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Powdered X-ray diffraction, FTIR, TGA and DTA studies of montmorillonite derivatives

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Montmorillonite derivatives prepared from natural source of mineral deposits have been characterized by PXRD and FTIR studies. Na-derivatives prepared by standard method may be studied for sorbent behavior with respect to the Cr and As samples collected from different sources of Hazaribagh district like Keswagaon, Rolagaon, Karbekla, Khambhioa, Oriya villages. A detailed investigation of the derivatives of the samples have been done for X-ray diffraction, FTIR and DTA. FTIR spectral analysis is used for detecting peaks of Mg-O, Al-OH, Na and other oxides. The dioctahedral clay is confirmed by Al-O peak at 978.2 cm^{-1}, OH^- is confirmed by peak at 3625 cm^{-1}. The bands at 1030 cm^{-1} show Si-O vibration, 785.1 cm^{-1} for MgO. The mineral montmorillonite is abundant in the inner part and layers of kaolin are also present. The differences in chemical characteristics of montmorillonite vary due to alternation conditions.

Keywords: Montmorillonite, PXRD, FTIR, TGA, DTA.

Introduction

The montmorillonites samples collected from different sources of Hazaribagh district gave blue coloration with benzidine solution[1,2]. The district is situated between 24°2′26″ North and 24°56′49″ North latitude and 85°18′24″ East and 85°25′25″ East longitude having an area of 4313 km^2. The thickness of the montmorillonite beds is 1–2 m in most of the cases. Rock fragments from volcanic rocks give rise to the formation of smectite group of minerals i.e. montmorillonite found in different colors and grades. When mined it is sometimes bluish green in colour which becomes brownish on exposure to light.The difference in chemical properties is attributed to the variable weathering conditions. The abundance of low-cost available montmorillonite minerals have been studied for adsorption behavior. Sorption is defined as a surface retention process. From literature review, montmorillonites have the capacity for adsorption of heavy metals. Na-derivatives of naturally abundant montmorillonites have been found to give better results for adsorption of heavy metals[3,4]. The possibility of using this mineral to remove Cr and As and fluoride from aqueous medium can be exploited on industrial scale too[5–7]. In addition to this sodium derivatives of montmorillonite may be exploited for other industrial applications.The chemical formula of montmorillonite is $(Na, Ca)_{0.3}(Al, Mg)_2SiO_4O_{10}(OH)_2.nH_2O$ and chemical composition of montmorillonite shows various oxides e.g. SiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O and K_2O and traces of TiO_2. In chemical formula tetrahedral sheet is occupied wholly by Si and number of octahedral cations is 2. The percentage of Al_2O_3 varies from 4% to 19% approax[8,9] and percentage of SiO_2 is up to 60%, Fe_2O_3 varies from (7.8 to 9.5)% and MnO varies from (2.6 to 3.3)%. Clay minerals in general have a layered structure based on sheet with 6 membered rings of silica tetrahedra e.g. pyrophyllite, beidellite, nontronite, saponite, iron saponite, vermiculite. The montmorillonite mineral in particular has layered structure of sheets of silica tetrahedra with Al or Mg octahedral. e.g. (2:1). One octahedral sheet is sandwiched between two tetrahedral sheets. Cation exchange capacity of montmorillonite is around 100 meq/100 g and the exchangeable cations are Na^+, K^+, Ca^{2+} and Mg^{2+} [10–12]. The montmorillonite lattice is negative in charge owing to isomorphous substitution of ions within the lattice. The negative charges are balanced by cations held on the surface which are responsible for the exchange[13–15]. The

exchange capacity is reduced on heating in montmorillonites and exchange reaction does not affect the structure of silica-alumina packet as a result of which during removal of fluoride from aqueous medium no free Al is released[16].

X-Ray diffraction technique has been used for characterization of montmorillonites. This method is applied for the quantitative analysis and imperfections in the lattice[17]. The reflection angle is 2θ of maximum intensity by which interplanar distance *d* of the diffracting plan *hkl* is known by Bragg's equation, $n\lambda = 2d \sin\theta$. This method is used to ascertain different crystalline phases in minerals. The data of a particular pattern is compared with parts of zero intensity in the pattern of the unknown samples. For getting better and accurate results, quality of radiation and randomization of the crystals in the sample and adjustment of the diffractometer needs to be considered[18–22]. Each crystalline substance has its own characteristic diffraction pattern. Different substances are identified by the patterns of component phases.

Experimental

Samples were freshly collected from different place of Hazaribagh, Sitalpur, Gogra hill of Jharkhand. The temperature of the collection places was also recorded. For the study laboratory facilities are made available by Central Institute of Mining and Fuel Research, a CSIR lab in Dhanbad for XRD tests, Department of Chemistry, Viswa Bharati, Santiniketan for providing FTIR analysis of the sample. The FTIR has been carried out using Perkin-Elmer Spectrum version 10.4.1. The PXRD studies of the collected samples have been done using Cu as anode material. The diffractometer type used was D8. The thermal behavior of montmorillonite has been carried out using TGA at different temperatures. Perkin-Elmer USA has been used for the said purpose. X-Ray diffraction patterns can be compared with theoretical patterns to ascertain montmorillonite minerals[23–26]. Estimation of elements has been done by quantitative chemical analysis for different elements. Fe has been estimated by titrating against standard potassium dichromate solution. Sodium and potassium have been estimated by flame photometry and EDTA titration has been carried out for estimation of magnesium and calcium. Again for aluminum colorimetric determination has been done as the Alizarin-red S-complex. Thus standard methods of qualitative analysis have been applied for estimation of elements. Clays other than montmorillonite mineral present may be illite and kaolinite[27,28].

FTIR of inorganic solids are done with a view to ascertain groups such as hydroxyl groups, trapped water and metal oxide bonds[29]. Sodium montmorillonite has been prepared by standard methods. 200 g of sample is taken in a beaker. 200 ml of 1 *N* NaCl solution is added and kept in contact for 20 days. After this period a clear liquid is decanted, and the beaker is refilled with 200 ml of 1 *N* NaCl and kept in contact for 20 days. After this period clear liquid is decanted and kept in contact for 25 days. External NaCl solution is removed by boiling with distilled water. This process is repeated till NaCl is removed completely. The residue is filtered with filter paper and washed with distilled water to make it free from chloride ion. The residue is dried and made ready for use.

The PXRD studies of the dried sample are done at 2θ position using Cu as anode material. The diffractometer type used is D_8 and Cu as anode material[30–33].

The FTIR is done by the apparatus Perkin-Elmer Spectrum version 10.4.1 for the dried sample derivatives[25]. S_6(2540) stands for the Hazaribagh montmorillonite sample collected from Village Khambha which is 35 km east from Hazaribagh keeping NH100 left. S_7(2541) stands for the Hazaribagh montmorillonite sample collected from Village Oriya which is 5 km east from Hazaribagh keeping NH100 right. SH_2(2543) stands for the Hazaribagh montmorillonite sample collected from Village Keswagaon, Hazaribagh.TGA and DTA studies are done to know thermal stability up to a range of 1000°C.

Results and discussion

The montmorillonites are represented by XRD patterns. Interplanar distance (Å) and corresponding relative intensities have been mentioned such as 4.414, 4.3534, 4.396, 4.1984 (Å) having relative intensities 19.63, 90, 17.40, 17.55 respectively. Among clay minerals, montmorillonites dominate. Small amounts of kaolinite were also detected in some percentage. In addition to this illite montmorillonite randomly mixed layer is present. Imperfections of crystals affect the diffraction characteristic arising due to highly symmetrical arrangement of atoms in the various layers and weak binding force between them. The layers may be displaced with respect to one another. The calculated XRD data of montmorillonite minerals is in agreement with the literature val-

ues of *d* (Å) for Jaipur and Bihar montmorillonites. The literature value of *d* (Å) of Bihar and Jaipur montmorillonites are 4.48 and 3.34 respectively reported by Guha and Sen[34]. Thus it has been confirmed that the samples have montmorillonite content Figs. 1, 2 and 3 show endothermic decomposition in TGA, DTA curves for SH_2 NaCl, S_7 NaCl and S_6 KCl respectively. The thermal studies have been done up to a temperature of 1000°C showing weight loss of 14% and 17% which is due to loss of hygroscopic water and dehydroxylation. Further weight loss of 6.65% in a sample shows presence of kaolinite along with montmorillonite. Elemental analysis done by standard method show the presence of SiO_2 up to 60%, Al_2O_3 up to (7.8 to 9.5)%., MnO up to (2.6 to 3.3)%, TiO_2 (0.07 to 0.63)%, CaO (0.95 to 1.21)%, MgO (0.61 to 2.41)%, Na_2O (0.56 to 1.53)%.

In the OH- stretching region bands around 3620 to 3698 cm^{-1} represent surface OHs and inner OH. Thus the absorption bands at 3446–3698 cm^{-1} represents fundamental stretching vibrations of different OH group e.g. Mg-OH-Al and Fe-OH-Al in the octahedral layer. The bands at 3698.03 and 3621.23 correspond to Al-OH vibration which characterizes montmorillonite. The higher bands are due to surface OHs and band at 3621.23 originates from the inner OH. A band at 3436 cm^{-1} observed, indicates the presence of natural disordered kaolinite in small proportion. 362 cm^{-1} vibration indicates Al-OH-Al. The bands around at 778.2 cm^{-1}, 995.60

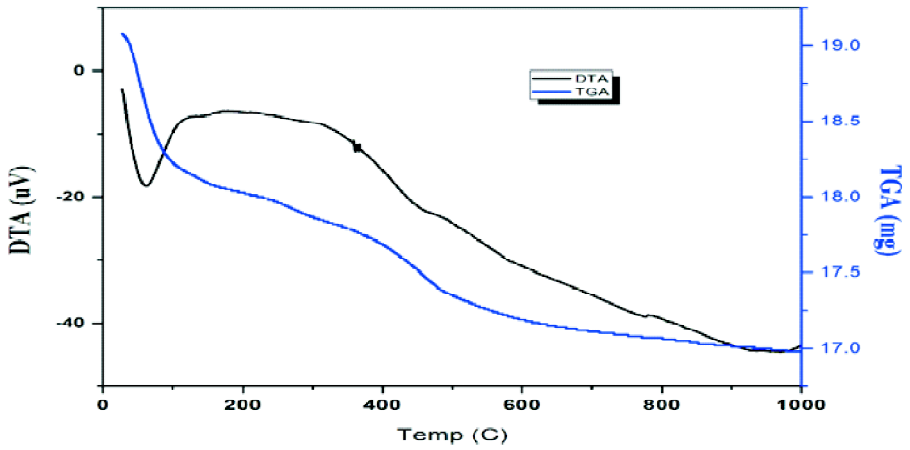

Fig. 1. TGA DTA graph for sample SH_2 NaCl(2543).

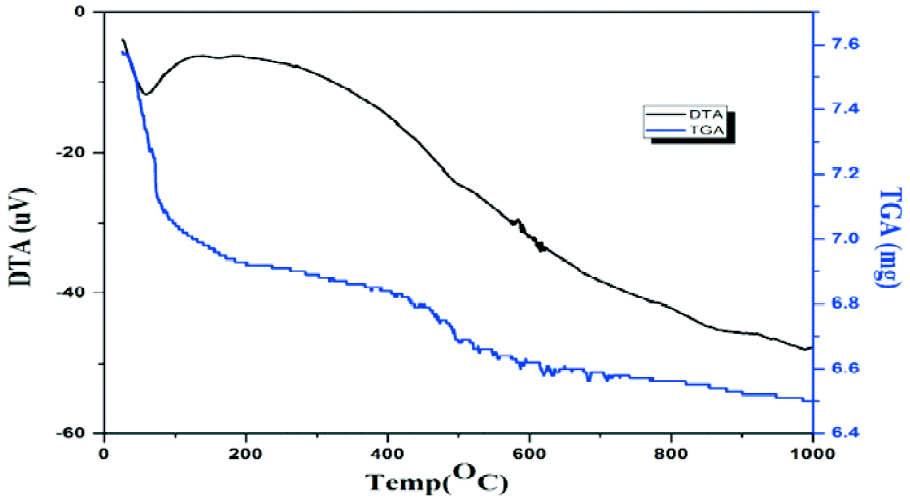

Fig. 2. TGA DTA curve for derivative S_7 NaCl(2541).

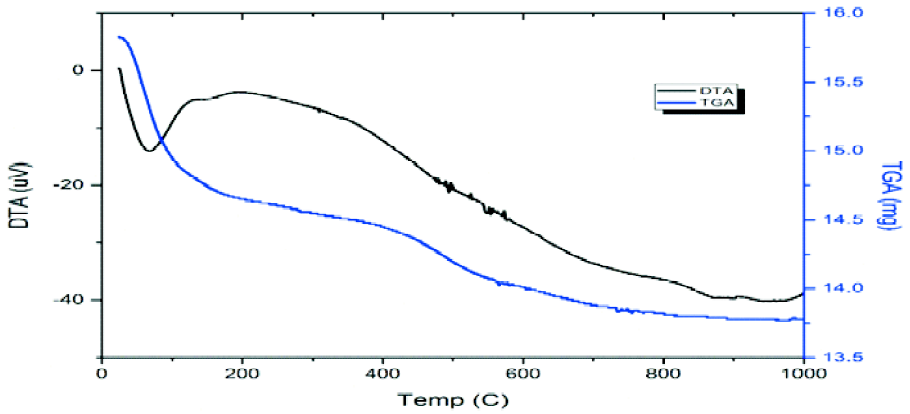

Fig. 3. TGA DTA curve for derivative S_6 KCl(2540).

cm^{-1}, indicate the presence of MgO and Al_2O_3 respectively. The peak at 1636.10 shows the absorbed water between the layers. The peaks obtained in FTIR analysis characterize the vibration bands of montmorillonite[35]. It may be concluded that peaks are identical to Na-montmorillonite derivative having trace of impurities e.g. kaolinite[36].

Conclusion

Samples of montmorillonites were collected from different parts of Jharkhand (Hazaribagh) hills after through survey, particularly for examining their properties to trace out good quality of montmorillonites and their derivatives to offer low cost method to remove arsenic, fluoride, hexavalent chromium and manganese from aqueous medium. XRD, FTIR, DTA and TGA studies have been performed to characterize the derivatives. The chemical composition of Jharkhand Hazaribagh montmorillonite is comparable to that of Rajmahal hills. Endothermic transition of derivative indicates the presence of montmorillonite.

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