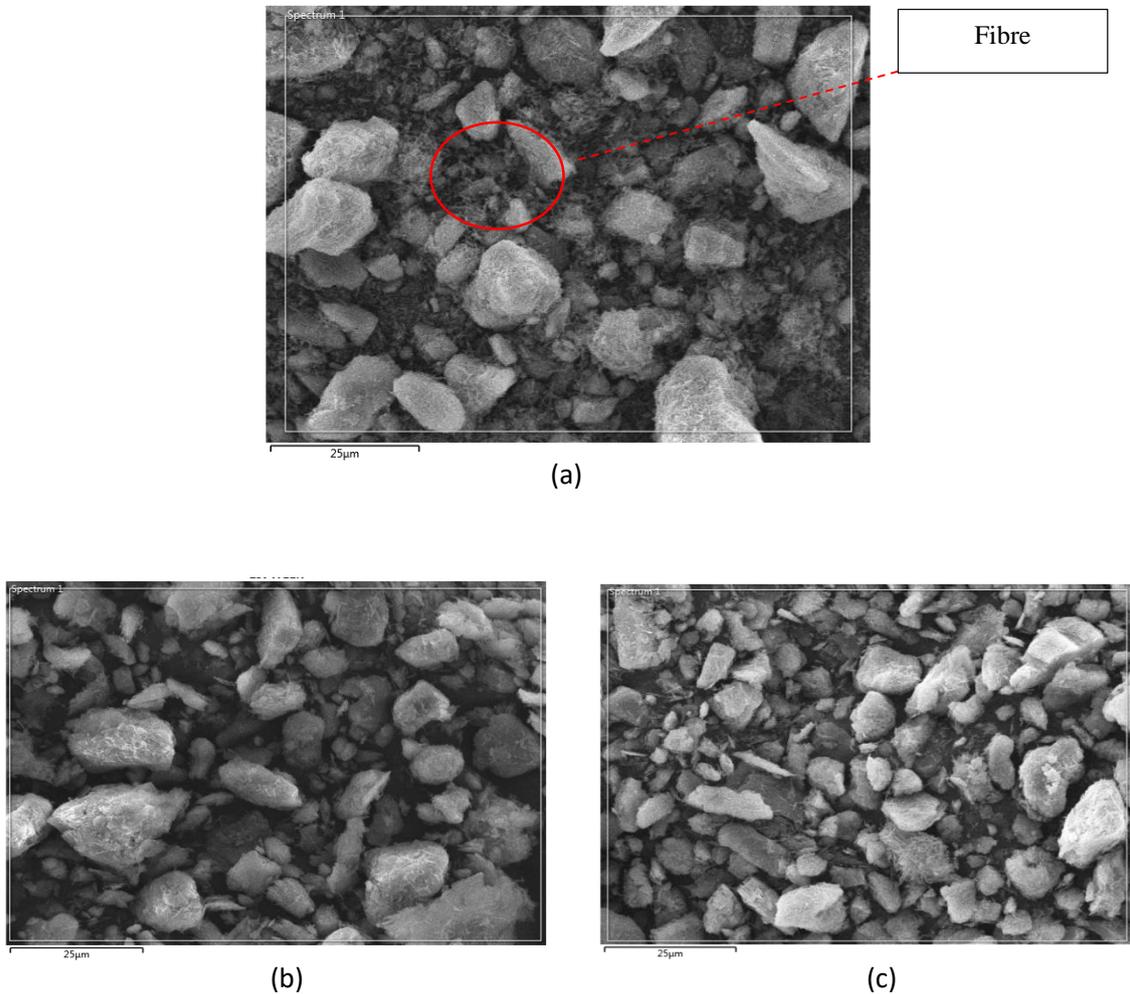


Figure 1: (a) Surface morphology for pre-detoxification process, (b) for first week (post-detoxification) process and (c) for second week (post-detoxification) process

Figure 1 (a) indicate that the surface morphology of pre detoxification sample contains fibre. It is present naturally in the soil and its play a role in determining soil's physical, chemical, and biological characteristics, which in turn influence plant growth. As shown in Figure 1 (b), the fibre are gradually

disappearing from the surface morphology of the soil and completely disappear as shown in Figure 1 (c) as the humic acid has dilute the fibre.

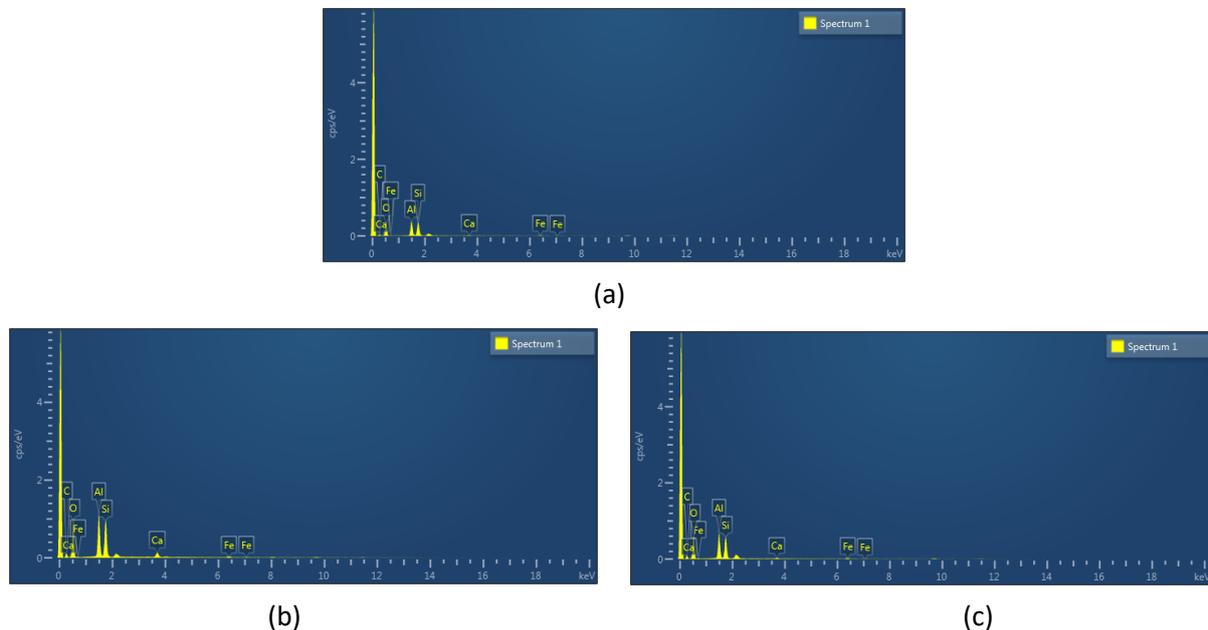


Figure 2: (a) EDX spectra image for pre-detoxification process, (b) for first week (post-detoxification) and (c) for second week (post-detoxification)

Based on Figure 2 (a), the data shows that the oxygen (O) is the heaviest element that present in the sample. The claim can be proved by the major composition of the raw soil sample from the EDX analysis reveals that it consists of 58.83% which is more than half from the total weight. Aluminum (Al) is the second highest among all elements with a percentage of 8.9%. The toxicity of Al is a major factor affecting the crop productivity in soil. Al is a crucial element of soil, and it dissolves in the soil in a variety of ionic forms, the most dangerous of which is Al^{3+} [7]. Followed by silicon (Si) with a percentage of 8.59%. Generally, silicon is the second most abundant element in the earth's crust. Silicon is not an essential element for plant because it may have an effect on the binding of nutrients to soil particles, making them more or less available for plant uptake [8]. Next, iron (Fe) receives the lowest analysis among the elements with the weight percentage of 0.35%. The most abundant form of iron in soils is ferric oxide (Fe_2O_3), often known as hematite, which is exceedingly insoluble and gives the soil a red colour as show in the Figure 3.2 (b) [9]. Iron oxides are major elements of most soils because they have a significant impact on the chemical, physical, and microbiological aspects of soils. Iron oxides have a large specific surface area and highly reactive surfaces due to their nanoparticulate size about 5-200 nm [10]. Other than 4 elements that have been mentioned earlier, there are also another element like carbon (C) with the percentage of 23.14% and 0.19% for calcium (Ca).

The EDX's spectra of post detoxification soil for 1 week of detoxification process is shown in Figure 2 (b), which shows the decreasing of oxygen (O) from 58.83% to 57.76%. The decreasing of oxygen content in the sample is due to the chronological order of formation of the humic substances in the soil [11]. The second highest element for first week of detoxification process is aluminum (Al) with the reduction of 8.9% to 8.13%. This is due to the drop of soil pH so the aluminum becomes soluble. Aluminum responsible for contributing acid in the soil.[7]. Thirdly, silicon (Si) drops from 8.59% to

7.41%. Si-O absorption was significantly reduced due to metalloid ion removal treatment [12]. Besides, there is a slightly of iron (Fe) increase from 0.35% to 0.37%. The presence of humified fraction of humic acid build up a reservoir of iron for plant [13]. There are also slightly change of other elements as well for example, carbon (C) increase from 23.14% to 25.48% and calcium (Ca) increase from 0.19% to 0.85%.

Figure 2 (c) shows the EDX's spectra for post detoxification soil for 2 weeks and it shows insignificant changes to the content of the element. However, oxygen (O) is still the highest element in the soil with a percentage of 57.76% from 53.58% which is good for plant growth. Oxygen allows for respiration of both plant roots and soil organisms. Plant physiological processes such as nutrient and water uptake will affected when its concentration in the soil is reduced [14]. The second highest element goes to aluminium (Al) also decreasing from 8.13% to 7.23%. The result is good for plant growth because Al toxicity only bring harm and stunt the plant growth. The percentage of silicon (Si) drop 7.41% to 6.45%. Silicon is not regarded as an essential element, most plants will grow adequately in the absence of it. However, a few plants have shown deleterious effects when silicon is not present [15]. Next, iron (Fe) has increased from 0.37% to 0.42%. Iron is a micronutrient that is required by almost all life forms because it involve in metabolic activities such as DNA synthesis, respiration, and photosynthesis. Although iron toxicity in soil is rare, some plants secrete acids through their roots, which lowers soil pH. These plants can absorb an excessive amount of iron, resulting in toxicity [16]. Other elements like carbon (C) is increasing with 32.08% and calcium is decreasing with 0.24%. Basically, carbon is the component of soil organic matter, and it contributes to the soil's water-retention capacity, structure, and fertility. Also, calcium (Ca) also promotes healthy soil structure by loosening soils and stabilising organic matter, which boosts the water and nutrient capacity of the soil.

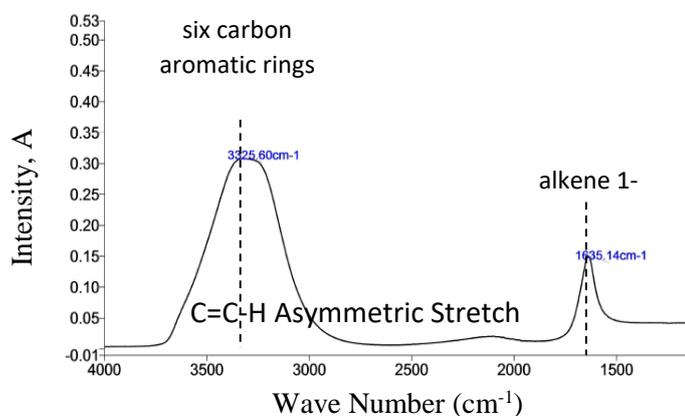


Figure 3: FTIR spectra of humic acid in liquid form

The FTIR spectrum of humic acid in liquid form are shown in Figure 3. The spectrum shows the first peak of 3325.60 cm^{-1} followed by the second peak which is 1635.14 cm^{-1} . The highest FTIR peak with absorption range of $3600\sim 3100\text{ cm}^{-1}$ is due to six carbon aromatic rings based on di- or tri-hydroxyl phenols. The phenolic and carboxylic functional groups contribute the most to the surface charge and reactivity of humic substances. Humic acid has make up a wide group of natural phenolic compounds. They are defined as dark-colored products in environment [17]. Next, the alkene 1-propene exist in the absorption range between $1675\sim 1600\text{ cm}^{-1}$ caused by infrared vibration of C-C=C symmetric stress.

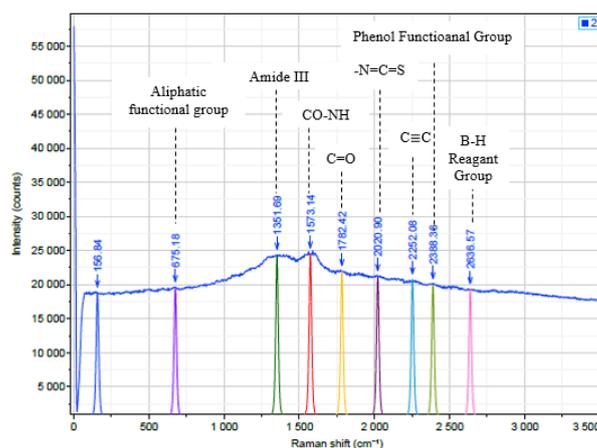


Figure 4: Raman spectrum of humic acid

Figure 4 represent Raman spectrum of humic acid which is representative of a biological molecule that present in the sample which responsible for metal cation binding and, as a result, their state and concentration in soils. The lowest peak which is 156.84 cm^{-1} is due to the lattice vibrations in the crystal cause by notch filter of the Raman system. Next, the peak at 675.18 cm^{-1} is due to the vibration of aliphatic functional group. It is classified as aliphatic if there is no aromatic ring immediately connected to a functional group. However, the Raman peak at 1351.69 cm^{-1} is the characteristic of amide III that have a carbonyl functional group that is linked to both an amine and a hydrocarbon group or hydrogen atom. This is because it is possible to have an aromatic molecule containing an aliphatic functional group if the aromatic ring is not directly attached to the functional group. Subsequently, amide aromatic ring produces the highest peak at 1573.14 cm^{-1} . The standard chemical formula for amide groups is CO-NH. It can be formed through the interaction of an amine (NH_2) group with a carboxyl (CO_2H) group. Hence, the characteristic of carbonyl C=O bonding is shown at the peak 1782.42 cm^{-1} . Carbonyl compounds such as anhydrides, acid halides, or strained ring carbonyls such as lactones and carbonates in five-membered rings are commonly above 1775 cm^{-1} bands. Next, the characteristic of 2020.90 cm^{-1} peak indicate the vibration of isothiocyanate ($-\text{N}=\text{C}=\text{S}$). Natural and synthesised isothiocyanates have anticarcinogenic effect because they reduce carcinogen activation and improve detoxification. Next, the peak at 2252.08 cm^{-1} is caused by the vibration of $\text{C}\equiv\text{C}$ and 2388.36 cm^{-1} is the characteristic of phenol functional group. Lastly, the Raman peak at 2636.67 cm^{-1} is due to the B-H reagent group. Hence, based on the data, it shows that the humic acid sample is amorphous in acidic version. This is because, humic acid are a natural amorphous colloid that is created as a result of numerous biological and abiotic breakdown processes of animal and plant residues [18].

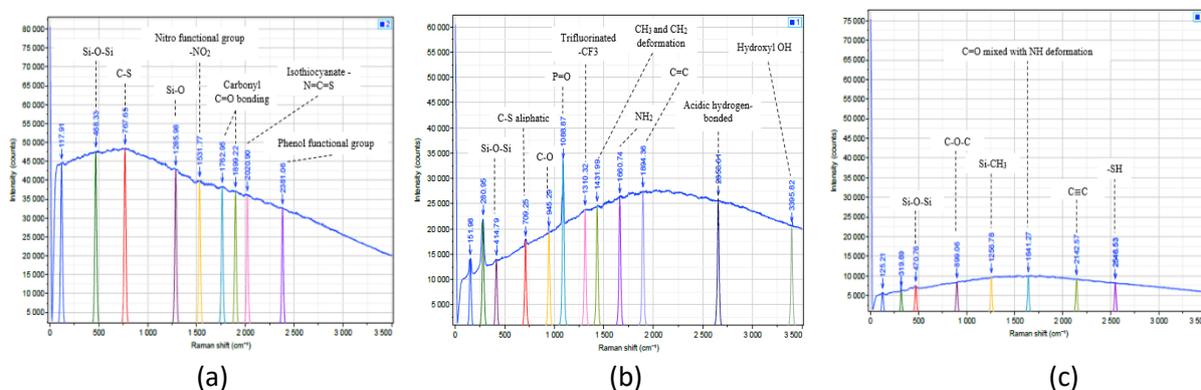


Figure 5: (a) Raman spectrum for pre-detoxification soil, (b) for first week (post-detoxification) and (c) for second week (post-detoxification)

Figure 5 (a) shows the Raman spectra for pre-detoxification soil. The Raman peak at 468.33 cm^{-1} indicates the presence of Si-O-Si bonding. For most cases, Si can be found in a variety of forms in the soil. The highest peak is 767.65 cm^{-1} which occurs as a result of the presence of C-S bonding. Furthermore, the peak at 1285.98 cm^{-1} is consequence of the existence Si-O bonding. Subsequently, Raman peak at 1531.77 cm^{-1} occur because of the nitro compound. It is an organic compound that contain one or more nitro functional groups ($-\text{NO}_2$). Moreover, the peak at 1762.95 cm^{-1} and 1899.22 cm^{-1} is the characteristic of the carbonyl C=O bonding stretching vibration. Next, 2020.90 cm^{-1} peak is due to the vibration of isothiocyanate ($-\text{N}=\text{C}=\text{S}$). Lastly, the functional group that resembles to the wavenumber between $2600\text{ ~}2100\text{ cm}^{-1}$ is phenol functional group.

Figure 5 (b) shows the Raman spectrum for post-detoxification soil within 1 week. Representing the strongest intensity peak with the vibration between the range of $1350\text{ ~}1080\text{ cm}^{-1}$ is the result of the P=O stretching vibration for organic phosphorus compounds. Adding phosphorus to the soil can promotes the root growth and help in the development of the new tissue. Also, the Raman peak at 414.79 cm^{-1} indicates the presence Si-O-Si bonding since silicon and oxygen are present naturally in the soil. Next, in the region $630\text{ ~}790\text{ cm}^{-1}$ are usually associated with the C-S aliphatic stretch of function group like carboxylic acid. Moreover, the peak with absorption within the range of $800\text{ -}970\text{ cm}^{-1}$ indicates the C-O stretch of C-O-C stretching vibrations. Next, the Raman peak at 1310.32 cm^{-1} is due to the vibrations of the trifluorinated compounds ($-\text{CF}_3$). Variety of plant species can take up fluorinated group from the environment. Moving on the next peak, the peak at 1431.99 cm^{-1} is the characteristic of CH_3 and CH_2 deformation. Additionally, the characteristic of amino group, NH_2 are shown at the ranges between $1660\text{ ~}2590\text{ cm}^{-1}$. Furthermore, the functional group that resembles to the wavenumber ranges between $1500\text{ ~}1900\text{ cm}^{-1}$ is carbonyl group due to the C=C stretching. Besides, the Raman peak at 2653.61 cm^{-1} which exist between $3100\text{ ~}2400\text{ cm}^{-1}$ typically due to acidic and strongly hydrogen-bonded hydrogen atoms. However, the main OH stretching bond for carboxylic acid dimers usually is fount at peak around 3000 cm^{-1} , as shown in the result, the peak is at 3396.82 cm^{-1} which prove the existence of hydroxyl OH stretching band.

The Raman spectrum of post-detoxification within 2 weeks is shown in Figure 5 (c) The highest peak of Raman shift which lie between the range $1620\text{ ~}1690\text{ cm}^{-1}$ indicate the presence of C=O mixed with NH deformation. In addition, the second highest peak goes to 1256.78 cm^{-1} , therefore prove the presence of Si- CH_3 bonding. Next, 2142.57 cm^{-1} which lie between the range of $2100\text{ ~}2300\text{ cm}^{-1}$ reveals the existence of C \equiv C. Subsequently, the peak which lie between $460\text{ ~}550\text{ cm}^{-1}$ indicate the absorption of Si-O-Si bonding. Hence, Raman shift at 899.06 cm^{-1} is the characteristic of carbonyl functional group, C-O-C. Lastly, thiol that contains the -SH functional group produce the Raman peak at 2546.53 cm^{-1} . Thiol is a sulfur analog of hydroxyl group.

Table 1: The change of pH value between pre and post treatment in duration of 2 weeks times

Soil Sample	pH
Pre-Treatment	8.71
First Week (Post-Treatment)	8.49
Second Week (Post-Treatment)	8.22

Table 1 above shows the pH reading for 3 soil sample, pre-treatment, first week and post-treatment using humic acid to detoxify the unnecessary element in the soil sample. Figure 4.7 shows the Ph meter that has been use to determine pH number for the sample. The readings are taken 3 times for each sample to obtain accurate reading. Raw soil sample indicate result with the reading of 8.71, which is the sample is in the alkali state. After a week of detoxification process, the reading decrease to 8.49. The pH number decrease gradually for post treatment which is from 8.49 to 8.22. It shows that the sample is not fully fertile yet and still in alkali state.

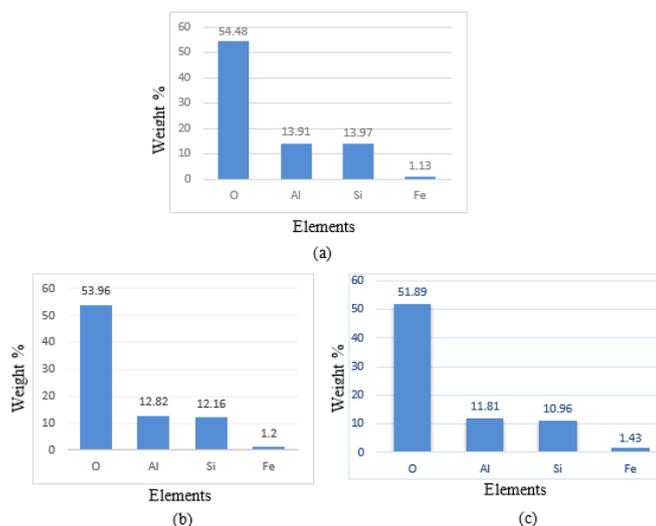


Figure 6: (a) EDX bar graph for main elements for pre-detoxification process, (b) for first week (post-detoxification) process and (c) for second week (post-detoxification) process

Figure 6 (a), (b) and (c) show the comparison of main elements that present in the soil for pre and post detoxification. The figure shows that there has been a slightly drop of oxygen weight percentage after 2 weeks of detoxification process with the value of 51.89%. Even the trend shows that the oxygen is slightly decrease, it is still above 50% of the overall elements which is good for plant respiration. Same goes to aluminum, it undergoes a steady decline from 13.91% to 11.81 as shown in EDX figure above. The reduction of aluminum will result in a low pH number which will be discussed in the previous chapter. Hence, the bar graph in Figure 4.12 reveals that the content of silicon also drops to 10.96% after two weeks of detoxification process. Lastly, what stands out in this chart is the steady increase of iron, from 1.13% to 1.43%. Iron is essential for practically all life forms because it contributes in metabolic activities such as DNA synthesis, respiration, and photosynthesis, all of which are necessary for plant growth.

4. Conclusion

As conclusion, almost every soil located at or near to Pagoh Education Hub contain heavy metal ion which can alter the structure and function of microbial species activity in the soil. From the data, humic acid shows its effectiveness to remediate laterite barren soil by balancing the metal concentration in the soil to the desirable atomic percentage, 51.89% for oxygen, 11.81% for aluminum, 10.96% for silicon and 1.43% for iron which can increases the microbial activity in the soil and making it an excellent root stimulator. Hence, from the data, it shows that the volume of humic acid applied to the laterite barren soil did not affect the concentration of the metal ion, but instead need to prolong the time of humic acid detoxification process. Also, FTIR data shows the presence of carboxylic acid (COOH) and six carbon aromatic rings which are amphoteric for binding cations or anions. Based on the Laser Raman analysis, it can be confirmed that humic acid's structural conformations which is amorphous in

acidic versions. A comparison of soil's molecular structure between pre and post-detoxification indicates that presence of humic acid substance which alter the molecular structure of the soil. A comparison between pre and post treatment indicate the different of the heavy metal ion concentration between pre and post detoxification process. In short, it proves the efficiency of humic acid as detoxification substance for heavy metal pollution in soil.

Acknowledgement

I would like to express my most gratitude and thanks to my lecturers, my friends and those who help me either directly or indirectly, for their efforts and for accompanying me on completing this research. This work would not have been possible without the constant support, guidance and assistance from everyone.

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