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Formation and Characteristics of Spodosols formed on Sandstone in the Extremely High Rainfall Area of Sarawak, Malaysia

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ABSTRACT – ***Two Spodosols occurring in Sarawak, Malaysia, were studied to elucidate the physico-chemical properties of the soils and to explain their formation. The pedons derived from sandstone are located at the elevation of 30 to 60 m above sea level. Under high temperature and extremely high rainfall prevailing in the area, the weatherable minerals in the sandstone have been mostly weathered and removed from the soil system, resulting in the accumulation of resistant minerals such as kaolinite, quartz and/or muscovite in the topsoil. The soil materials were subjected to podzolization which eventually formed spodic horizon in the soils at varying depths. At 60 m above sea level where the drainage is excessive, the spodic horizon is about 50 cm thick (having Bhs and Bs horizons (Arenic Alorthods), while at the lower position with poorer drainage condition, the thickness of Bs horizon is only about 7 cm (Lithic Alaqoud). The spodic horizon in both pedons is compacted, not penetrable by plant roots. The samples from spodic horizons contain carbonyl group conjugated with aromatic ring (having band at 1615 cm^{-1}). This peak is probably attributed to the vibrations of aromatic C–C structural vibrations and C–O stretching of amide, quinone and H–bonded conjugated ketone groups. Carbonyl group occurring in the soils was probably involved in the metal complexation (or ligand exchange) during the podzolization process. The migration of the organo-metallic complexes and its deposition into the subsoil leads to the formation of spodic horizon. The spodic horizon in both profiles is characterized by low pH and high exchangeable Al with trace amount of hematite. Throughout the profiles, basic cations and CEC are very low, consistent with the sandy nature of the soils.***

Keywords – Chemical weathering, sandstone; Spodosol, spodic horizon, Sarawak

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1. INTRODUCTION

In the humid tropics with high annual rainfall, most of soils formed are highly weathered and acidified due to intensive leaching over a long period of time [1] and they are usually dominated by kaolinite and sesquioxides which are variable charge minerals [2,3,4]. Under the prevailing intensive leaching coupled with high temperature, common rocks and/or minerals would undergo a high degree of chemical weathering forming highly leached soils which are deprived of basic cations. In Peninsular Malaysia, where the annual rainfall ranges from 2000 to 2500 mm, sandstone would weather to form Ultisols, having sandy clay loam texture [2,5]. The original minerals in the sandstone are altered to kaolinite, halloysite, gibbsite, goethite and/or hematite [6]. However, in Sarawak, East Malaysia, with the evenly distributed annual rainfall exceeding 3770 mm, the same rock type would form Spodosols with sandy textures. The formation of such Spodosols formed under extremely high annual rainfall and temperature has not been clearly explained.

Spodosols are very common either in the cool regions of the world [7,8] or in the lowlands of the tropics, forming from very sandy parent materials [9,10]; they are formed by the process of podzolization. These soils are characterized by the presence of spodic horizon, which is defined as an illuvial layer with spodic materials (organic matter and/or oxides complexes), and this illuvial layer is often overlain by an albic horizon. Spodic materials are associated with vertical movement of organo-Al and/or Fe oxides complex [11]. The symbol used for the spodic horizon is Bh, Bs or Bhs. To qualify for a spodic horizon, there must be a pH (1:1) in water of ≤ 5.9 and an organic carbon (OC) content of $\geq 0.6\%$ [12].

Two major groups of processes can be used to explain the process of podzolization in the cool regions of the world [13]. Firstly, it is the formation and downward transport of complexes of organic acids in association with Al and/or Fe. Leaching of dissolved organic carbon (DOC) from the O horizon is an important process involved in the eluviation and illuviation of complexing Al and Fe with organic acids in Spodosols [14]. They showed that DOC plays an important role in the eluviation of Al and Fe in the Ultisols formed on sedimentary rock (sandstone) in East Kalimantan Province, Indonesia, which is consistent with the observation of the Spodosols formed under temperate forest [15]. However, the soils studied by Fuji et al. [14] cannot be classified as Spodosols due to the absence of spodic B horizon, and the amount of amorphous Al and Fe (Al_o and Fe_o) was lower compared to the spodic B horizons of normal Spodosols (0.50% or more $Al_o + 1/2Fe_o$) [12]. The absence of the spodic B horizons in the Ultisol studied was probably due to warm, humid climate and low soil pH, which could enhance mineralization of metal-humus complexes and mobilization of Al and Fe.

The second theory of podzolization by De Coninck [13] is the weathering of silicate, followed by downward transport of Al and Si as inorganic colloidal materials. The immobilization of the organic complexes in the illuvial horizon has been described in detail by Lundstrom et al. [16] and Lundstrom [17]. These are the precipitation/adsorption of organic metal complexes due to a decreasing carbon to metal ratio, and the microbial degradation of organic complex formed during migration through the profile, followed by precipitation of inorganic Al and Fe. The immobilization process takes place after the decomposition of easily degradable low molecular weight organic acids, while the precipitation/adsorption process is attributed to the presence of metal complexes of fulvic and humic acids in the soils.

In Peninsular Malaysia, Spodosols have been found to occur sporadically on the sandy beach ridges of the coastal plains [10, 18, 19]. Other areas in the country where Spodosols can occur are in the cool forest of Cameron Highlands and Genting Highlands in the Main Range of the Malay Peninsula. It is interesting to find out how the Spodosols (or spodic horizon in the soils) formed on sandstone come into being under the weather conditions prevailing in Bintulu, Sarawak, Malaysia, where the annual rainfall is extremely high. The objectives of this study were: 1) to determine the physico-chemical properties of the sandstone-derived Spodosols in Bintulu Sarawak, Malaysia; and 2) to explain how the spodic horizons in the soils were formed.

2. MATERIALS AND METHODS

2.1. Details of the Study Area

The study area is the Universiti Putra Malaysia (UPM) Bintulu Campus, Sarawak, Malaysia, located approximately at the latitude of 3^o 12 N and the longitude of 113^o 05 E. The terrain of the area is highly dissected with a small stream cutting across the campus, draining rainwater into the nearby sea. The common plant species present are dipterocarp (*Dipterocarp* spp, *Shorea parvifolia, Shorea leprosula and Hopea* spp) and non-dipterocarp (*Syzygium* spp, *Mallotus leucodermis, Macaranga gigantean and Pomea pinnata*). The soils found in the area are Jerijeh, Nyalau and Bekenu Series as defined by the Keys to Soil Classification of Sarawak [20]; the first soil is Spodosols which are found on the rocks dominated by sandstone occasionally intercalated with shale and the last two soils are Ultisols which were formed on rocks dominated by ferruginous shale.

The area under study is characterized (or covered) by the rocks of Nyalau Formation of Miocene age (5-20 million years old), which are composed of moderately hard sandstone occasionally intercalated with shale [21]. According to this author, the sandstone contains mainly quartz with 10-15 % feldspars; other minor minerals are muscovite, biotite and iron ores. This area has been exposed to wet condition throughout the year for a long period of time. Monthly rainfall is in excess of 200 mm and the annual rainfall is about 3770 mm; higher rainfall occurs in the months of October, November and December [22]. The mean maximum temperature is > 40^oC, while the mean minimum is 22^oC; the average mean temperature is 30^oC.

2.2. Soil Sampling and Soil Analyses

Spodosols occur sporadically throughout the UPM farm, Bintulu Campus, Sarawak. For this study, two locations in the UPM farm were selected based on the elevation and drainage condition. Soil pits were dug and the profiles described. The soils can be classified as Jerijeh Series using the Keys to Soil Classification of Sarawak [20]. The two pedons are henceforth referred to as Jerijeh 1(located at 60 m above sea level) and Jerijeh 2 (located near a small stream at 30 m above sea level). The former profile is disturbed area which cultivated by mango tree and the latter profile is undisturbed area under natural forest known as Nirwana forest. Soil samples were taken according to the genetic horizons observed in the profiles.

The sand, silt and clay fractions in the soils were separated by successive sedimentation after treating with 30 % H_2O_2. X-ray diffraction analysis (using Philips PW 3440/60 X'Pert PRO) was performed to identify the minerals present in the silt plus clay fraction of the soils. Selected soil samples from the spodic horizons of the two soils were subjected to studies using scanning electron microscope (SEM). The elemental composition of the materials of interest in these samples was identified and subsequently estimated by the energy dispersive X-ray (EDX) accessory attached to the SEM (JEOL® 400, Japan).

Soil pH was determined in water at the soil to solution ratio of 1:1 and cation exchange capacity (CEC) was determined by the method using 1 M NH_4OAc buffered at pH 7. The basic cations (Ca, Mg, K and Na) in the NH_4OAc extract were determined by atomic absorption spectrophotometer (AAS; Perkin Elmer 5900 AAS Instrument); the cations are regarded as exchangeable cations. Exchangeable Al was extracted by 1 M KCl and the Al in the solution was determined by AAS. Total C was analyzed by the C analyzer (model LECO CR-412), while total nitrogen was determined by the Kjeldahl method.

Extractable inorganic and organic Fe and Al in the soils were determined by three selective dissolution methods. The methods were the dithionite-citrate-bicarbonate extraction (DCB) of Mehra and Jackson [23], acid ammonium oxalate method [24] and pyrophosphate method [24]. The main functional groups present in the organic matter of the spodic horizons were inferred from spectroscopy measurements using Fourier Transform Infrared (FTIR Perkin Elmer). These analyses will provide useful information about functional group, chemical bond and molecular structure of the organic acids present in the soil of spodic horizon.

3. RESULTS AND DISCUSSION

3.1. Chemical weathering of the sandstone

The area under study is either steep or undulating with differing drainage conditions, depending on the location. The rocks forming the soils belong to the Nyalau Formation of Miocene age, which are composed of moderately hard sandstone occasionally intercalated with shale [21]. This sandstone is composed of quartz and feldspars with minor amount of muscovite, biotite and iron ores. Being exposed to the high temperature and extremely high annual rainfall prevailing in the area for a long period of time, feldspars and biotite are readily weathered to form secondary minerals. Even the moderately resistant muscovite (mica) cannot withstand the onslaught of extreme weather condition prevailing in the area. However, some white mica flakes (muscovite) were found in the E horizon of both soil profiles. The stability sequence of the minerals undergoing weathering in the tropics is: quartz > muscovite > feldspars > biotite [25].

Feldspars under tropical environment starts to alter along their cleavage and fracture planes and muscovite begins to alter at later stage [26]; these are consistent with the findings of Zauyah et al. [25]. According to Muggler et al. [27], mica in shale under tropical climate is transformed to hydroxyl-Al interlayered vermiculite and kaolinite. The vermiculite would then transform to kaolinite on further weathering if the environmental condition is conducive to its formation. Feldspars can directly be weathered to kaolinite [28]. Mica and feldspars in granite of Peninsular Malaysia (annual rainfall is 2,000-2,500 mm) will weather to kaolinite, halloysite and gibbsite [29], while mica and feldspars in sandstone will weather to kaolinite, halloysite, gibbsite and goethite [6]. These same processes could have happened continuously to the feldspars and mica in the sandstone of Bintulu, Sarawak, except that the alteration process might have occurred more aggressively due to the extreme weather condition prevailing in the area where the mean temperature exceeds 30^oC and annual rainfall is about 3770 mm. The downward movement of soil materials in the Spodosols of the current study is probably controlled by the surface negative and positive charges present in the soils [4].

3.2. Morphological Features and Physico-chemical Properties of the Soils

Jerijeh Series occurs in two distinct areas of the UPM campus. The first (referred to as Jerijeh 1) is the soil located at 60 m above sea level which is subjected to excessive drainage. The profile is deep with very thick (50 cm) spodic horizon. The second type (referred to as Jerijeh 2) is the soil that is located on a flat area near a small stream and so the drainage is less excessive than that of the former. As such, the spodic horizon is thinner (7 cm) in this particular profile.

In the field, it was easy to recognize the morphological features of the Spodosols. The Ap horizon of Jerijeh 1 is characterized by a dark brown (10YR 4/3) loamy sand, underlain by a white (10YR 8/1) sand (Table 1) containing some muscovite flakes. The spodic horizon in this pedon is thick, breaking into Bhs and Bs horizons. The Bhs horizon is characterized by a dark reddish brown (2.5YR 2.5/4) sand, underlain by a dark brown (7.5YR 4/4) Bs horizon which is not cemented. The C horizon is a loose sand of light brown (2.5Y 6/4) color, underlain by indurated ferruginous shale. The light color of the C horizon has probably resulted from groundwater perching on the impervious shale. Total C and exchangeable Al in this horizon is 1.58% and 1.44 $cmol_c$/kg soil (Table 2).

Jerijeh 2 pedon has an Ao horizon characterized by a dark brown (7.5YR 4/2) loamy sand, underlain by a light grey (10YR 7/1) loamy sand (E horizon). Below this horizon is a spodic Bs horizon having loamy sand texture. The color of this horizon is dark reddish brown (5YR 3/3). The C horizon is consisted of indurated ferruginous shale resulting in impeded drainage; hence, the drainage is imperfect.

Since the soils are derived from sandstone which contains abundant of quartz, they are sandy textured with sand content ranging from 69 to 91% (Table 1). Some horizons contain no clay fraction at all (for example Ap and E horizons of Jerijeh 1 and E horizon of Jerijeh 2). This means that the clay materials in these horizons which are produced during the process of weathering of the minerals in the sandstone have either been completely broken down and subsequently leached into the groundwater or transported downwards under the strongly leaching environment. Hence, the coarse fraction of topsoil contains mainly quartz with minor amount of muscovite (resistant mica).

The chemical properties of the soils are given in Table 2. The pH values for all the horizons in both pedons are less than 5.9 and that of Bhs and Bs horizons are lower than the maximum defined for spodic materials (pH≤5.9). The pH of the Jerijeh 1 tends to decrease with depth from 5.89 at topsoil to 4.24 in the Bhs. The pH of Jerijeh 2 increases from 4.08 in horizon Ao to 5.10 in the E and decreases to 4.39 in the Bs horizon. Exchangeable Al is high in the spodic horizon of Jerijeh 1. Its value in the Bhs and Bs horizons of Jerijeh 1 is 1.44 and 3.88 $cmol_c$/kg soil, while the exchangeable Al in the Bs horizon of Jerijeh 2 is very low which is 0.5 $cmol_c$/kg soil. The CEC is very low, consistent with very low clay content; the value is higher in the spodic horizons due to the contribution of organic matter. Total C is maximal in the spodic horizon of both soils. These organic materials probably exist in the form of organo-Al-Fe complexes, accumulated in this horizon via podzolization process [13, 16, 17].

Table 1: Particle-size distribution of the soils.

Soil	Horizon	Depth (cm)	Granulometric composition (%)			Soil Texture (USDA)
			Clay	Silt	Sand	
Jerijeh 1	Ap	0 - 5	0.00	22.5	77.35	Loamy sand
	E	5 - 40	0.00	8.47	91.36	Sand
	Bhs	40 - 70	1.40	8.29	90.09	Sand
	Bs	70 - 90	1.704	14.09	84.03	Loamy sand
Jerijeh 2	Ao	0 - 8	0.92	19.90	79.03	Loamy sand
	E	8 - 38	0.00	21.60	78.27	Loamy sand
	Bs	38 - 45	4.69	15.79	79.30	Loamy sand

3.3. Soil Classification

The pH of the soils in Bhs and Bs horizons for both pedons is < 5.9, while the organic C is > 0.6%. The color of these horizons is redder than 7.5YR. The values of oxalate-extractable materials (Al_o + 0.5 Fe_o) in the Bhs and Bs horizons were more than 0.5 % and much greater than twice those in upper layer. Hence, these three parameters satisfied the criteria defined in spodic materials based on Soil Taxonomy [12]. Jerijeh 1 contains < 0.1% Fe and the albic layer has sandy-skeletal particle-size class. Therefore, this pedon can be classified as Arenic Alorthod. Within 50 cm of the mineral surface of Jerijeh 2 occurs redoximorphic features. The amount of Fe in the spodic horizon is < 0.1%. A lithic contact was observed within 50 cm of the mineral surface. Hence, this pedon can be classified as Lithic Alaquod.

Table 2: Chemical properties of the soils

Soil	Horizon	Depth	pH	Exchangeable Cations						T.C	N
		(cm)	H_2O	Ca	Mg	K	Na	Al	CEC	%	
				cmol$_c$/kg							
Jerijeh 1	Ap	0 - 5	5.89	0.42	0.21	0.04	0.40	0.02	0.91	0.68	0.46
	E	5 - 40	5.49	0.01	0.01	0.00	0.39	0.01	0.07	0.03	0.01
	Bhs	40 - 70	4.38	0.01	0.02	0.05	0.40	1.44	5.32	1.58	0.23
	Bs	70 - 90	4.24	0.00	0.04	0.06	0.40	3.88	3.83	1.88	0.39
Jerijeh 2	Ao	0 - 8	4.08	0.02	0.05	0.05	0.41	0.18	1.36	1.07	0.44
	E	8 - 38	5.10	0.00	0.01	0.00	0.40	0.05	0.26	0.05	0.02
	Bs	38 - 45	4.39	0.00	0.02	0.02	0.41	0.05	7.42	1.86	0.32

3.4. Mineralogy and Scanning Electron Microscopic Study

The samples from topsoil and spodic horizons (Bhs and Bs) of both soil profiles were selected for mineralogical study using XRD analysis. Since the clay content in the topsoil of Jerijeh 1 was very low (0 – 0.92 %), clay and silt for this horizon were X-rayed together as suggested by Roslan et al. (2010). The XRD diffractograms for the untreated samples of topsoil and spodic layer of Jerijeh 1 and Jerijeh 2 are presented in Figure 1 and 2, respectively. The results showed that quartz (4.23 – 4.26 Å and 3.33 – 3.34 Å) and kaolinite (7.08 – 7.25 Å and 3.55 – 3.57 Å) are the dominant minerals present in the topsoil and spodic horizon of both pedons. The XRD patterns show a strong peak of mica (most likely to be muscovite) in the spodic layer of both pedons at 9.96 – 10.33 Å, 4.99 – 5 Å and 3.33 – 3.37 Å. Mica flakes (muscovite) were observed in the eluvial layer during the soil sampling of Jerijeh 1.

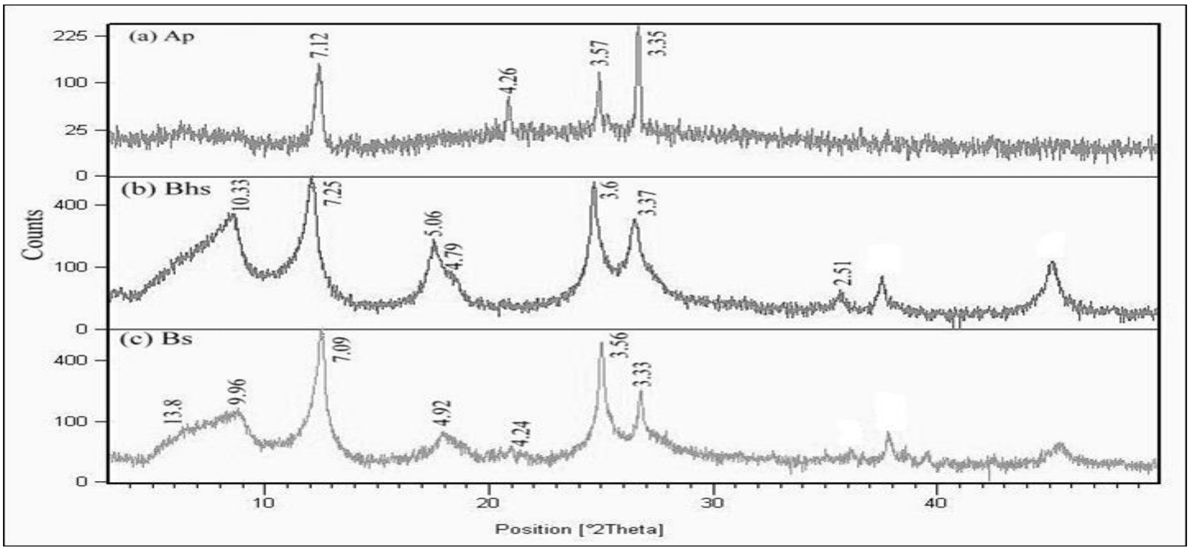

Figure 1: X-ray diffraction pattern for untreated clay sample from Jerijeh 1.

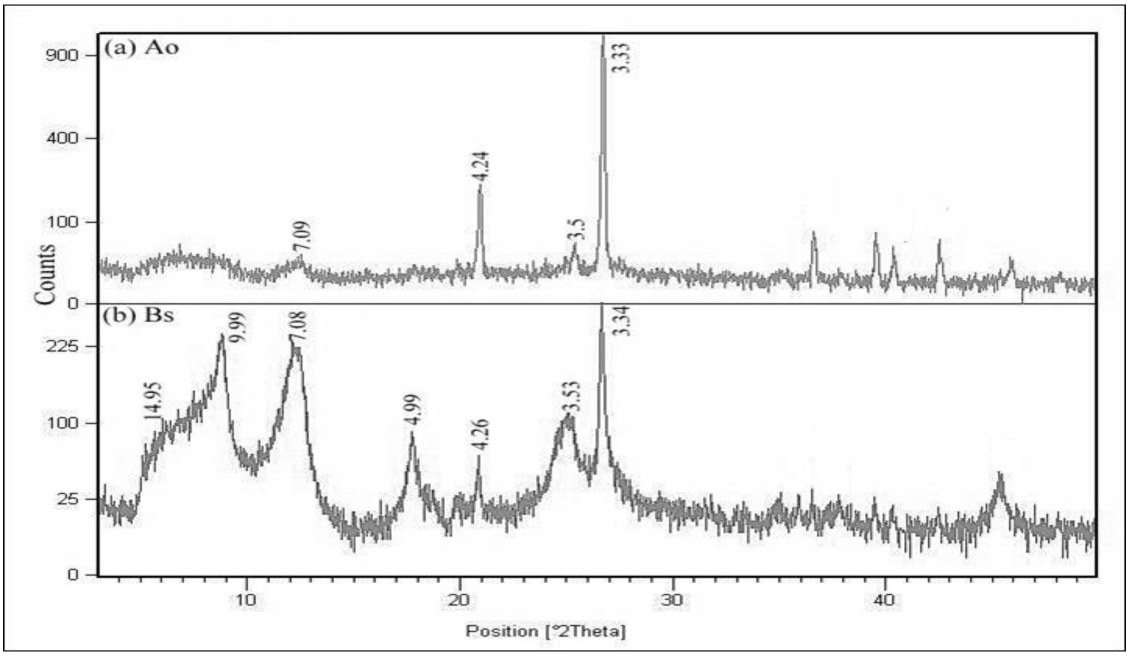

Figure 2: X-ray diffraction pattern for untreated clay sample from Jerijeh 2.

Some vermiculite was present in the Bs horizon of Jerijeh 1 and Jerijeh 2. This vermiculite most probably originated from biotite, formed under impeded drainage due to compaction of the spodic horizon. Identification of the vermiculite was based on the detection of peak at 13.8 Å in the Bs horizon of Jerijeh 1 and peak at 14.95 Å in the Bs horizon of Jerijeh 2, and its failure to expand beyond these peaks after Mg saturation and glycerol solvation (Figure 3, 4 and 5). This vermiculite is most likely coming from the weathering of biotite originally present in the sandstone [21]. This is consistent with the findings of Muggler et al.[27]. A weak peak of hematite was detected at 2.51 Å in Bhs horizon of Jerijeh 1. The dark reddish brown (2.5YR 2.5/4) color of the soil in the horizon further supports the presence of hematite. This hematite is most probably the weathering product of goethite. Gibbsite was only present in the spodic horizon of Jerijeh 1, shown by the weak peaks at 4.79 – 4.92 Å.

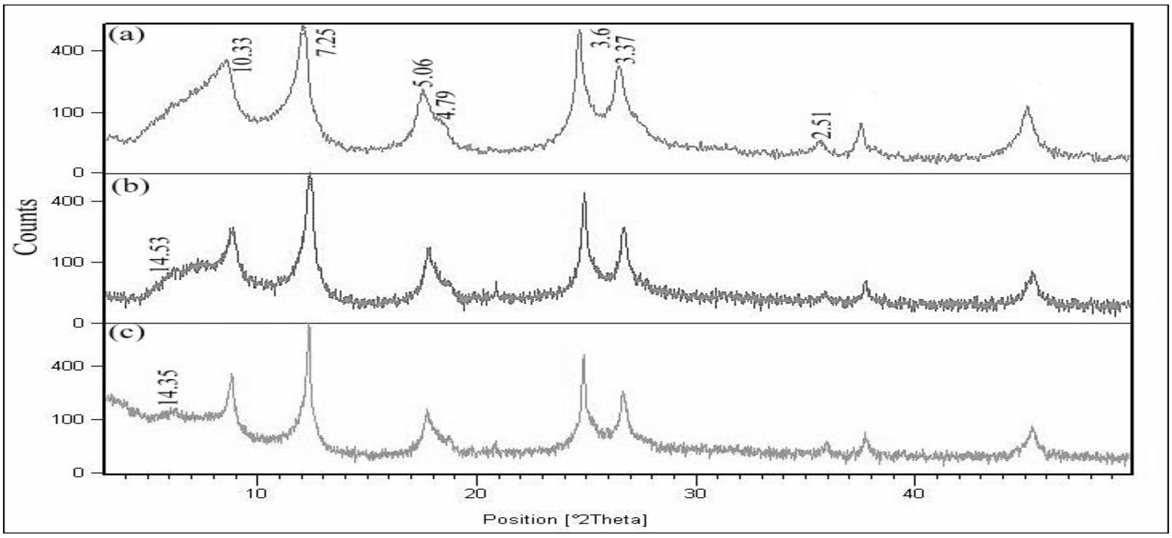

Figure 3: X-ray diffraction pattern for treated clay sample from Bhs horizon of Jerijeh 1; (a) untreated sample, (b) Mg-saturated, and (c) Mg-saturated, glycolated.

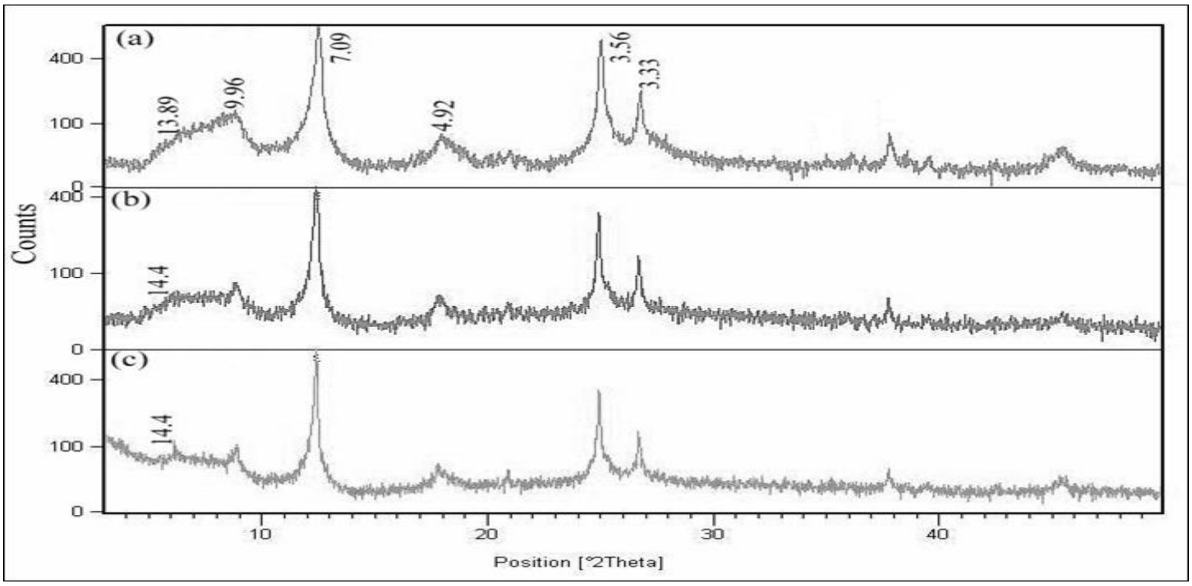

Figure 4: X-ray diffraction pattern for treated clay sample from Bs horizon of Jerijeh 1; (a) untreated sample, (b) Mg-saturated, and (c) Mg-saturated, glycolated.

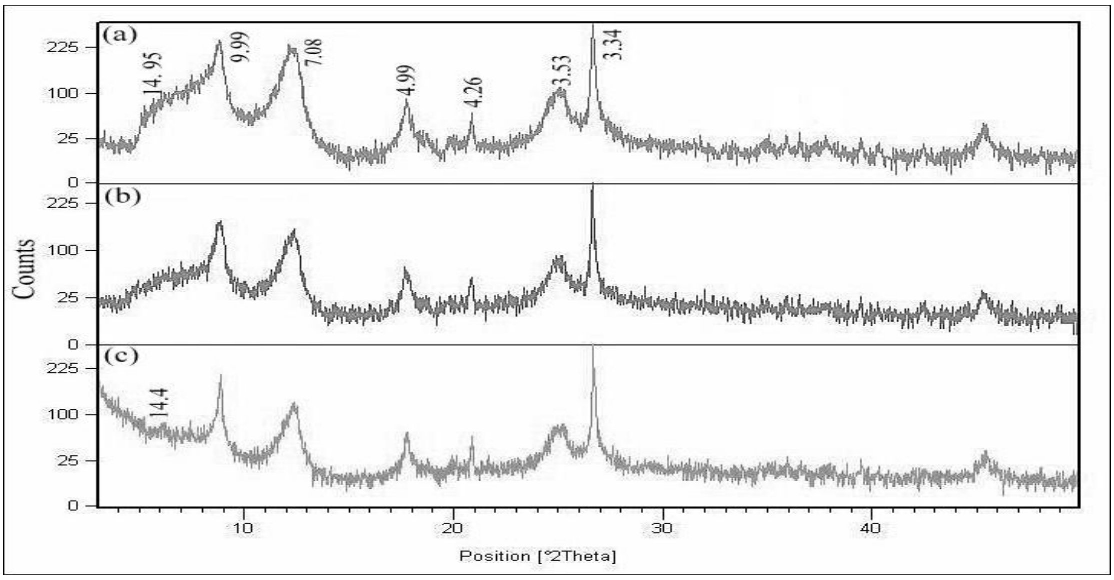

Figure 5: X-ray diffraction pattern for treated clay sample from Bs horizon of Jerijeh 2; (a) untreated sample, (b) Mg-saturated, and (c) Mg-saturated, glycolated.

Quartz is the major component of the sandstone which is the parent materials of the soils under study and it is a tough mineral [10]. It is very resistant and therefore remains in the soils for a long time. Feldspar and mica (biotite) in the sandstone have been weathered to form secondary minerals such as vermiculite, kaolinite, gibbsite and hematite. The presence of kaolinite and gibbsite indicates that the soils have undergone through an advanced stage of weathering. In the Spodosols under study, kaolinite was found in the surface, while gibbsite was detected in a small amount in the spodic horizon of Jerijeh 1. Most of the Al in the spodic horizon probably exists in the form of amorphous Al-hydroxides, which could not be detected by XRD analysis. Weathering process proceeds under high rainfall and rapid removal of bases through intensive leaching leads to the accumulation of kaolinite in the topsoil, which is consistent with the finding of Sakurai et al. [30]

The minerals containing Fe and Al are present in the spodic horizons (either Bhs or Bs) but not in the topsoil. These results are in agreement with the findings of Roslan et al. [10] who studied the Spodosols in the Kelantan-Terengganu Coastal Plains, Peninsular Malaysia. Our research show that Fe-bearing minerals were absent in the topsoil, which is a clear evidence of their disintegration and subsequent eluviation into the spodic horizons. Note that the parent materials of the soils contain very little of Fe-bearing minerals.

Figure 6 shows the SEM micrograph of the Bhs horizon from Jerijeh 1. EDX was taken at spectrum 1 where organic matter was accumulated. This organic matter was eluviated from the topsoil and accumulated in the spodic horizon during the process of podzolization. The EDX graph indicates the presence of C, O, Fe, Al, Si and K. These C, Fe, Al, Si and K are most probably the chemical components of organic matter, hematite, Al-hydroxides and/or kaolinite, quartz and muscovite, respectively. The presence of these minerals was proven by XRD analysis (Figure 3).

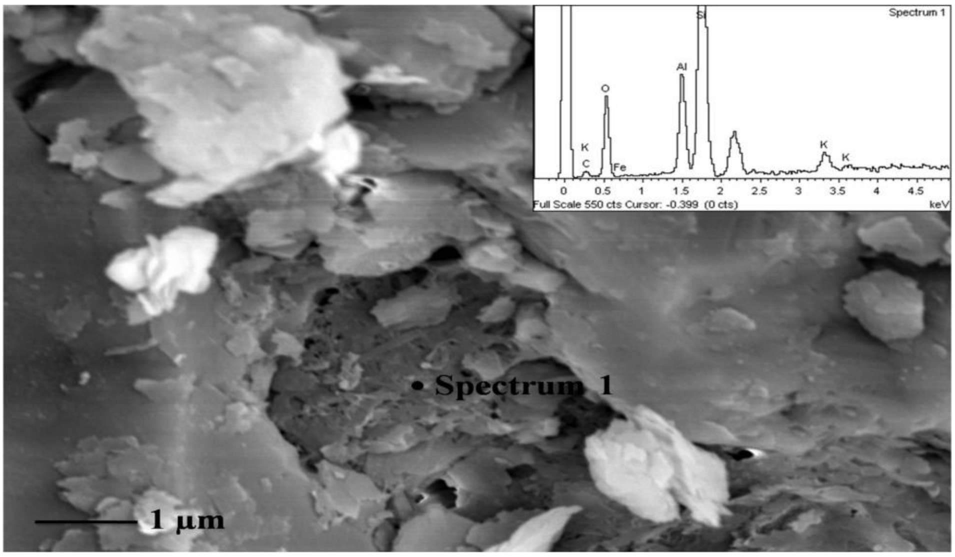

Figure 6: SEM micrograph of Bhs horizon from Jerijeh 1.

The chemical composition at spectrum 3 of the Bs horizon from Jerijeh 1 is shown in Figure 7. It is almost similar to that of Bhs horizon, except for the presence of Ti, which is a component of anatase (TiO_2). However, the presence of anatase in this soil was not detected by XRD analysis (Figure 1). The Bs horizon of Jerijeh 2 contains kaolinite and/or muscovite as shown by the flaky structure of the minerals in the middle of the top part of the SEM micrograph given in Figure 8. The presence of these minerals is consistent with the XRD analysis (Figure 5). Spectrum 2 in Figure 8 shows the presence of C, K, O, Fe, Al and Si. C is the component of organic matter which is coating the mineral grains, mainly quartz. The stability of the organic matter in this soil probably occurs through physical protection in the mesopores and cation bridging as suggested by Anda et al. [31]. Fe, Si and Al are the chemical component of hematite, quartz and kaolinite and/or Al-hydroxides, respectively.

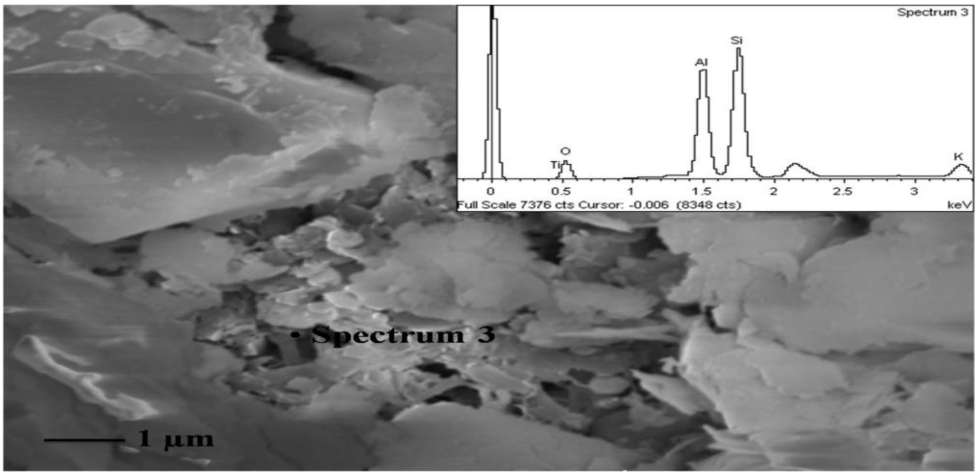

Figure 7: SEM micrograph of Bs horizon from Jerijeh1.

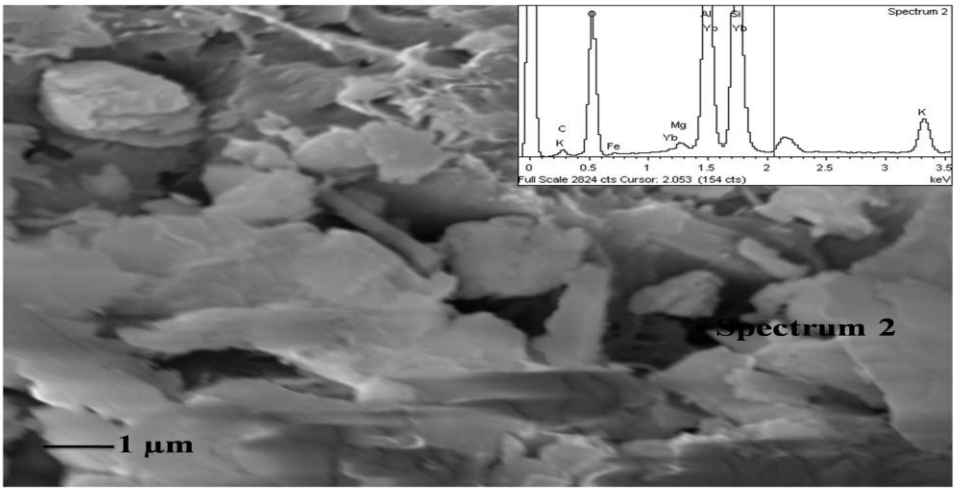

Figure 8: SEM micrograph of Bs horizon from Jerijeh 2.

3.5. Selective Dissolution Studies

The extractable Fe and Al contents in both the studied profiles are summarized in Table 3. The dithionite-, oxalate- and pyrophosphate-extaractable Fe were very low in both profiles and some of the results showed no difference in spodic horizons compared with either the E or A horizons. However, the dithionite-, oxalate- and pyrophosphate-extaractable Al showed the maximal accumulation in spodic horizons compared to upper layer.

Table 3: Selected extractable Fe and Al of the soils.

Soil	Horizon	Depth	Dithionite		Oxalate		Pyrophosphate		
		(cm)	Fe_d (%)	Al_d (%)	Fe_o (%)	Al_o (%)	Fe_p (%)	Al_p (%)	$Al_o + 0.5\ Fe_o$
Jerijeh 1	Ap	0 - 5	0.020	0.016	0.007	0.005	0.006	0.005	0.008
	E	5 - 40	0.008	0.012	0.002	0.002	0.006	0.003	0.003
	Bhs	40 - 70	0.014	0.178	0.006	0.095	0.006	0.102	0.098
	Bs	70 - 90	0.027	0.153	0.004	0.069	0.016	0.121	0.071
Jerijeh 2	Ao	0 - 8	0.018	0.021	0.011	0.009	0.007	0.009	0.014
	E	8 - 38	0.006	0.023	0.005	0.001	0.007	0.003	0.004
	Bs	38 - 45	0.047	0.261	0.032	0.133	0.008	0.138	0.149

The distribution of the different forms of Al with depth indicated that large amounts of Al were eluviated from the A/E horizons and accumulated in underlying spodic horizon (Bhs and/or Bs). This Al is more soluble and may move earlier and deeper into the pedon than Fe because it has smaller solubility constant (pK values) compared to that of Fe [32]. The distribution of extractable Fe forms was similar to the extractable Al forms, but the amounts of these Fe forms were much lower than those of Al in both soil profiles. Low content of extractable Fe in both soils was probably due to nature of the parent material which is dominated by quartz with minor amount of Fe-bearing minerals. Weathering of Fe-poor minerals throughout the history of the parent materials had released low amount of Fe that required for podzolization process in the soils.

It is generally accepted that the dithionite values provide an approximation of the combined content of amorphous forms of Fe and crystalline iron oxides, while oxalate value give an approximation of the degree of accumulation of amorphous products of recent weathering in the horizons [33]. The oxalate-extractable Fe and Al also have often been used to estimate the translocation of organo-metallic complexes [34, 35]. Therefore, Al_o + 0.5 Fe_o or ratio of extractable Fe to Al can be used to determine sesquioxides or spodic materials accumulation. In this study, the values of Al_o + 0.5 Fe_o in the spodic horizons were more than 0.5 %, greater than twice those in the upper layer, and therefore indicate that sesquioxides or spodic materials have been translocated and subsequently accumulated in the Bhs or Bs horizon. Pyrophosphate value provides the data for organo-metallic complex forms of Fe and Al in the horizon [34, 35]. High Al_p in the spodic horizons (horizons having the highest organic matter content) suggest that accumulation of organic complex of Al have occurred in them compared to Fe.

3.6. Fourier Transform Infrared Spectroscopy Study

The FTIR spectra from the spodic layer of both profiles were very similar (Figure 9). The FTIR spectra have low absorption band at 2400 to 3400 cm^{-1} region, indicating the presence of –OH groups stretching. This region also may be assigned to the aliphatic primary amine stretching. All the investigated samples have the band at 1615 cm^{-1} due to the presence of carbonyl group conjugated with aromatic ring. This peak generally attributed to the vibrations of various groups including aromatic C–C structural vibrations and C–O stretching of amide, quinone and H–bonded conjugated ketone groups. The carbonyl group was probably involved in the metal complexation (or ligand exchange) during the podzolization process. The weak band at about 1418 cm^{-1} suggests that the carboxyl groups (–COOH or $–COO^-$) of the organic matter in the spodic horizon are complexed with Fe and/or Al. The sharp and strong bands at the 1000 and 1300 cm^{-1} region represents alcohol, phenol, ether, and carbohydrate compound related to C–O complexes. The bands at 3690, 3698 and 3619 and 911 cm^{-1} may be related to Si–OH as found by Horbe et al. [36] The organo-halogen compounds also present in the region between 500 to 1000 cm^{-1}. These organic groups, alcohol, carboxylic, phenol, ether, carbohydrate and fulvate, are acidic and hydrophilic, having negative energy and being able to reduce the pH, facilitating the dissolution of silicates and iron oxides, and corroding quartz through the formation of organic complexes and colloids [37].

3.7. Formation of the Spodic Horizon

The mobilization and migration of Al and Fe as organic complexes is probably the dominant mechanism of podzolization in the Spodosols of the studied areas. The high temperature coupled with extremely high annual rainfall prevailing in the area for a long period of time accelerated the weathering of primary silicates and clay minerals leading to the release of Al, Fe and other cations such Ca and Mg. The studied Spodosols are located under heath forest with constant supply of leaf litters which contribute to the formation of organic acids through microbial decomposition. Presence of the organic acids is likely to enhance the weathering of silicates and minerals to release cations. Many of these organic acids have both acidic and strong complexing power [38, 39, 40, 41]. The organic acids can be considered as drivers in the weathering of oxide and silicate minerals as well as carriers of polyvalent metals such as Fe and Al [42]. The trivalent cations such as Fe and Al are less leached because they can form more stable bond with organic acids [13] to form the organo-metallic complexes. Overall, continuous leaching condition in the study area enhances the translocation of the unsaturated organo-metallic complexes.

The Fe and Al in the topsoil are mobilized and subsequently translocated downwards in organically-bound form with the organic acids from the organic matter. The high accumulation of Fep and Alp have been found in spodic horizons of both profiles. This indicated that a large amount of Fe and Al is translocated to the spodic horizon in association with organic acids from the upper horizon. This migration turns the E horizon even more bleached. Al is the more dominant complexation cation compared to Fe. The Fe seems to be less associated with organic compounds, as it is likely to be present in solutions as Fe^{2+} which tends to be leached out easily. Many investigations have shown that organic acids with the –COOH and phenol –OH groups have the highest complexing tendencies with cations [13].

Both functional groups were detected in the spodic horizon of the soil by FTIR. Dissociation of –COOH and phenol –OH radicals contribute to the formation of surface charges. The surface charges can be neutralized through chemisorptions with the trivalent cations such Fe^{3+} and Al^{3+}. This process corresponds in reality to the formation of organo-metallic compounds. Jansen et al. [43] stated that binding of Fe and Al to the functional groups influence the mobility of Fe, Al and organic acids itself in several ways. The insoluble complexation of Fe and Al with the organic acids will immobilize both organic acids and metals. However, soluble complexation could either mobilize or immobilize Fe, Al and organic acids, depending on whether sorption is prevented or cation bridging is stimulated. Therefore, insufficient availability of Fe and Al in the soils to completely neutralize the organic acids and immobilized them immediately in the upper horizon caused the organo-metallic complexes to move down the soil profiles. These are in line with the suggestion of De Coninck [13].

The immobilization of the organo-metallic complexes in the illuvial B horizon could be ascribed either due to microbial decomposition of the organic complexes during migration or because the complex becomes saturated with sesquioxides as suggested by Lundstrom et al. [16].

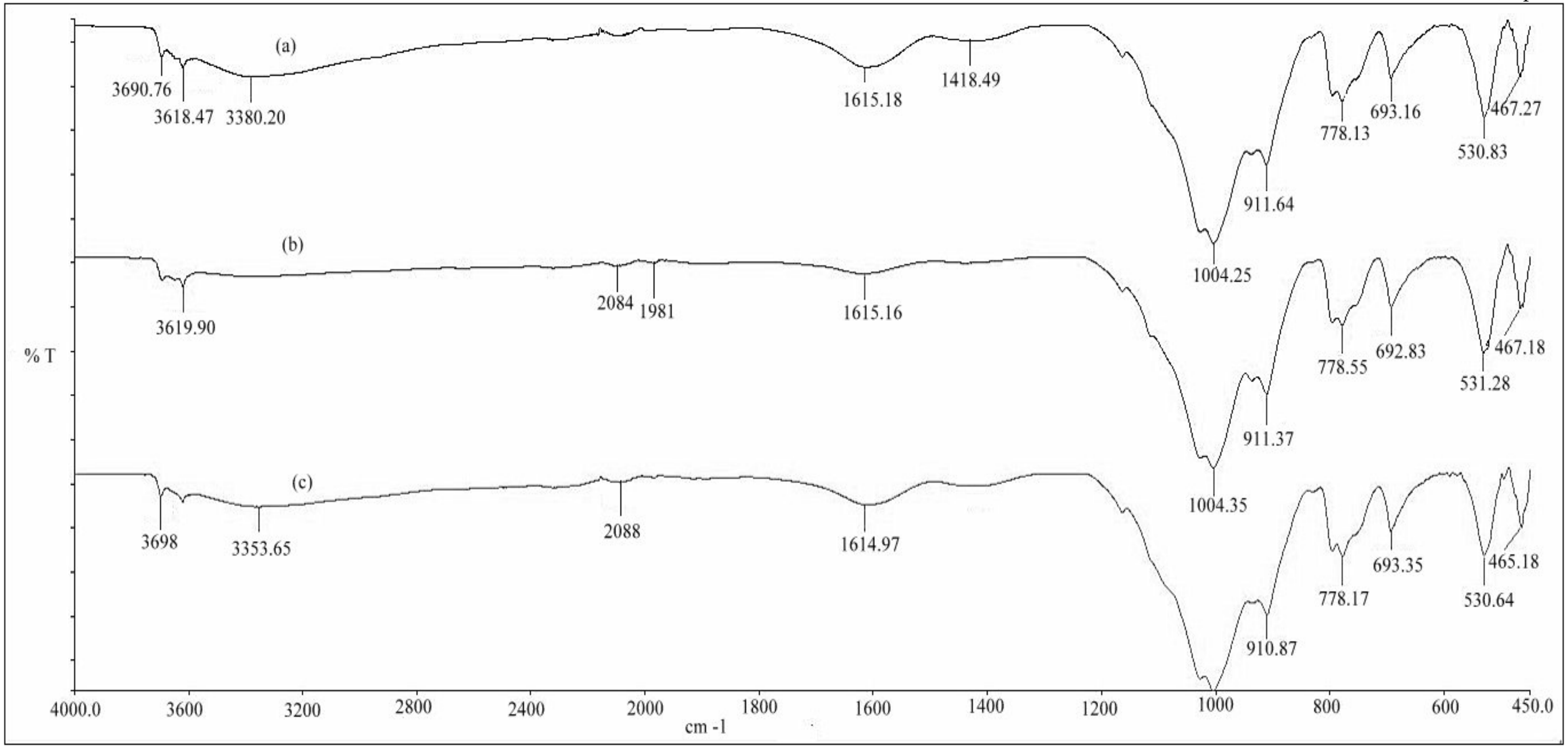

Figure 9: Infrared spectra for spodic horion of the soils; (a) Bhs horizon of Jerijeh 1, (b) Bs horizon of Jerijeh 1 and (c) Bs horizon of Jerijeh 2.

4. CONCLUSION

This study showed that the Spodosols in the high rainfall area of Sarawak, Malaysia, are almost similar to those found anywhere else in the tropics, the differences being the kind of parent materials and environmental condition under which they are formed. The Sarawak Spodosols are characterized by the presence of quartz, muscovite and kaolinite in the topsoil, indicative of the strongly leaching environment the soils have undergone through. However, vermiculite is still present in the spodic horizon, most like to be formed by the weathering of mica (biotite) originally present in the parent material (sandstone). Other minerals present in this horizon are gibbsite and hematite; the latter make this horizon slightly reddish in color. Interactions with organic acids released by the leaf litter derived from tropical plant species over a long period of time are generally believed to play a crucial role in the translocation of Fe and Al in this Spodosols. The translocation of the organo-metallic complexes from the upper horizon and their accumulation in spodic horizon is believed to be the important process in the formation of this tropical Spodosols.

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