CHARACTERIZATION OF ORGANIC MATTERS IN MOLLISOLSOF PAKISTAN

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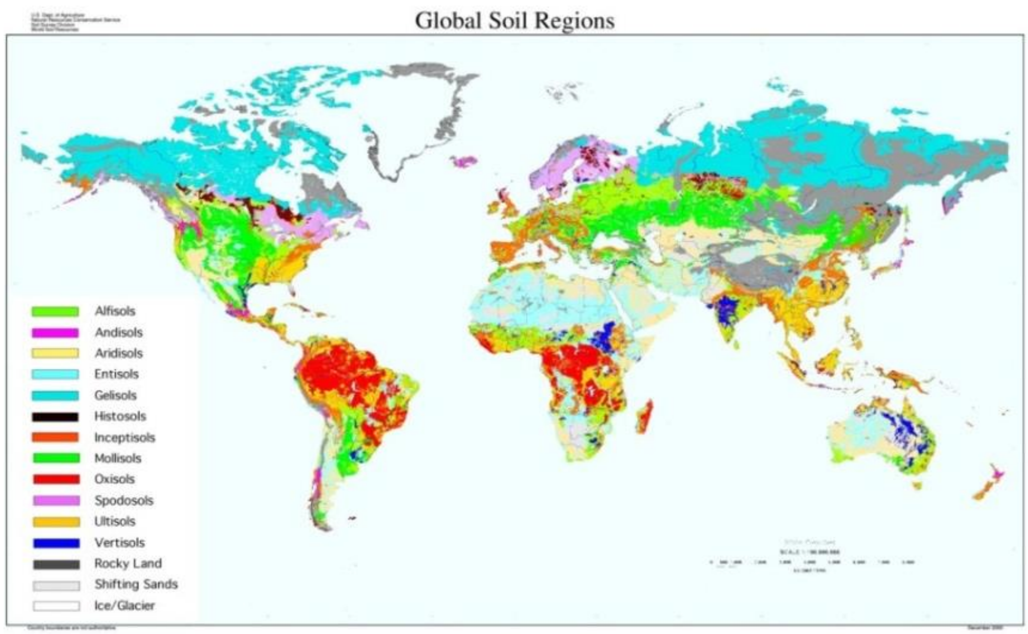
ABSTRACT: Mollisols are soils enriched with organic matter and typically composed of calcareous materials like loess, limestone or wind blown sands. 7 % of the total available soils of the world are mollisols including over 7,500 square kilometer spanning area of soils in north western part of Pakistan. From geotechnical engineering perspective, mollisols are naturally weak in its bearing capacity and exhibit substantial settlement when subjected to loading. Mollisols are required to be stabilized chemically before carrying out any infrastructure development on it. For that purpose, itsorganic matter characterization is desired because organic matter in mollisols strongly influence sits behavior during chemical stabilization. This research has been carried out to identify the organic matter constituents of mollisols available in Pakistan. Selected mollisols samples having over 8 % organic matter content from Murree district has been tested by X-Ray Diffraction (XRD) technique. The engineering properties of soils were also determined. Nineteendistinctive types of different organic compositions has been observed in the mollisols like Magnesium diisopropoxide, 9H-Flourine, 3-(p-Toluenesulfonyl)-4-cyano-5-methylthioisothiazoleetc. Monoclinic, orthorhombic and anorthic are three crystal systems identified in the mollisols. Inorganic zeolites have also been detected in the organic compositions of mollisols.

Key words: Organic, Mollisols, Soils, X-Ray diffraction, Chemical.

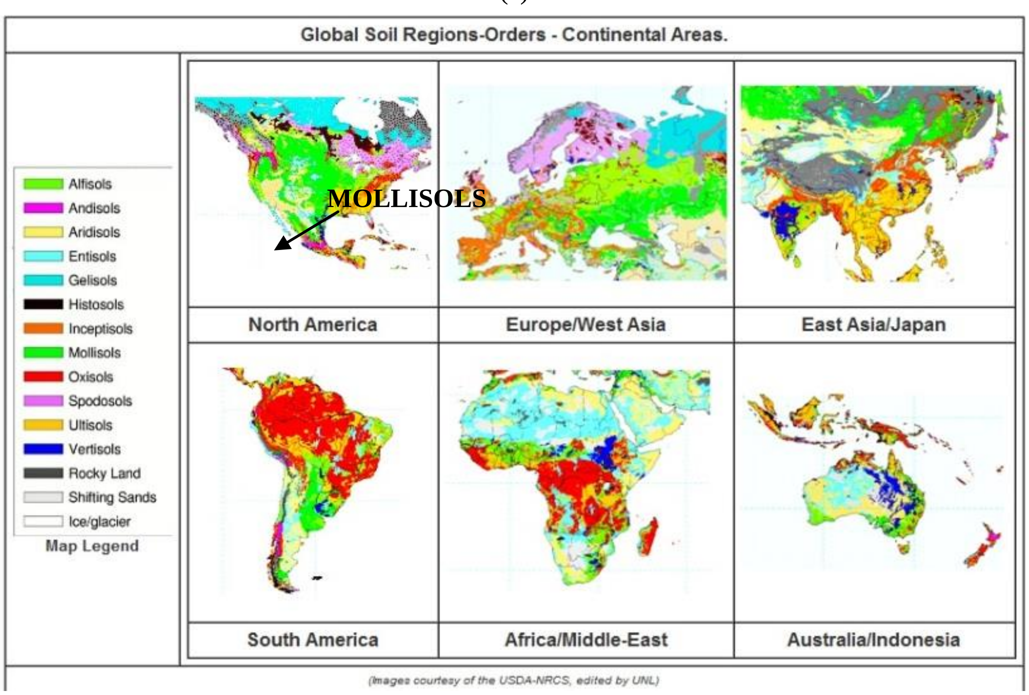
INTRODUCTION

Mollisols are found on deposits and landscapes with a wide range of ages. Many mollisols occur on deposits associated with glaciations (unconsolidated quaternary materials) where calcareous rich aolian deposits have supported its formation. In other areas these soils develop in residuum, weathered from sedimentary rocks. One of the main characteristics of mollisols is the high accumulation and decomposition of organic matter which includes a variety of materials ranging from newly added material to the thoroughly decomposed and polymerized residual matter (humus). The grassland or prairie vegetation yields high amount of organic matter, where as much as 80 % of the total biomass is in the roots. As a result, most of the organic matter is deposited within the profile itself, the highest amount within the mollicepipedon. Due to decomposition and humification, stable humus is formed, which is composed of complex organic compounds synthesized by the soil organisms and resistant polymers of phenolic and aromatic functional groups. Mollisols exhibit a mollicepipedon, which is dark in color, humus-rich, relatively fertile, and show a thickness of about 40 to 75 cm. Other factors that are associated with the accumulation of organic matter in mollisols are a high base saturation (> 50 %), high cation exchange capacity, and high water holding capacity. There are two main acidic fractions of organic matter present in organic soils, namely humic acid and fulvic acid. Based on several studies carried out by previous researchers, it was agreed that humic acid is the main constituent of organic matter affecting the strength development of stabilized soil (ClareandSherwood (1956), Onitsuka et al. (2002), Puppala et al. (2007).

X-ray diffraction (XRD) testing is used worldwide to identify the different minerals present in the soil mass. About 95% of all solid materials can be described as crystalline. X-rays when interact with a crystalline substance (phase), one gets a diffraction pattern. The same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. The X-ray diffraction pattern of a pure substance is therefore like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. Today about 50,000 inorganic and 25,000 organic single components, crystalline phases, and diffraction patterns have been collected and stored on magnetic or optical media as standards in XRD. The main use of powder diffraction is to identify components in a sample by a search or match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. Solid matter can be described as amorphous and crystalline. In amorphous materials the atoms are arranged in a random way similar to the disorder we find in a liquid. Crystalline materials composed of atoms those are arranged in a regular pattern and there is as smallest volume element that by repetition in three dimensions describes the crystal. This smallest volume element is called a unit cell. An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However, the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another. This model is complex to handle mathematically, and in day to day work we talk about X-ray reflections from a series of parallel planes inside the crystal.



(a)



(b)

(c)

Figure-1: (a) Global distribution of mollisols (Courtesy US Department of Agriculture) (b) Continents wise presence of mollisols (Courtesy US Department of Agriculture) (c) Area of mollisols in Pakistan (Courtesy Soil Survey of Pakistan).

It is desired to achiev equality mollisols stabilization (economy and performance) for construction and infrastructure development purposes in Pakistan. This research was conducted with objective to determine the chemical composition of organic matter found in typical mollisols available in Pakistan. So that when for construction (geotechnical) purposes these soils will be chemically stabilized than the best affinity of reactivity of soil organic matter with admixtures like flyash, cement, bitumen or lime will be proposed.

MATERIALS & METHODS

The objectives of the research have been achieved by adopting following methodology:

- Extensive literature survey from the database of departments like Soil Survey of Pakistan, Geological Survey of Pakistan, Agriculture Department etc. for the identification of mollisols potential regions in Pakistan.
- After identification of mollisols soil regions, the engineering properties of soils in these regions has been reviewed by consulting different geotechnical engineering reports of the projects.
- Collection and transportation of representative samples of mollisols for evaluation in laboratory. According to the reports of Soil Survey of Pakistan, Murree district has extensive deposits of mollisols. Representative samples of mollisols soils were collected from Murree district from different locations i.e. Angoori, Ghora Gali, Phagwari etc. as shown in Figure 2. The samples were collected by digging test pits of shallow depths up to 2 m.
- Determining organic content of mollisols by loss in ignition test method (ASTM F-1647).
- Determining basic geotechnical engineering characteristics of mollisols by performing laboratory tests like gradation (ASTM D-422), hydrometer (ASTM D-422), Atterberg Limits (ASTM D-4318), modified proctor compaction (ASTM D-698) and unconfined compression (ASTM D-2166).
- Identifying composition of organic matter in mollisols by performing X-Ray diffraction (XRD) test (ASTM D-4452).
- Analysis of XRD test data for recognition of chemicals composition of organic matters found in mollisols.

(a) (b)

Figure-2: Sampling locations of mollisols from Murree district

RESULTS AND DISCUSSION

In representative soil samples the organic matter content determined by loss in ignition test method was obtained as 8 %. The mollisols containing over 2 % organic matter are rated as high organic content mollisols (Wood, 1971). The mollisolssamples were found mildly alkaline with pH of 7.6.The mollisols soil samples also contained partially carbonized vegetable matter resembling Peat. Further, sample was moist throughout. According to Geological Survey of Pakistan, the mollisols (Udolls and Hapludolls) were formed over Mureeshales with mixed mineralogy comprising of dark reddish brown moist silty clay loam, weak medium sub-angular blocky structure, friable, slightly sticky, very plastic, few very fine and very coarse and common fine, medium and coarse roots, many continues and distinct clay films on vertical faces of peds and in pores, common continues moderately thick clay films in root channels and or pores, thin organic coats in pore and or root channels. Soils appeared to be formed from the underlying bedrock that have undergone varying rates of weathering depending upon the hardness and kind of inter bedded material.

Further findings using testing techniques as described under materials and methods heading are as follow;

- Figure 3 shows the grain size distribution curve of the mollisols obtained from sieving and hydrometer analysis. Based on the observed grain sizes, the soil sample comprised of about 34 % clay, 54 % silt, 10 % fine sand and fractions of medium and coarse sands.
- 49 % and 32 % are the respective values of liquid and plastic limits of the mollisols obtained from Atterberg Limits tests resulting into plasticity index of 17 %.
- Figure 4 show the modified proctor based compaction characteristics of mollisols. The maximum dry density (16.59 kN/m^3) of sample was obtained against optimum moisture content of 14.6 %.
- Figure 5 shows the results of unconfined compressive strength of three soil samples reconstituted in the laboratory at maximum dry density and optimum moisture content. The soil showed an average unconfined compressive strength of 300 kPa against axial strain of 2.25 %.
- Figure 6 shows the main XRD trend observed in the mollisols against 2 theta positions.
- Table 1 presents the results of the analysis of the XRD test performed on mollisols for the determination of the organic matter composition using X-PERT PRO software. The results show the various organic acids present in the soil like (dl-Tartaric acid, 5-Formylvanillic acid, p-Phenylenediacetic acid, 3, 3-Dimethylacrylic acid, r-Pentyloxybenzoic acid, Glycolic acid, Mesaconic acid, Picolinic acid along with other compounds of benzene. Moreover results also show the presence of various Aluminum Silicon Phosphate Quinuclidine (0.11C7H13N Al0.57Si0.07P0.36O2), Sodium Aluminum Silicate Choline Hydrate (C13.8H38.64N2.76O2.76 Na0.40Al2Si64.2O133 xH2O), Aluminum Phosphate Dipropylamine Hydrate (C3H7.5N0.5 AlPO4 20H2O) and many others which are the complex compounds of various Clay minerals including Halloysite (Si4Al4O10 (OH)8 4H2O), Montmorillonite Si8Al4O20 (OH)4 nH2O), Kaolinite (Si4Al4O10 (OH)8), The presence of Illite (Si8(Al, Mg, Fe)4~6O20(OH)4 (K,H2O)2) has not been identified through XRD testing.

Based on the results of grain size distribution and Atterberg limits,mollisols can be classified as organic silty clay of low plasticity (OL) according to Unified soil classification system and A-7 as per AASHTO soil classification system. OL / A-7 soils are rated as poor subgrade material in terms of capacity and settlement behavior (Bowles, 1996).

The results of XRD test confirm the presence of organic matter in the Mollisols. Organic matter when reacts with water forms organic acid which is a complex mixture of different acids. So in mollisols organic acid is present. The results of XRD show the various organic acids present the soil like (dl-Tartaric acid, 5-Formylvanillic acid, p-Phenylenediacetic acid, 3, 3-Dimethylacrylic acid, r-Pentyloxybenzoic acid, Glycolic acid, Mesaconic acid, Picolinic acid along with other compounds of benzene.

As typical composition of mollisols is colluvial and residual material from inter bedded shales, sandstones and slates.The presence of different clay minerals including Halloysite, Montmorilloniteand Kaolinite showsmixed mineralogical composition of mollisols.

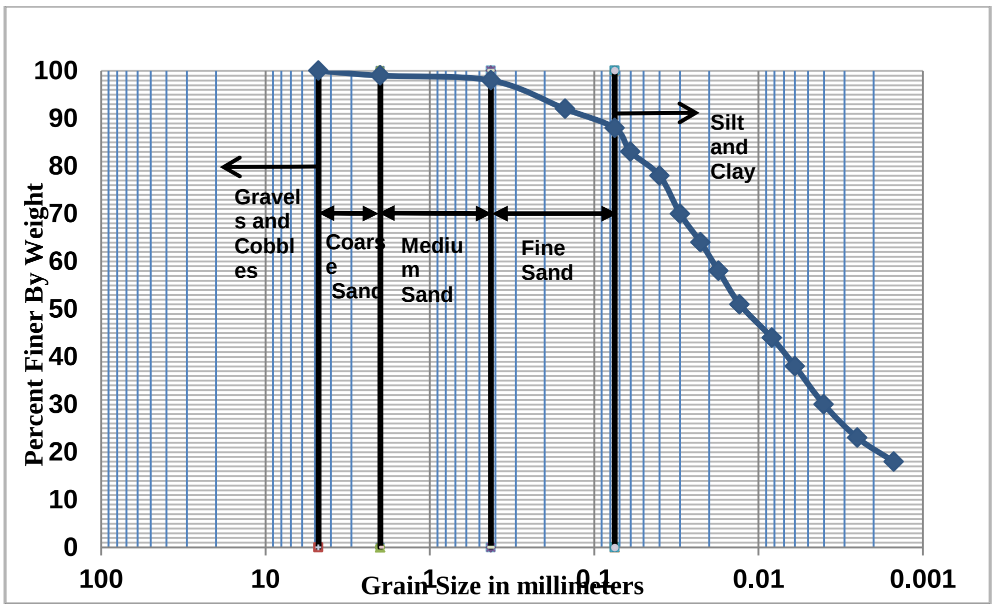


Figure-3: Grain size distribution curve of mollisols

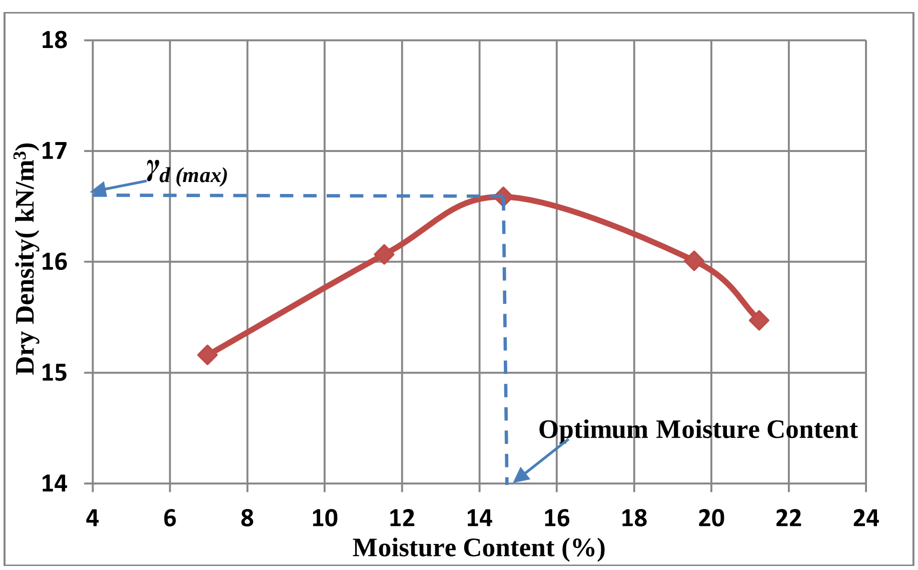


Figure-4: Compaction characteristics of mollisols

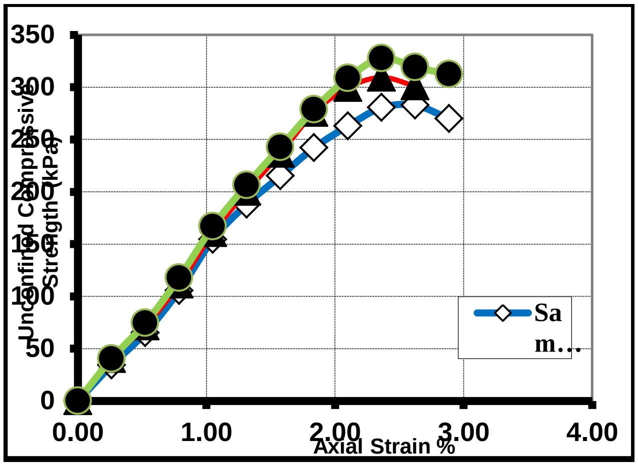


Figure-5: Strength characteristics of mollisols

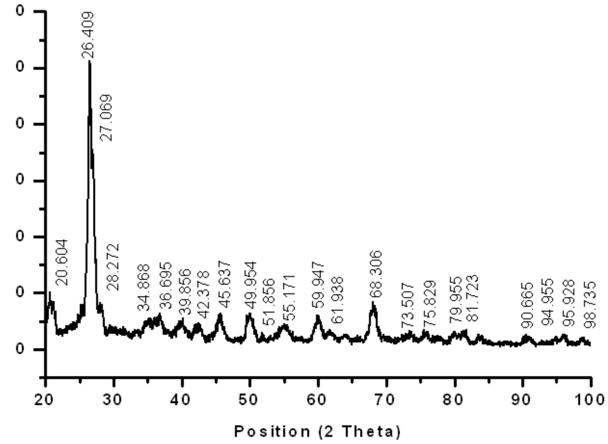
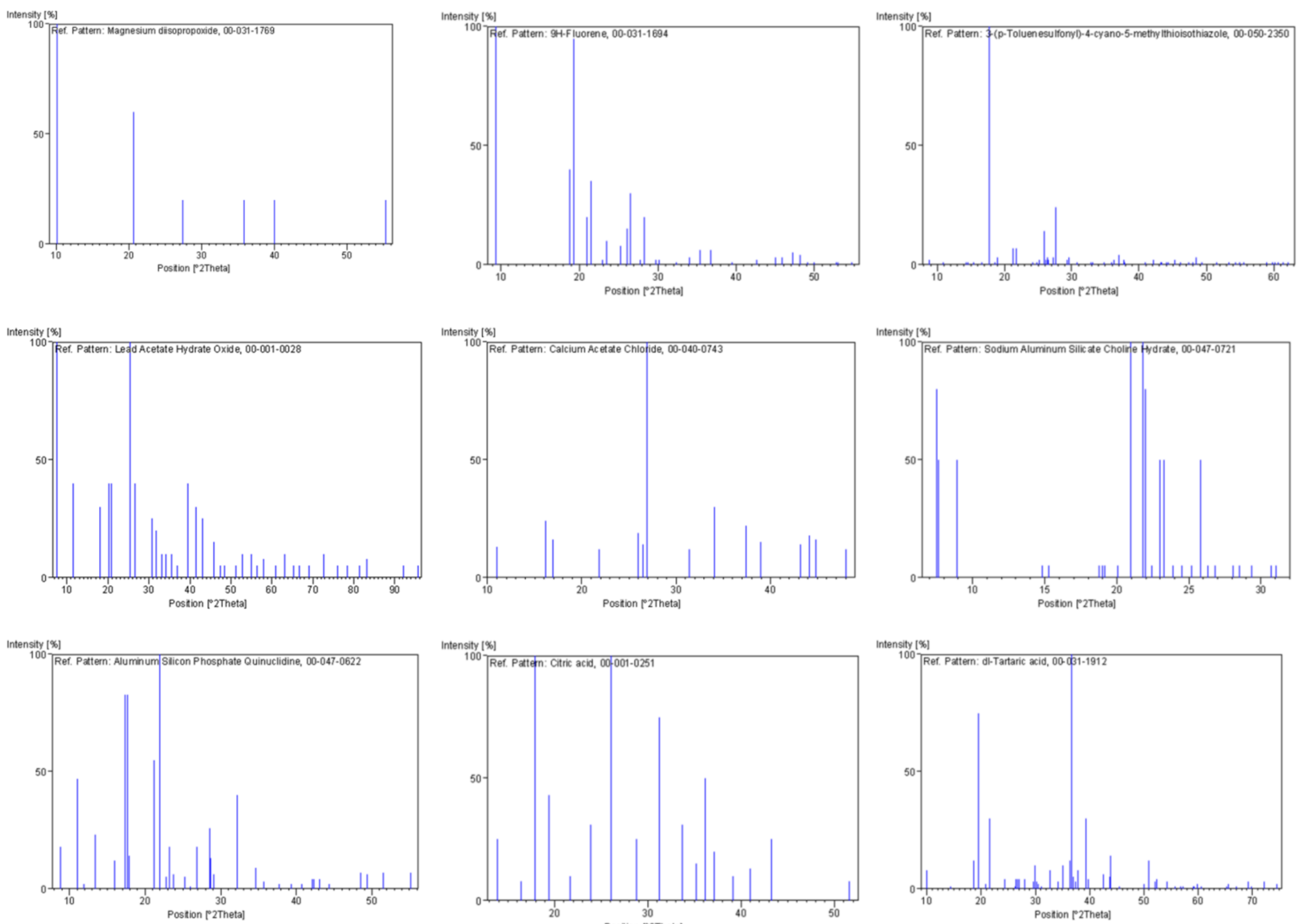


Figure-6: XRD trend observed during testing of mollisols

Table 1: Summary of XRD test analysis of mollisols

XDR Stick Pattern	Index Name	Empirical Formula	Chemical Formula	Crystal System	Type	Melting Point (^{O}C)	Color	XRD Software Ref.
a	Magnesium disopropoxide	$C_6H_{14}MgO_2$	$C_6H_{14}MgO_2$	Unknown	Organic	-	-	Ashby et.al (1979)
b	9H-Fluorene	C13H10	C13H10	Orthorhombic	Organic	116-117	White	Gong et.al (1980)
c	3-(p-Toluenesulfonyl) -4-cyano-5-methylthioisothiazole	C12H10N2O3S3	C12H10N2O3S3	Monoclinic	Organic	111.5-112.5	Colorless	Lin et.al (1998)
d	Lead Acetate Hydrate Oxide	C4H12O7Pb	Pb ($C_2H_3O_2$)$_2$ •3H_2O	Unknown	Organic plus Inorganic	75	White	Hanawalt et.al (1938)
e	Calcium Acetate Chloride	C4H6Ca2Cl2O4	C4H6CaO4 CaCl2	Unknown	Organic plus Inorganic	-	-	Stoilova et.al (1987)
f	Sodium Aluminum Silicate Choline Hydrate	C13.8H38.64 N2.76O2.76 Na0.40Al2Si6 4.2O133 ·xH2O	Na0.40Al_2Si_{64}.2O_{13} 2.76C_5H_{14}NO •xH_2O	Unknown	Organic plus Inorganic (Zeolite)	-	-	Miller et.al (1982)
g	Aluminum Silicon Phosphate Quinuclidine	C0.77H1.43Al0.57N0.11O2 P0.36Si0.07	0.11C7H13N Al0.57Si0.07P 0.36O2	Unknown	Organic plus Inorganic (Zeolite)	-	-	Lok et.al (1984)
h	Citric acid	C6H8O7	H3C6H5O7	Unknown	Organic	-	-	Hanawalt et.al (1938)
i	dl-Tartaric acid	C4H6O6	C4H6O6	Anorthic	Organic		White	Visser (1979)
j	5-Formylvanillic acid	C9H8O5	C9H8O5	Monoclinic	Organic	-	-	Kodama et.al (1964)
k	p-Phenylenediacetic acid	C10H10O4	C10H10O4	Unknown	Organic	-	-	Rose et.al (1981)
m	3,3-	C5H8O2	C5H8O2	Unknown	Organic	68-69 C	-	Rose et.al

	Dimethylacrylic acid							(1986)
n	r-Pentyloxybenzoic acid	C12H16O3	C12H16O3	Unknown	Organic	-	Colorless	Kudoh (1984)
p	Glycolic acid	C2H4O3	CH2OHCOOH	Monoclinic	Organic	-	-	Hanawalt et.al (1938)
q	Mesaconic acid	C5H6O4	C5H6O4	Monoclinic	Organic	-	-	Canfield et.al (1988)
r	Aluminum Phosphate Dipropylamine Hydrate	C3H47.5AlN 0.5O24P	C3H7.5N0.5 AlPO4 ·20H2O	Unknown	Organic plus Inorganic (Zeolilte)	-	-	Davis et.al (1989)
s	Picolinic acid	C6H5NO2	C6H5NO2	Monoclinic	Organic	136-137	White	Jaw et.al (1979)
t	Sodium 4-amino-2-hydroxybenzoate dihydrate	C7H10NNaO 5	$NH_2C_6H_3$ (OH) COONa •$2H_2O$	Monoclinic	Organic	-	White	University College, Cardiff, Wales, UK
u	Manganese chloride 1,2-diammoniobethane	C2H10Cl4Mn N2	C2H10Cl4Mn N2	Monoclinic	Organic	-	Dark Yellow	Tichy (1976)



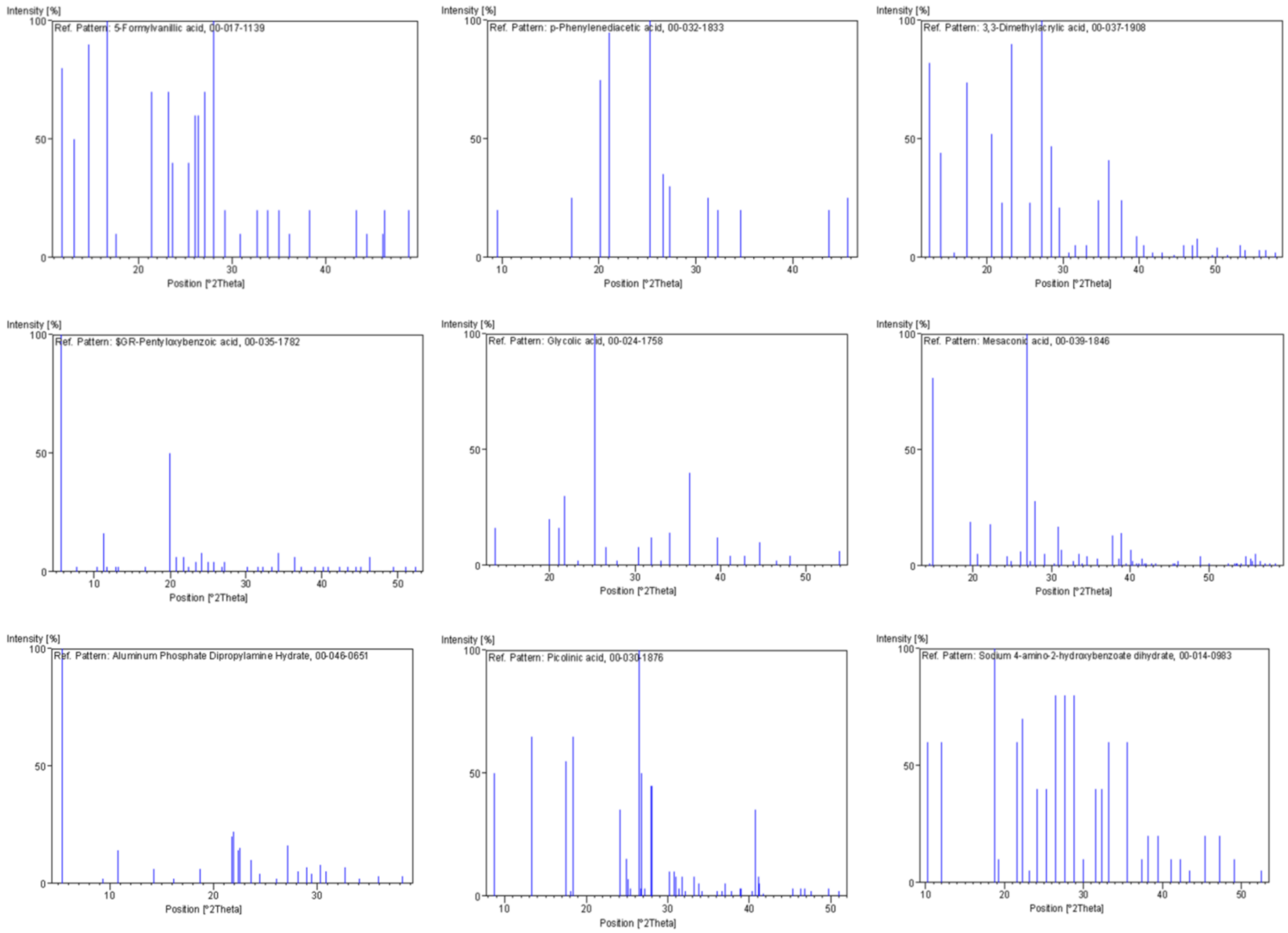


Figure-6: XRD test results analysis for determination of organic matter composition.

Conclusions: Mollisols soils after determination of its engineering properties has been evaluated through XRD for evaluation of the composition of its organic matters. Following conclusions can be drawn from it:

1. Mineralogical compositions of mollisols include combination of montmorillonite and kaolinite. No illite mineral was found.
2. Mollisols composed of nineteen distinctive types of organic matter compositions including Magnesium diisopropoxide, 9H-Flourine, 3-(p-Toluenesulfonyl)-4-cyano-5-methylthioisothiazole etc.
3. Monoclinic, orthorhombic and anorthic are three crystal systems identified in the mollisols.
4. Inorganic zeolite has been detected in the organic compositions of mollisols.

Recommendations: Mollisols are required to be stabilized chemically by additives (common additives include lime, flyash, cement or bitumen) before undertaking any infrastructure development on it. The mineralogy and chemical composition of mollisols obtained from this research will be useful in selection of appropriate additive based on its chemical affinity with such soils. Based on the findings of this research, it has been recommended to conduct a research for identification of most suitable and appropriate additive for mollisols stabilization before its use for infrastructure development.

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