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MINERALOGICAL CHARACTERISTICS OF SOIL OF PANCHANGANGA RIVER BASIN FROM INFRA-RED ANALYSIS

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ABSTRACT

Infra-red spectroscopy is a well known technique for the characterization of the substances. The principle of the technique is to pass infra-red radiation (4000 to 400 cm^{-1}) through a sample and the absorbed radiation is dispersed through a grating or a set of gratings and is allowed to fall on the detector. Vibrations in the region 550 to 960 cm^{-1} can be attributed to R – OH bending vibrations. Strong vibrations in the region below 550 cm^{-1} arise principally from in – plane vibrations of octahedral ions and their adjacent oxygen layers. The detector signal is amplified and recorded. There will be absorption peaks at frequencies corresponding to the substances. In certain cases, it may be possible to see the influence of rotation of the molecules. From the analytical point of view, the type of chemical bond present, the quantitative estimation of the components of a mixture, the association constant and the binding energy of the complexes can be determined. The Infra-red spectroscopy soils of Panchanganga river basin revealed the presence of kaolinite, halloysite, montmorillonite, attapulgite, nontronite and illite in all the soil samples though in different proportions in association with Quartz and humic acid.

KEY WORDS : Absorption, Clay minerals, Frequencies, Infrared, Panchanganga, Weathering process.

INTRODUCTION

Atoms in the molecules or in the crystal lattice are never at rest and the energy of the characteristic vibration lies in the infra-red region and hence anything happening to the molecular framework finds its effect on the infra-red absorption. The infrared studies are most useful for the identification of the clay constituents and also for the study of fine points of the structure of the clay. The clays from the weathered rocks fall into three main classes in the order of decreasing chemical complexity: the smectite, the illite and the kaolinite clay minerals. Deer *et al.* (1978) classified the clay minerals into five main groups, based on the basal spacing viz. kandite group (7A*), illite group (10A*), smectite group (15A*), vermiculite group (14.5A*) and palygorskite group. Grim (1968) suggested a classification based on the distinction of shape of the clay minerals and expandable or non-expandable characters of the 2:1 and 1:1 and 1:1 layer silicates into amorphous, allophone group and crystalline group.

Study area: The study area of the Panchanganga river basin selected is bonded between latitude 16^0 18′ 00"N to 16^0 50′00" N and longitude 73^0 50′ 00" E to 74^0 16′ 6.42" E . The river basin has been carved out in basalt flows of the Deccan Volcanic Province. These rocks now form the valley side, hills and ridges within the basin. At higher altitudes they have been converted into laterites that contain pockets of bauxites. The soils derived from these rocks form a thin veneer on the valley floor. Because of the intensive weathering of parent rock and their transportation downstream, well developed alluvial deposits are formed on the banks of rivers. The thickness of the alluvial soil varies from 5 to 10 m in the valley portions of the Panchanganga river basin. As shown in Fig.1. within the river basin, three types of soils can be demarcated. Black cotton soil is well developed in the north and north-western part of the basin and all along the bank of the river Bhogawati. Reddish brown lateritic soil is well developed on the plateau in the western and central part of the basin. In the southern part of the Kolhapur city a thin layer of coarse soil is developed on weathered basalts.

Soil sampling: Fifteen representative soil samples were collected from cropland, from a depth of 10-15 cm. About 1.5 kg.of sample was collected in a polythene bag and dried in the laboratory before grinding and sieving. The location of these soil samples are shown in Fig.1.

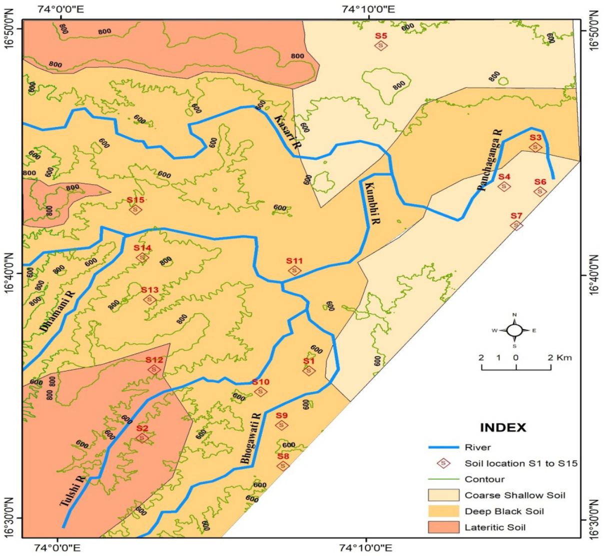

Fig. 1. Location map of soil samples

Methodology

The representative soil samples were crushed and the clay fraction was separated by International Pipette Method as per the procedure given by Carver (1971).

The sample was sieved through 300 mesh and fine fraction was collected on pan and transferred to 1000 mL graduated cylinder. About 15 mL of 10% solution of sodium hexametaphosphate (dispersing agent) was added, and sample was stirred for five to ten minutes in order to ensure an even distribution of sediment throughout the cylinder. After 24 hours, the dispersal of the particles were checked, and distilled water was added up to 1000 mL mark, and the sample was stirred again and kept for overnight 250 mL of this solution was collected from the cylinder from a depth of 10 cm by dipping the pipette into the solution. The solution so collected was centrifuged and the residue was dried under room temperature. This clay fraction was then used for IR analysis. Historically, two main regions in the IR are used for spectroscopy: near infrared (NIR, 700–2500 nm [14,000–4000 cm^{-}1]) and mid-infrared (MIR,4000–400 cm^{-}1 [2500 nm–25,000 nm]) (Sherman Hsu, 1997). While the NIR range is dominated by these broad overtone and combination patterns, the MIR range shows more fundamental absorptions and a clearer peak resolution (Hutengs *et al.,* 2019).

In the present study, the infrared spectroscopic studies were used to find out different constituents of the clay fractions by using pellet method of Schiedt and Reinwein (1952), on Perkin Elmer-883 model in the wave length range of 400 to 4000 cm^{-1}. The scanning was done in 12 minutes. The different mineral phases were identified by comparing the data with those given by Gadsden (1975) and Vander Merel and Beutel Spacher (1976).

RESULTS AND DISCUSSION

In the infrared spectroscopic studies, the radiations absorbed by a substance are plotted against the incident wavelength or frequency and the graph obtained is interpreted in terms of intermolecular vibrations. (This graph is characteristic of the material and can be used in its identification). In the infrared spectrum, every band should be assigned to a particular vibration. This is comparatively easy for simple molecules like H_2O, CO_2 and SiO_2. But in more complicated structures, it is controlled by many factors like masses of atoms, their distances, symmetry, bond strength and dipole momentum during vibrations, particle size, wave length and the difference in refractive index between the absorbing substance and the dispersion medium. Broadening of bands, loss of intensity and decrease of frequency are caused by isomorphous substitutions and poor crystallinity of the analyzed substance. The characteristic frequencies mainly fall in the region 3500 – 3750 cm^{-1} and 400 - 1150 cm^{-1}.

Buswell and Dudenbostel (1941) first showed that the absorption in the region 3500 – 3750 cm^{-1} is due to hydroxy1 group. Serratosa (1962) stated that the absorption frequency of O – H band depends on the degree of association of these groups. For free groups the frequency is around 3700 cm^{-1}. With increasing association, the frequency decreases depending on the strength of the hydrogen bond. Structural OH group shows the frequency in the range 3600 – 3700 cm^{-1} whereas absorbed water shows lower frequency at 3400 cm^{-1} and another at 1640 cm^{-1} The first is stretching mode while latter is deformation mode. The changes observed in the intensity of the bands during dehydration show the analogy between absorption at 915 cm^{-1} (montmorillonite) and at 820 cm^{-1} (nontronite), their origin being a deformation vibration of OH groups. The regular decrease of these bands with the loss of OH and their positions indicate that these absorptions correspond to a deformation vibration of the O-H bond. This has been confirmed by Stubiean and Roy (1960) on the basis of comparison of spectra of kaolinite and nontronite with those of their deuterated synthetic analogs.

In the region of 400 – 1500 cm^{-1} the frequencies are due to lattice vibrations. In this range, the layered silicates in which aluminium for silicon substitution is absent or low, give the sharpest spectra. Infrared spectra of silicates are dominated by the strong and broad band in the range 1200 – 800 cm^{-1} due to Si – O bending and a broad, medium absorption between 2400 – 2320 cm^{-1} representing a harmonic of Si – O stretching. The absorption bands between 1120 to 1025 cm^{-1} was attributed to Si – O stretching by Former and Russel (1964).

Vibrations in the region 550 to 960 cm^{-1} can be attributed to R – OH bending vibrations. Strong vibrations in the region below 550 cm^{-1} arise principally from in – plane vibrations of octahedral ions and their adjacent oxygen layers. The presence of Fe, Mg replacing Al causes a shift from higher to lower frequencies but however the substitution in tetrahedral site does not affect these absorption bands.

Clay mineral assemblage: The spectral characteristics of the representative samples are shown in Fig. 2.

Kaolinite : It was identified by the absorption band of larger intensity at 3694, 3621, 913, 540, 430 cm^{-1} and less intense bands at 1100, 539 and 471 cm^{-1}. Some kind of kaolinite overlaps with the bands of halloysite. However, the absorption bands at 1902, 1015, 830 and 690 cm^{-1} are indicative of halloysite.

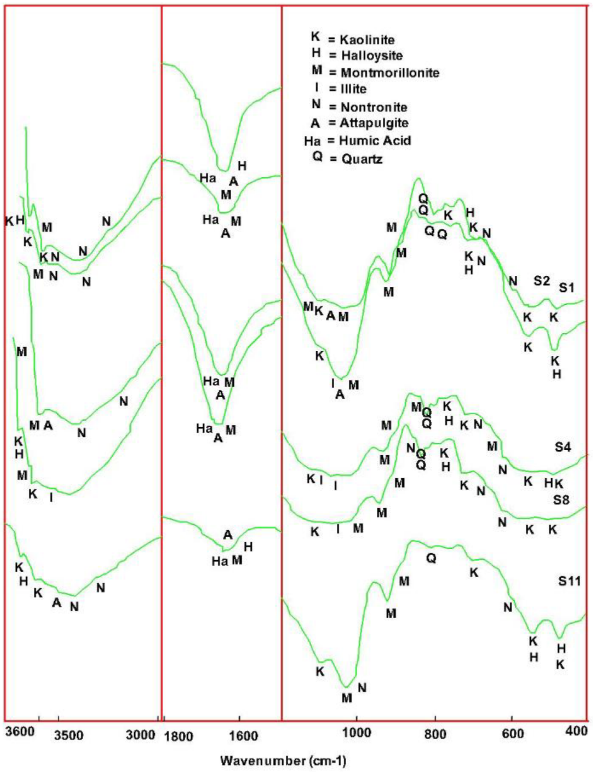

Fig. 2. The IR spectral characteristics of the representative samples

The absorption bands at 3694 cm^{-1} may be caused by stretching mode of vibration due to hydroxyl group and the band between 1000 – 1120 cm^{-1} may be attributed to the Si – O stretching mode of vibration. Almost all the samples showed the presence of kaolinite.

Montmorillonite : It was identified by the characteristic absorption bands at 3642, 3624, 915, 845-835, 976-790, 623 and 467 cm^{-1}. However, some bands of montmorillonite such as 3696, 3668, 752 cm^{-1} overlap with kaolinite (Van del Marel and Beutelspacher, 1976). It was observed that the soil samples (No. S$_4$, S$_5$, S$_6$ & S$_7$) showed comparatively strong peaks at 3642 cm^{-1} and 915 cm^{-1}, whereas in other samples the peak at 3642 cm^{-1} is either absent or less intense. Even in these samples, the kaolinite bands are strong at higher frequencies.

In clay minerals it is generally observed that the layer silicate structural OH groups which are comparatively associated appear at 3600 to 3700 cm^{-1}, but superficially absorbed, loosely held water gives band at 3400 cm^{-1} and sharp band at 1640 cm^{-1} are commonly observed in almost all the samples. Attapulgite (polygroskite): The characteristic bands occur at 3620, 3400, 1037, 987, 513 and 482 cm^{-1}. The samples (No. S$_1$ to S$_7$) showed the presence of this mineral. These samples showed strong peak at 3620 cm^{-1} and broad peak at 3400 cm^{-1}.

Illite : The bands of illite occur at 3643, 3622, 1166, 1025, 523 and 475 cm^{-1} and weak bands at 1022, 692 and 560 cm^{-1}. These peaks were commonly observed in all the samples. However, few samples (No. S_1, S_2, S_{11} & S_{12}, S_{13}, S_{14}) showed the strong peak at higher frequencies (3560 cm^{-1}).

Quartz : Quartz has strong peaks at 1172, 1082, 798, 778, 512, 478, 460 cm^{-1} of which doublet at 798 and 778 cm^{-1} distinguishes quartz from the clay admixture. The doublet at 798 and 778 cm^{-1} was commonly found in all the samples.

Humic acid : The presence of humic acid was observed in the clay samples and is of great significance for soil fertility. Humic acid was identified by the characteristic peaks at 1656, 1616, 1464 and 1081 cm^{-1}.

From the IR study, it was evident that almost all the samples contain kaolinite, montmorillonite as dominant clay minerals along with illite, nontronite, quartz and humic acid as accessory clay minerals. The proportion of these constituents may vary depending upon the soil type and degree of weathering. In natural environment the trend of chemical weathering can be predicted on the basis clay assemblage. In this regard, Carrol and Hathaway (1963), have suggested the following general sequences of mineral alteration which is a modification of the sequence given earlier by Jackson *et al.* (1948).

Table 1. Clay minerals identified on IR in soils of Panchanganga River Basin

Sample No.	Minerals identified
S_1	K, H, I, M, N, A, Q, & HA
S_2	K, H, M, A, N, I, Q & HA
S_3	K, H, M, A, N, I, Q & HA
S_4	K, M, A, N, I, Q & HA
S_5	K, H, N, M, A, I, Q & HA
S_6	K, H, N, M, A, Q & HA
S_7	K, H, N, M, A, Q & HA
S_8	K, N, M, I, Q & HA
S_9	K, H, M, N, Q & HA
S_{10}	K, H, M, N, Q & HA
S_{11}	K, M, N, Q & HA
S_{12}	K, H, M, I, N, Q & HA
S_{13}	K, H, M, N, Q & HA
S_{14}	K, H, M, N, I, Q & HA
S_{15}	K, H, M, N, I, Q & HA

Abbreviations :

K = Kaolinite
H = Halloysite
M = Montmorillonite
I = Illite
N = Nontronite
A = Attapulgite
Q = Quartz
HA = Humic acid

Progressive weathering →

Fresh mineral → montmorillonite → halloysite → kaolinite → gibbsite. This sequence suggests that the presence of montmorillonite is indicative of an early stage of chemical weathering, while an advanced stage is indicated by the presence of kaolinite. It has also been shown that plagioclase from basalt may directly alter to halloysite (Bates, 1962) or to gibbsite (Abbott, 1958; Swinedale, 1966). Area selected for study confined to an elevation of maximum 800m MSL. At higher altitude i e. more than 1000 m MSL, bauxite is found in the form of blanket deposit which is by and large gibbsite is nature.

The IR studies revealed that the clay is an admixture of minerals in different proportions with kaolinite and montmorillonite are the dominant clay minerals with other clay minerals. Sample wise assemblage of clay minerals in soils of Panchanganga River Basin is given in Table 1.

CONCLUSION

The IR studies revealed that the clay is an admixture of minerals in different proportions. However, kaolinite and montmorillonite are the dominant clay minerals. Other clay minerals identified are nontronite, halloysite, attapulgite , illite along with quartz and humic acid. The above study shows that there is co-existence of kaolinite with montmorillonite and this suggests variable extent of weathering. As indicated above, these minerals have high nutrient intake capacity and are hence able to absorb heavy metals from effluents and fertilizers. Hence, there is a tendency for the pollutants to be retained in the soil. The position though not grave at present is likely to worsen. Once absorbed in the soil in relatively large amounts, pollutants can be passed to humans and live-stock through vegetables, fruits etc. obtained from plants grown on such polluted soils. Infrared studies for the soils of Panchanganga river basin revealed the presence of kaolinite, halloysite, montmorillonite, attapulgite, nontronite and illite in all the soil samples though in different proportions. Quartz and humic acid were also identified in the IR studies.

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