

## Instrumental characterization of clay by XRF, XRD and FTIR

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**Abstract.** Instrumental characterizations of the clay were performed by different techniques such as XRF, XRD and FTIR. XRF shows the chemical compositions of the clay where Al-oxide and silica oxide are present in major quantity whereas XRD confirms the presence of these minerals in clay. FTIR studies show the presence of quartz, alumina, haematite and different mineral matters.

**Keywords.** Instrumental characterization; XRF; XRD; FTIR.

### 1. Introduction

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents. Clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite (Shichi and Takagi 2000). The adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity (Alkan *et al* 2004). Montmorillonite clay has the largest surface area and highest cation exchange capacity. Its current market price (about US\$ 0.04–0.12/kg) is considered to be 20 times cheaper than that of activated carbon (Babel and Kurniawan 2003). In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and fullers earth for their capacity to adsorb not only inorganic but also organic molecules. They showed that this naturally occurring material could act as a substitute for activated carbon as an adsorbent due to its availability and low cost, and its good sorption properties.

Clay is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalis and alkali earths (Ralph 1968). Two structural units are involved in the atomic lattices of most clay minerals. One unit

consists of closely packed oxygens and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons. The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition,  $\text{Si}_4\text{O}_6(\text{OH})_4$  (Ralph 1968). A large number of researchers determined semi-quantitative clay mineral composition on the basis of area under X-ray diffraction peak duly corrected by appropriate factors accounting for variation of scattering due to variation of angle. The literature on quantitative clay mineral analysis has been reviewed from time to time (Mukherjee *et al* 1971; Ghosh and Raychaudhuri 1974; Ghosh and Kapoor 1982; Ghosh and Datta 1996). Later on, many others (Bhattacharyya and Sidhu 1987; Ravikumar *et al* 1991; Agrawal and Singh 1995; Sidhu and Ghosh 1996) revealed the occurrence of a wide spectrum of minerals.

Numerous studies have been carried out on the behaviour of the exchanged, now organophilic clay (Gibbons and Soundararajan 1988; Conner 1990; Montgomery *et al* 1991; Faschan *et al* 1993). Dentel *et al* (1995) used trimethylammonium for the removal of 1,2,4-trichlorobenzene in the presence of tannic acid. The FTIR study of water adsorption was carried out by Stevens and Anderson (1996a). Similarly, the orientations of trimethyl phenylammonium (TMPA) in montmorillonite, as well as its implications in the adsorption of aromatic compounds, have been studied by Stevens and Anderson (1996b). Kramer (2000) and Uribe (2000) studied the adsorption behaviour of this type of organoclays. This will pave the way for using the results of clay research in a mutually beneficial way for increasing soil productivity. The knowledge developed in the field of clay mineralogy have been of some use in genetic and taxonomic studies of soil as well. Hence, this paper deals with the characterization of clay with the help of this technique.

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## 2. Experimental

The characterization of clay is carried out with a number of experimental approaches in order to investigate all the relevant features. Clay was obtained from the mines of Katni district of Madhya Pradesh. This sample was fractionated into different fractions of varying particle sizes using standard sieves of mesh sizes having geometrical mean particle diameters 140, 100 and 50  $\mu\text{m}$ . The chemical constituents and LOI at 800°C were determined by the Indian standard method (Indian Standard Methods of Chemical Analysis of Fireclay and Refractory Materials 1960).

The clay was analysed for its vibrational spectra with the aid of Fourier transform infrared spectroscopy using Perkin Elmer 1800 model instrument in the range 450–4000  $\text{cm}^{-1}$  as potassium bromide pellet.

XRD patterns of clay were obtained on a powder X-ray diffractometer Model Philips with  $\text{CuK}_\alpha$  radiation having a scanning speed of 0.04°/s. The clay was subjected to XRF to analyse the chemical composition or elements present in the sample.

## 3. Results and discussion

### 3.1 Characterization of clay particle

It is clear from table 1 that the chemical analysis of the clay contains alumina, silica and calcium in major quantities and other elements in minor quantities. The loss on ignition value indicates that clay has lower carbonaceous matter and higher mineral matter contents. For understanding the nature of phenol sorption on clay, XRF, XRD and FTIR studies were performed using raw sorbents, which are described in the following sections.

### 3.2 XRF characterization

It was performed to know the chemical compositions of the minerals that are present in the clay. The data given in table 2 shows that the alumina and silica oxide are present in major quantities while other minerals are present in trace amounts. This confirms the chemical analysis of clay.

**Table 1.** Chemical analysis of clay.

Chemical composition	Weight (%)
$\text{SiO}_2$	48.12
$\text{Al}_2\text{O}_3$	34.54
$\text{Fe}_2\text{O}_3$	2.48
CaO	0.83
MgO	0.50
$\text{TiO}_2$	0.40
LOI (800°C)	12.44

### 3.3 XRD characterization

The presence of above minerals were further tested by XRD studies. XRD is used to determine the mineralogical composition of the raw material components as well as qualitative and quantitative phase analysis of multiphase mixtures. The occurrences of minerals in clay were identified by comparing 'd' values (Selected Powder Diffraction Data for Minerals 1974; Powder Diffraction File Search Manual Minerals 1974). The possible minerals with their 'd' values present in the adsorbents are given in table 3. No quantitative estimation phases in these adsorbents have been made but their characterization of XRD patterns indicates the presence of quartz, kaolinite, hematite, illite, and tridymite as the major phases. Further the occurrence of the above minerals in the aforesaid adsorbents was confirmed by FTIR study.

### 3.4 FTIR characterization

FTIR studies of these adsorbents help in the identification of various forms of the minerals present in the clay. The coupled vibrations are appreciable due to the availability of various constituents. Nevertheless, observed bands (in the range, 4000–500  $\text{cm}^{-1}$ ) have been tentatively assigned. In the IR studies of clay, the Si–O stretching vibrations

**Table 2.** Chemical analysis of fractions of clay.

Chemical composition	Weight (%)
$\text{SiO}_2$	28.977
$\text{Al}_2\text{O}_3$	14.081
$\text{Fe}_2\text{O}_3$	1.201
CaO	0.183
MgO	0.638
$\text{TiO}_2$	0.875
$\text{K}_2\text{O}$	0.382
MnO	0.036
SrO	0.001
$\text{Na}_2\text{O}$	2.547
Ni	0.003
Zn	0.005
V	0.011
P	0.018
Cr	0.009
Cu	0.003

**Table 3.** X-ray diffraction 'd' values of clay fraction.

d(Å)	Possible mineral
4.2754, 1.5441, 1.3864	Quartz
3.4354, 2.5505, 1.3781	Alumina
2.6990, 1.6957, 2.2001	Hematite
3.8057, 3.4354, 2.2903	Tridymite
3.3462, 3.0965, 2.2844	Illite
4.1876, 2.5509, 3.4023	Kaolinite

**Table 4.** Important IR bands of clay along with their possible assignments.

Band (cm <sup>-1</sup> )	Transmittance (%)	Assignments
3696.7	27.3	Al---O-H str.
3622.5	13.5	Al---O-H (inter-octahedral)
3450.4	50.2	H-O-H str.
1633.4	91.4	H-O-H str.
1033.3	7.2	Si-O-Si, Si-O str.
914.5	32.6	Al---O-H Str.
790.9	27.5	Si-O str., Si-O-Al str. (Al, Mg)---O-H. Si-O- (Mg, Al) str.
693.4	66.8	Si-O str., Si-O-Al str.
538.8	29.9	Si-O str., Si-O-Al str.
468.9	12.3	Si-O str., Si-O-Fe str.

were observed at 790.9 cm<sup>-1</sup>, 693.4 cm<sup>-1</sup>, 538.8 cm<sup>-1</sup> and 468.9 cm<sup>-1</sup> showing the presence of quartz (Marel and Bentelspancher 1976). The appearance of  $\nu$  (Si-O-Si) and  $\delta$  (Si-O) bands also support the presence of quartz (Marel and Bentelspancher 1976), a strong band at 3696.7 cm<sup>-1</sup>, 3622.5 cm<sup>-1</sup> and 3450.4 cm<sup>-1</sup> indicate the possibility of the hydroxyl linkage. However, a broad band at 3450.4 cm<sup>-1</sup> and a band at 1633.4 cm<sup>-1</sup> in the spectrum of clay suggests the possibility of water of hydration in the adsorbent. The inter layer hydrogen bonding in clay is assigned by a characteristics band at 3622.5 cm<sup>-1</sup>. Most of the bands such as 3696.7 cm<sup>-1</sup>, 3622.5 cm<sup>-1</sup>, 3450.4 cm<sup>-1</sup>, 1033.3 cm<sup>-1</sup>, 914.5 cm<sup>-1</sup>, 790.9 cm<sup>-1</sup>, 693.4 cm<sup>-1</sup>, 538.8 cm<sup>-1</sup>, 468.9 cm<sup>-1</sup> show the presence of kaolinite (Tuddenham and Lyon 1960). The vibrations observed at 914.5 cm<sup>-1</sup> indicate the possibility of the presence of hematite (Gadsen 1975). The presence of bands at 3696.7 cm<sup>-1</sup>, 3622.5 cm<sup>-1</sup>, 3450.4 cm<sup>-1</sup>, 2369.8 cm<sup>-1</sup>, 1633.4 cm<sup>-1</sup>, 1033.3 cm<sup>-1</sup>, 914.5 cm<sup>-1</sup> and 790.9 cm<sup>-1</sup> indicate the possibility of the presence of illite (Wolf 1963), whereas 3622.5 cm<sup>-1</sup>, 1633.4 cm<sup>-1</sup>, 1033.3 cm<sup>-1</sup> are indicative of gypsum and 693.4 cm<sup>-1</sup> shows the possibility of the presence of calcite (Gadsen 1975). The corresponding values are given in table 4.

Thus the results of IR are quite helpful in the identification of various forms of minerals present in the used sorbents. IR spectra of these sorbents show adsorption band at 3622.5 cm<sup>-1</sup> of clay corresponding to H<sub>2</sub>O vibrations, indicating the hydrous nature of these materials and the presence of hydroxyl linkage. However, owing to the mixing of various overtones and complexity of the spectrum of clay, distinct assignments of various other vibrations have not been made.

#### 4. Conclusions

The chemical analysis, XRF, XRD and FTIR show that clay is mainly constituted of alumina and silica in major quantities and iron, calcium, magnesium oxide and other ele-

ments in minor quantities. The loss on ignition value indicates that clay has lower carbonaceous matter and higher mineral matter contents. X-ray diffraction study shows the presence of quartz, kaolinite, hematite, illite and tridymite as major phases. The presence of above minerals were further confirmed by FTIR analysis.

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