In this chapter all the experimental details regarding the proposed research work are embodied, which are as follows:-

2.1 Characterisation of clays

Characterisation of clay is an elaborate process consisting of several steps, such as, Purification, Identification by X-ray diffraction (XRD) measurement, Infra-red (IR) spectrophotometric analysis and thermal studies (TG-DTG-DTA), CEC determination, Chemical analysis and so on. Two montmorillonite (hereafter Mnt) clays are chosen for the studies - (i) Bentonite from Neelkanth Sodaclays and Pulverizers, Jodhpur, India (Mnt\textsubscript{i} hereafter) (ii) Wyoming bentonite (SWy2). Crook County, from clay repository (Mnt\textsubscript{2} hereafter).

2.1.1 Purification of Mnt by Sedimentation

Usually clays like bentonite contain coarser impurities such as sand and silt. The lower fractions (-2 \textmu m particle size) were rich in Mnt. Sedimentation under gravitation is a common technique of separating clay-rich fraction from the crude form. The Stoke's law is applied to separate the different particle size fractions of the clay. The Stoke's law is represented as

\[ R = \left[ \frac{9gh/2(d_1-d_2)\eta t}{\pi r^4} \right]^{1/2} \]

Where, 
\( g = 980.66 \text{ cm/sec}^2 \); 
\( r = \text{radius(\textmu m)} \); 
\( \eta = 0.008937 \text{ poise [gm/cm sec]} \); 
\( d_1 = \text{density of the clay} \); 
\( d_2 = \text{density of water} = 0.9978 \text{ gm/cc} \); 
\( h = \text{depth of the suspension} \); 
\( t = \text{time in sec} \).
The rate of fall of different sized particles through a certain distance was calculated from this equation and accordingly used for separation of the desired size fractions of the clay. Thus the Mnt rich -2 μm fraction was separated from a 2% aqueous suspension of the bentonite prepared by dispersing about 20 gm of clay (ground and dried) in 1000 ml of distilled water. This suspension was allowed to stand for 8 hrs and then siphoned out from 20cm depth of the vessel, which was allowed to dry in an air oven at around 50 ± 5°C in flat trays. The clay after drying was hand ground in agate mortar and kept in dry bottles.

2.1.2 Transformation into homoionic Na-Mnt

Natural Mnt, after purification was found to contain more than one exchangeable cations. It is seldom found in homoionic state. For convenience in identification and other experiments, it was converted into homoionic form, usually, Na-form. The -2 μm particle size of the Mnt was taken and dispersed in distilled water as a 2% suspension and stirred well for half an hour. About 100 ml of 2M NaCl solution was added to 100 ml of clay suspension and stirred overnight and set aside for settling. The supernatant salt solution was removed and fresh NaCl solution was added again. This step was repeated to ensure complete exchange of all other interlayer cations like Ca²⁺, Mg²⁺ etc. After exchanged with Na⁺ ions enough fresh distilled water was added, stirred, settled
and decanted off. The large excess of salt was removed by this process. When the clay stopped settling, the remaining salt was removed by dialysis technique.

The clay suspension was taken in dialysis bags (pore size <0.2 μm) which were immersed in large quantity of distilled water. Water was kept on mild stirring and replaced with fresh water till the NaCl concentration was well below detection ascertained by AgNO₃ test for Cl⁻ ions and the conductivity value of the water which should be below 20 μS/cm. The clay was then dried in flat dishes in an air oven at around 50±5°C. Finally, the Na-Mnt was collected and kept in air-tight bottles.

2.1.3 Identification of the clay mineral

Identification of the clay mineral was done by XRD measurement substantiated by IR spectroscopy and thermal analysis.

2.1.3.1 Identification by XRD technique

The dry Na-Mnt was well dispersed in water as 2% suspension by sonication. A little of the suspension was allowed to drop slowly on a clean glass slide and allowed to dry undisturbed. One of such slides was used for XRD measurement. Another slide was dried at around 110°C in an air oven and was kept over ethylene glycol in an evacuated desiccator overnight. The XRD patterns for Na-Mnt₁ and Na-Mnt₂ and their ethylene glycol treated form were shown in
Fig. 2.1. The room temperature dried Na-Mnt$_1$ and Na-Mnt$_2$ showed basal spacing ($d_{001}$) of 12.4 and 12.5 Å respectively. Ethylene glycol treated Na-Mnt$_1$ and Na-Mnt$_2$ showed basal spacing of 16.1 Å and 16.5 Å respectively. These are the characteristic values for ethylene glycolated smectite (128).

2.1.3.2 Identification by IR spectroscopy

IR spectra of Na-Mnt$_1$ and Na-Mnt$_2$ (Fig. 2.2) showed characteristic peaks of smectite type clays. In the IR spectra of Na-Mnt$_1$ the peak in the range of 3630-3620 cm$^{-1}$ arose from OH-stretching vibrations in AlAlOH and AlMgOH environment. The peaks around 3430 and 1635 cm$^{-1}$ were due to OH-stretching and bending vibrations respectively for adsorbed water. The bands in the region 950-600 cm$^{-1}$ were for OH vibrations in different environments, e.g. peak at 917-916 cm$^{-1}$ was for AlAlOH, at 890 cm$^{-1}$ for AlFeOH and at 847 cm$^{-1}$ for AlMgOH bending vibrations while the peaks at 791 cm$^{-1}$ and at 688 cm$^{-1}$ were due to OH out-of-plane and in-plane bending vibration respectively. The Si-O stretching vibrations showed bands near 1050-1020 cm$^{-1}$ and Si-O bending vibration occurred in the region 550 - 460 cm$^{-1}$ (129, 130).

Similarly, the IR spectra of Na-Mnt$_2$ showed the characteristic bands for different vibrations at wavelengths 3630, 3432, 1637, 1045, 996, 890, 847, 798, 523 and 465 cm$^{-1}$. The peak at 847 cm$^{-1}$ is for AlMgOH bending vibration while others are similar to that of Na-Mnt$_1$. 
Fig. 2.1. XRD diffraction patterns of Mnt₁ (Neelkanth) and Mnt₂ (Wyoming) in Na-Mnt (A & C) and ethylene glycolated Mnt (B & D) form.
Fig. 2.2. Infrared spectra for Mnt$_1$ (a) (Neelkanth) and Mnt$_2$ (b) (Wyoming) in Na-Mnt form.
2.1.3.3 Identification by Thermal analysis

The TG-DTG curves for Na-Mnt (dotted line) and Na-Mnt$_2$ (solid line) showed mass loss in the regions 50-150°C and 450-700°C (Fig. 2.3). The first mass loss in the region 50-150°C was 13.9 and 11.95% for Na-Mnt$_1$ and Na-Mnt$_2$ respectively which was attributed to loss of adsorbed water. The second mass loss in the region 450-700°C was 3.8 and 4.2% for Na-Mnt$_1$ and Na-Mnt$_2$ respectively, which was due to dehydroxylation of the clay structure. The DTA curve showed two endothermic peaks in the regions 50-150°C and 450-700°C, which occurred due to the loss of interlayer and structural water respectively. The third small endothermic peak in the region around 900°C was due to dehydroxylation of the clay structure, which was immediately followed by an exothermic peak without any corresponding mass loss. The latter indicates phase transformation in the clay lattice (29).

2.1.4 Determination of Cation Exchange Capacity (CEC)

CEC was determined by standard methods after converting the clays into homoionic Na-Mnt form (131).

A standard CaCl$_2$ solution was prepared by dissolving fused CaCl$_2$ salt in absolute alcohol and standardized against ethylene-di-amine-tetraacetic acid (EDTA) solution. The EDTA solution was standardized with a primary standard such as Zn-acetate or Zn-sulphate solution (132). The titrations were carried out in a buffer medium (NH$_3$/NH$_4$Cl, pH-10) with Eriochrome black T or Solochrome.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Deriv. Wt. (%/°C)</th>
<th>Temp. Differ. (°C/mg)</th>
<th>Wt. Loss (%)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
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</tr>
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<td>0</td>
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</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>700</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>900</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

Fig. 2.3. TG-DTA-DTG curves for Mnt₁ (Neelkanth) and Mnt₂ (Wyoming) in Na-Mnt form
black T (EBT) as indicator. The wine red solution turned into a deep blue solution at the stable end point. For CEC determination, about 0.5 gm of dried Na-Mnt was treated with excess CaCl₂ solution over 24 hrs, the suspension was filtered and washed repeatedly with alcohol into a 100 ml volumetric flask. The volume was made up with distilled water. The complete washing was ascertained by AgNO₃ test for Cl⁻ ion. The amount of Ca²⁺ ions present was determined by titration against the EDTA solution. The difference between Ca²⁺ ion concentration before and after the exchange was the amount of Ca²⁺ ions adsorbed by the clay. This value expressed in meq / 100 gm (or mmol / 100 gm) of the dry clay gave the CEC of the clay. The amount of exchangeable Ca²⁺-ions was known by treating about 0.5 gm of dry clay with 1M NH₄-acetate solution for 24 hrs with constant stirring. The Ca²⁺ ions on the clay surface and interlayer were eluted into solution that was filtered and washed well with more NH₄-acetate. As the Ca²⁺ ion concentration was low in the filtrate, a dilute solution of standard EDTA was used for the titration. For Na-Ca-clay, both types of exchangeable ions were determined separately by the above mentioned methods and the sum of both values were taken as the total CEC (130). The CEC values for Mnt₁ and Mnt₂ clays are 114 and 90 meq/100gm respectively.
2.1.5 Chemical analysis of clay minerals

Chemical analysis of the clays Mnt₁ and Mnt₂ were carried out following standard procedures(131).

2.1.5.1 Loss on ignition (LOI)

The LOI was determined by heating almost 0.5 gm dry clay at 1000°C for 1 hr and weighed after cooling down in a desiccator. The difference in the weight was expressed as the percentage of the weight of the clay taken.

2.1.5.2 Determination of Silica

The clay was fused with about 2.5 gm of Na₂CO₃ at 950°C for half an hour in platinum crucible. The fused mass was extracted with hot 1:1 HCl. The crucibles were washed thoroughly with hot HCl followed by water and the washings were added to the extract. The extract was evaporated to dryness and then kept at 110°C in an oven for an hour, to which 5 ml of concentrated HCl was added followed by water. The mass was filtered through Whatman 40 quantitative filter paper and washed well with dilute HCl through the filter paper into the same filtrate (Filtrate No.1) in a 250 ml volumetric flask and the volume was made up with distilled water. The residue was freed from chloride ions by washing with small volumes of warm water. It was then burnt in a weighed platinum crucible at 1000°C for half an hour to a constant weight. In order to determine the possible
presence of other metal oxides, 5 ml of HF with a little H₂SO₄ was added and ignited at 1000°C to remove the silica.

2.1.5.3 Determination of Fe, Al as mixed oxide

About 50 ml of the Filtrate No.1 was taken in a 250 ml beaker and saturated with NH₄Cl. Excess of NH₄OH was added to it when Fe(OH)₃ and Al(OH)₃ was precipitated. It was heated to 40 – 60°C to coagulate the precipitate. A drop of NH₄OH was added to the supernatant solution to ensure complete precipitation and then filtered through Whatman Quantitative filter paper (No. 40 or 41) into a 250 ml volumetric flask (Filtrate No. 2); the residue was washed with dilute NH₃ solution and 1% NH₄NO₃ followed by distilled water. The residue was burnt at around 800°C to a constant weight. From the weight difference the amount of mixed oxide (Fe₂O₃·Al₂O₃) was determined. The volume of Filtrate No. 2 was made up to the mark and kept for further analysis.

2.1.5.4 Determination of Fe by titrimetric method

To determine the amount of Fe, about 25 ml of Filtrate No. 1 was taken out and taken into a 250 ml conical flask. To ensure reduction of all Fe³⁺ to Fe²⁺, the acidic solution was heated (70-90°C) and concentrated Stannous chloride (SnCl₂) solution was added to it drop wise with constant stirring until the yellow colour of the solution had nearly disappeared. The reduction was then completed with dilute Stannous chloride till the solution was of faint green colour. The
reduced solution was rapidly cooled and the slight excess of SnCl₂ was removed by adding 5% mercuric chloride solution. A silky white precipitation of mercurous chloride was observed.

About 8 drops of the indicator, sodium diphenylamine sulphonate(I) was added to the Fe²⁺ solution followed by 200 ml of 2.5% of H₂SO₄ acid and then 5 ml of 84% phosphoric acid. This was titrated slowly against standard potassium dichromate solution until it showed a bluish-green/greyish-blue tint near the end point. The titration was continued by drop wise addition of potassium dichromate solution till one drop turned the colour into intense purple or violet blue at the stable end point.

2.1.5.5 Determination of Ca and Mg

50 ml of Filtrate No. 2 was taken out into a 250 ml conical flask. 5 ml NH₃/NH₄Cl buffer (pH-10) was added followed by 20 mg of EBT (Eriochrome black T). The wine red titrate turned to blue sharply at the end point on titration with EDTA. The value obtained from it gave the total Ca and Mg content.

For Ca, Patton and Reeder's indicator (HHSSNA) was used with EDTA as the titrant. At the end point, the colour changed sharply from wine-red to blue. Before determining Ca, the Mg present in the solution was precipitated by adding 8 M KOH. The amount of Mg was determined by subtracting the amount of Ca from total Ca and Mg. The chemical composition of the clays Mnt₁ and Mnt₂ are given in the Table 2.1.
Table 2.1: The oxidic composition of Mnt₁ and Mnt₂

<table>
<thead>
<tr>
<th>Constituents (Wt%)</th>
<th>Mnt₁ (Neelkanth)</th>
<th>Mnt₂ (Wyoming)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.42</td>
<td>60.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.02</td>
<td>21.69</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.49</td>
<td>4.58</td>
</tr>
<tr>
<td>CaO</td>
<td>0.69</td>
<td>2.67</td>
</tr>
<tr>
<td>MgO</td>
<td>2.82</td>
<td>2.68</td>
</tr>
<tr>
<td>Others</td>
<td>1.74</td>
<td>0.13</td>
</tr>
<tr>
<td>LOI</td>
<td>17.51</td>
<td>7.75</td>
</tr>
</tbody>
</table>

2.1.6 Synthesis and characterization of metal complexes

Most of the metal complexes used for the present study were of the type [M(L-L)₃]X₂/X'. [M = Ni & Fe, L-L = 1,10-phenanthroline, (hereafter phen), 2,2'-bipyridyl, (hereafter bpy), X' = SO₄²⁻, X = Cl⁻, CH₃COO⁻ etc.] and [M(L-L-L)₂]X₂, [M = Ni, L-L-L = (2-aminoethyl)amine and 2,2':6',2''-terpyridine, X = ClO₄⁻, Cl⁻. These compounds were synthesized by following known methods.

2.1.6.1 Synthesis of [Ni (phen)₃]X₂/X' and [Ni (bpy)₃]X₂/X'

Metal salt (NiX₂/NiX') and phen were taken in a stoichiometric ratio of 1:3 and each was dissolved separately in distilled water and absolute alcohol respectively (133,134). Both the solutions were mixed together to give a deep burgundy colour solution. Light pink crystals of [Ni(phen)₃]X₂/X' were crystallized from this solution. These were recrystallized from alcohol and dried at 80-110°C in an oven and stored in airtight bottles.
Similarly, metal salt (NiX$_2$/NiX') and bpy were taken in a stoichiometric ratio of 1:3 and each was dissolved separately in distilled water and absolute alcohol respectively. Both the solutions were mixed together to give a deep burgundy colour solution. Light pink crystals of [Ni(bpy)$_3$]X$_2$/X' were crystallized from this solution. These were recrystallized from alcohol and dried at 80-110$^0$C in an oven and stored in airtight bottles.

2.1.6.4 Synthesis of [Fe (phen)$_3$]SO$_4$ and [Fe(bpy)$_3$]SO$_4$

Ferrous sulphate and phen were taken in a stoichiometric ratio of 1:3 and each was dissolved separately in distilled water and absolute alcohol respectively. Both the solutions were mixed together to give a blood red solution. Bright red crystals of [Fe(phen)$_3$]SO$_4$ were crystallized from this solution. These were recrystallized from alcohol and dried at 80-110$^0$C in an oven and stored in airtight bottles.

Similarly, ferrous sulphate and bpy were taken in a stoichiometric ratio of 1:3 and each was dissolved separately in distilled water and absolute alcohol respectively. Both the solutions were mixed together to give a blood red solution. Bright red crystals of [Fe(bpy)$_3$]SO$_4$ were crystallized from this solution. These were recrystallized from alcohol and dried at 80-110$^0$C in an oven and stored in airtight bottles.
2.1.6.5 Synthesis of [Ni{Di(2-aminoethyl)amine}2][Cl2]

A solution of Nickel chloride in a small volume of water was added to a slight excess of 2-aminoethyl amine in ethanol (1:2.2 mole ratio). The mauve product was filtered off from the cold solution and recrystallized from hot water and dried at around 80-110°C in an air oven and stored in airtight bottles.

2.1.6.6 Synthesis of [Ni(2,2': 6',2''-terpyridine)2](ClO4)2.

The pale brown crystalline compound was obtained from Prof. A. T. Baker. University of Technology, Sydney, as a gift for the study.

2.1.7 Hydration of Mnt under restricted conditions

Mnt1 was purified and transformed to Na form as described in previous sections. Mnt in ½Na-½Ca form was taken in comparison with Na-Mnt and Ca-Mnt.

2.1.7.1 Transformation to Ca-Mnt

1.0 gm of Na-Mnt was dispersed in 100 ml of distilled water and treated with 100 ml of 1M CaCl2 repeatedly for 72 hrs. Then, the clay was washed with distilled water to remove the large excess of salt by decantation and was finally dialysed in dialysis bags till the conductivity of the water was below 20 μS/cm and showed negative test for chloride ion by AgNO3 test. The clay was dried at around 50±5°C in air oven and ground in an agate mortar to powder.
2.1.7.2 Transformation to $\frac{1}{2}$Na-$\frac{1}{2}$Ca-Mnt

1 gm of Na-Mnt was dispersed in 100 ml of distilled water and treated with 0.6 ml of 1M CaCl₂ repeatedly for 72 hrs. The clay was then washed with distilled water to remove the large excess of salt by decantation and dialysed in dialysis bags till the conductivity of the water show a value below 20 μS/cm and negative test for chloride ion by AgNO₃ test. The clay was dried at around 50±5°C in air oven and ground in an agate mortar to powder.

2.1.7.3 Hydration of clay films under restricted condition

Oriented films for each of the clays i.e., Na-Mnt, Ca-Mnt and $\frac{1}{2}$Na-$\frac{1}{2}$Ca-Mnt were prepared on slides. Desiccators were charged with saturated aqueous salt solutions of LiCl, CrO₃, Zn(NO₃)₂·6H₂O, KBr, CuCl₂·2H₂O and water. The relative humidities (RH-hereafter) at 20°C in the desiccators were 11, 32, 42, 68, 84 and 100 % respectively. The clay films were heated in air oven at 110°C for about one hour and allowed to cool in desiccator over P₂O₅ and XRD patterns were taken. The dried films were then kept in respective desiccators and XRD patterns were taken after 24, 72, 168 and 240 hrs of hydration.

2.1.8 Intercalation and intersalation reactions of trisdiimine metal complexes with Na-Mnt

Mnt₁ was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of trisdiimine metal
complexes of the type \([M(L-L)\_3]^X_2, [M = Ni, L-L = phen, bpy and X = SO\_4^{2-}.Cl^-]\) was also done as described before.

### 2.1.8.1 Adsorption (intercalation/ intersalation) reactions

**a) Under ultrasonic irradiation**

About 50 mg of finely ground clay (dried at 50 ± 5°C) was directly added to each of 10 ml solution containing 0.1, 0.5, 1.0, 2.0 and 4.0 CEC-Eqv. of metal complexes. Alternately, 50 mg clay was dispersed in 10 ml water under ultrasonic vibration for about 10 min and the respective solution of metal complex was added to it. The whole mass was ultrasonicated under closed condition for 30 min with the help of an ultrasonic bath. In another experimental condition, 50 mg of finely ground clay (dried at 50 ± 5°C) was directly added to 10 ml solution containing 4.0 CEC-Eqv. of metal complexes and ultrasonicated under closed condition from 1 to 60 min. The clay-adsorbed products were filtered through sintered bed under mild suction and the filtrate was analysed for unadsorbed metal complex. The residue was washed thoroughly with distilled water and dried at 50 ± 5°C in an air oven.

**b) Under refluxing condition**

Dry clay or slurry of it was directly added to the solution of metal complexes and the mass was refluxed at about 100°C under stirring condition for about 30 min followed by filtration and drying as in 2.1.8.1a.
(c) Under autoclaving condition

Dry clay or slurry of it was added directly to the metal complex salt solution (as in 2.1.8.1a) and was autoclaved in a closed steel reactor lined with teflon at 120°C (at 2 atm. pressure) for a period of 30 min under a rolling condition in a roller oven. In another experimental condition, 50 mg of solid clay was directly added to 10 ml solution containing about 4 CEC-Eqv. of \([\text{Ni(phen)}_3]\text{SO}_4\). The mass was autoclaved separately in closed teflon coated pressure reactor for 30 min at 80, 90, 100, 110 and 120°C (corresponding pressure 0.5, 0.7, 1.0, 1.4 and 2.0 atm.). The adsorbed products were then washed and dried as in 2.1.8.1a.

(d) Under vigorous stirring

Dry clay or slurry of it was added directly to the metal complex salt solution and the whole mass was vigorously stirred under closed condition with the help of magnetic stirrer for about 30 min and then filtered and dried as in 2.1.8.1a.

2.1.8.2 Intercalation reactions of \([\text{Ni(phen)}_3]\text{SO}_4/\text{Cl}_2\) with Na-Mnt in presence of \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{Cl}\)

Mnt\text{t} was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of trisdiimine metal
complexes of the type $[\text{M(L-L)}_3X_2/X']$ [M = Ni, L-L = phen, $X' = \text{SO}_4^{2-}$, $X = \text{Cl}^{-}$] was also done as described before. The effect of salts $(\text{NH}_4)_2\text{SO}_4$ and $\text{NH}_4\text{Cl}$ was observed on intersalation reaction of dispersed clay with the metal complexes.

(a) 0.025 gm of Na-Mnt was dispersed in about 5.0 ml of distilled water by sonication. To it 5.0 ml of solution containing of 4.0 CEC Eqv of $[\text{Ni(phen)}_3]\text{SO}_4$ was added and stirred for 24 hrs. The slurry was centrifuged and analyzed as in 2.1.8.1a.

(b) 0.025 gm of Na-Mnt was dispersed in about 5.0 ml of distilled water by sonication. To it 5.0 ml of solution containing of 4.0 CEC Eqv of $[\text{Ni(phen)}_3]\text{SO}_4$ and 4.0 CEC Eqv of $(\text{NH}_4)_2\text{SO}_4$ was added to the dispersion followed by stirring for 24 hrs. The slurry was centrifuged and analyzed as in 2.1.8.1a.

(c) 0.025 gm of Na-Mnt was dispersed in about 5.0 ml of distilled water by sonication and 5.0 ml of solution containing about 4.0 CEC Eqv of $[\text{Ni(phen)}_3]\text{Cl}_2$ was added to it and stirred for 24 hrs. The slurry was centrifuged and analyzed as in 2.1.8.1a.

(d) 0.025 gm of Na-Mnt was dispersed in about 5.0 ml of distilled water by sonication. 5.0 ml of solution containing about 4.0 CEC Eqv of $[\text{Ni(phen)}_3]\text{Cl}_2$ and 4.0 CEC Eqv of $\text{NH}_4\text{Cl}$ was added to it and stirred for 24 hrs. The slurry was centrifuged and analyzed as in 2.1.8.1a.
2.1.8.3 Intercalation reactions of trisdiimine metal complexes with different fractions of Na-Mnt

Mnt\textsubscript{i} was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of trisdiimine metal complexes of the type \([M(L-L)_3]X_2/X', [M = Ni, L-L = phen, bpy and X' = SO_4^{2-}, X=Cl, CH_3COO^-]\) was also done as described before.

(a) Separation of Na-Mnt\textsubscript{i} into fractions

The size fractions (-2.0 +1.5) \(\mu\text{m}\), (-1.5 +1.0) \(\mu\text{m}\), (-1.0+0.5) \(\mu\text{m}\) and -0.5 \(\mu\text{m}\) were separated from a 2\% suspension of -2\(\mu\text{m}\) Na-Mnt following Stokes' law. The procedure followed was similar to section 2.1, with a little modification.

The clay suspension was allowed to stand for 16 hrs. The fraction withdrawn from the depth of 10 cm was -1.5 \(\mu\text{m}\), while the remaining lower portion was (-2+1.5) \(\mu\text{m}\) fraction, where <1.5 \(\mu\text{m}\) was absent. This was allowed to dry around 50± 5\(^{\circ}\)C in air oven. The suspension containing -1.5 \(\mu\text{m}\) size fraction was again allowed to stand for 24 hrs. The suspension withdrawn from the depth of 10 cm after 24 hrs contained -1.0 \(\mu\text{m}\) size fraction, while the remaining lower portion contained (-1.5+1.0) \(\mu\text{m}\) fractions. The suspension containing -1.0 \(\mu\text{m}\) fraction was allowed to stand for 32 hrs. The fraction withdrawn from 5 cm depth was -0.5 \(\mu\text{m}\) and the remaining part was (-1.0+0.5)
μm size fraction of Mnt. All the size fractions were dried around 50± 5°C in air oven, ground in an agate mortar to a fine powder and kept in air-tight bottles.

(b) Intercalation (under sonication by horn)

-0.5 μm, (-1.0 +0.5) μm, (-1.5 +1.0) μm and (-2.0+1.5) μm size fractions of Mnt were taken in four separate glass tubes (0.025 gm each) and dispersed in 2.5 ml of distilled water by sonication for 2 min. To it 2.5 ml of 0.0228 M solution of [Ni(phen)₃]SO₄ was added and sonicated with an ultrasonic horn for 2, 6 and 10 min. The slurries were centrifuged at 10,000 rpm and supernatant solutions were estimated by UV-VIS spectrophotometer. XRD patterns for the metal complex-clay composites were taken. Similarly, for other metal complexes the experiment was carried out with all the four fractions.

(c) Intercalation (under microwave irradiation)

The intercalation reaction of metal complexes with the different size fractions of clay were observed under microwave heating similarly as in case of sonication. The heating was done in 'simmer' (~100°C) and 'low' (~80°C) regions and to avoid evaporation of the metal complex solution, heating was done stepwise i.e. 2 min at a step. The reaction time was taken as 2, 6 and 10 min.
Intercalation (under stirring condition)

The intercalation reactions of metal complexes with the different size fractions of clay were observed under stirring condition at room temperature similarly as in 2.1.8.3.c.

2.1.9 Adsorption reaction of [Fe(phen)₃]SO₄ with Na-Mnt in different states of aggregation

Na-Mnt was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of [Fe(phen)₃]SO₄ was also done as described previously.

(a) Adsorption of [Fe(phen)₃]SO₄ by Na-Mnt in dry, highly aggregated state

Na-Mnt, dried around 50 ± 5°C for 48 hrs. was stirred with aqueous solutions of [Fe(phen)₃]SO₄ containing 1.0 and 4.0 CEC Eqv of metal complex. Aliquots were drawn at 2 min, 30 min, 1 day, 7 days, 15 days, 21 days and 24 days. The slurries were centrifuged at 10,000 rpm. XRD patterns for the metal complex – clay composites were taken.

(b) Adsorption of [Fe(phen)₃]SO₄ by Na-Mnt in dispersed state

Na-Mnt was sonicated in an ultrasonic bath for 10 min in water (1% w/w aqueous suspension) and stirred with 1.0 and 4.0 CEC-Eqv. of metal complex. The reaction was carried out as in 2.1.9.a.
(c) Adsorption of $[\text{Fe(phen)}_3]\text{SO}_4$ by Na - Mnt in delaminated state

Na - Mnt was stirred in water as 1% w/w suspension for 7 days and stirred with 1.0 and 4.0 CEC-Eqv. of metal complex. The reaction was carried out as in 2.1.9.a.

2.1.9.1 Adsorption of $[\text{Fe(phen)}_3]\text{SO}_4$ by Na-Mnt in presence NaCl

Here, four reactions were carried out with 0.015 gm of 2 μm Na-Mnt each. Clay was dispersed in 3 ml of distilled water.

(a) To the clay slurry 1.5 ml of 0.0228 M solution of $[\text{Fe(phen)}_3]\text{SO}_4$ (about 4.0 CEC-Eqv) was added.

(b) 0.04 ml of 1 M NaCl (about 1.0 CEC-Eqv) was added to the clay slurry and stirred for 2 min. Aqueous solution containing 4.0 CEC-Eqv of $[\text{Fe(phen)}_3]\text{SO}_4$ was added and stirred for 30 min.

(c) 0.14 ml of 1 M NaCl (about 3.0 CEC-Eqv) was added to the clay slurry and stirred for 2 min. Aqueous solution containing 4.0 CEC-Eqv of $[\text{Fe(phen)}_3]\text{SO}_4$ was added and stirred for 30 min.

(d) Finally, excess of 1 M NaCl (in about 0.6 ml) was added to the clay slurry and stirred for 2 min. Aqueous solution containing 4.0 CEC-Eqv of $[\text{Fe(phen)}_3]\text{SO}_4$ was added and stirred for 30 min.
The suspensions were centrifuged at 10,000 rpm for 15 min and the centrifugates were analyzed by UV-VIS spectrophotometer. XRD patterns were taken from the oriented slides prepared from the washed residues.

2.1.10 Intercalation reactions of [Ni(di(2-amino ethyl)amine)₂]Cl₂ and [Ni(2,2':6',2''- terpyridine)₂](ClO₄)₂ with Na-Mnt

Mnt₁ was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of the metal complexes was also done as described previously.

(a) Intercalation reaction of [Ni(di(2-amino ethyl)amine)₂]Cl₂

A 0.0228M solution of the metal complex [Ni(di(2-aminoethyl)amine)₂]Cl₂ (hereafter[Ni(den)₂]Cl₂) was prepared by dissolving 0.1858 gm of it in 25 ml of distilled water.

0.025 gm of Na-Mnt was dispersed in distilled water by 10 min sonication. 1.0 CEC-Eqv. of metal complex in 0.63 ml of water was added to the clay slurry. The total volume of the suspension was almost 10 ml which was stirred for 30 min.

0.025 gm of Na-Mnt was dispersed in distilled water by 10 min sonication. 4.0 CEC-Eqv. of metal complex in 2.52 ml of water was added to the clay slurry and stirred for 30 min. The total volume of the suspension was almost 10 ml.
All the suspensions were centrifuged at 10,000 rpm and the residues were washed 3-4 times with distilled water. The centrifugate was analyzed by UV-VIS spectrophotometer and XRD. IR spectroscopic and Thermal analysis of the clay composites were done.

(b) Intercalation reaction of \([\text{Ni (2,2':6',2''-terpyridine)}_2\text{(ClO}_4\text{)}_2]\)

\([\text{Ni (2,2':6',2'' - terpyridine)}_2\text{(ClO}_4\text{)}_2\text{, (hereafter [Ni (tpy)}_2\text{(ClO}_4\text{)}_2\text{). was not much soluble in water. 0.105 gm of the metal complex was dissolved in warm water and allowed to stir for 30 min with clay suspension containing 0.025 gm of Na-Mnt. The metal complex was about 1.0 CEC-Eqv. of the clay.}

Again, another clay suspension was prepared with 0.025 gm Na-Mnt in 5 ml distilled water. 4.0 CEC-Eqv of the metal complex (0.423 gm) was dissolved in 5 ml of warm water and added to the clay slurry which was stirred for 30 min.

The clay suspensions were centrifuged at 10,000 rpm and the residues were washed with distilled water. The amount of adsorbed metal complex was determined by Elemental (C, H, N) analyzer. XRD, IR spectrometric and Thermal analysis of the clay composites were done.

2.1.11 Synthesis of phosphate-bridged-Mnt from Na-Mnt and their intercalation properties:

2.1.11.1 Synthesis of phosphate-bridged-Mnt
0.025 gm of Na-Mnt of size fraction -2 μm was dried and dispersed in 100 ml of 1×10^{-2} M ortho-phosphoric acid solution by ultrasonication for about 15 min. The turbid suspension thus formed was allowed to stand. The mass settling down to give a clear supernatant solution was the phosphate-linked-Mnt (hereafter, Po-Mnt). The supernatant was discarded while the clay was washed with distilled water several times. Finally, it was dialyzed to remove the excess acid and dried at room temperature. XRD, IR spectrometric, SEM-EDX and thermal analysis of Po-Mnt were carried out.

A film prepared from Po-Mnt was kept in hot water (~90°C) for several hrs., which remained stable. While another film prepared from Na-Mnt delaminated after sometime, even at room temperature.

2.1.11.2 Determination of total acidity of Po-Mnt

About 0.2 gm of Po was suspended in 100 ml of water and treated repeatedly with small volumes of 1M KCl. All of the treated KCl was collected together along with the washings of the clay. This was titrated against standardised NaOH. The amount of NaOH required gave the total acidity of the clay which was about 18 meq/100 gm.

2.1.11.3 Intercalation reaction of [Ni(phen)₃]SO₄ with Po-Mnt
0.025 gm of Po-Mnt was suspended in 10 ml of distilled water by sonication. To it 0.2, 1.0, 2.0 and 4.0 CEC-Eqv of [Ni(phen)$_3$]SO$_4$ in solution was added separately and stirred for 30 min. The slurries were centrifuged at 10,000 rpm and the remaining metal complexes in the centrifugates were estimated by UV-VIS spectrophotometer. The metal complex-Po-Mnt composites were analysed by XRD and IR spectrometric methods. The CEC of the Po-Mnt was estimated from the amount of metal complex adsorbed on addition of about 114 meq of metal complex to dispersed Po-Mnt.

2.1.12 Synthesis of the pillared clay composites useful as solid acid catalysts

(a) About 1.0 gm of dried Na-Mnt$_2$ clay (Wyoming) was dispersed in 250 ml of distilled water by stirring and then by sonication for 10 min. To it 10 ml of aqueous solution containing 0.156 gm (0.5 CEC-Eqv.) of [Ni(phen)$_3$]Cl$_2$ was added and stirred for 1 hr. The mass was centrifuged at 12,000 rpm for 15 min and washed well with distilled water. It was redispersed in 250 ml of distilled water and 0.0724 gm AlCl$_3$ in 20 ml of water was added to it. The slurry was stirred for 48 hrs and centrifuged again. The mass was washed and dried at 200°C for about 3-4 hrs.

(b) About 1.0 gm of dried Na-Mnt$_1$ clay (Jodhpur) was dispersed in 250 ml of distilled water by stirring and then by sonication for 10 min. To it 10 ml of aqueous solution containing 0.198 gm (0.5 CEC-Eqv) of [Ni(phen)$_3$]Cl$_2$ was
added and stirred for 1 hr. The mass was centrifuged at 12,000 rpm for 15 min and washed well with distilled water. It was redispersed in 250 ml of distilled water and 0.0917 gm AlCl$_3$ in 20 ml of water was added to it. The slurry was stirred for 48 hrs and centrifuged again. The residual mass was washed and dried as in 2.1.12(a).

2.1.12.1 Benzylation reaction

The Al-[Ni(phen)$_3$]-Mnt composites for both the clays Mnt$_1$ and Mnt$_2$ are used as Friedel-Crafts catalyst in the benzylation reaction. Benzene (~15 ml) and benzyl chloride (~0.5 ml) were taken and stirred at room temperature with the catalytic composite (~1.0 gm) containing about 0.5 CEC-Eqv. of the metal ion. The product diphenylamine was analysed by GC.

2.1.13 Application of some metal-metal complex-Mnt composites as deodorants

Mnt$_1$(Neelkantha clay) was purified and transformed to Na form as described in previous sections. The characterisation of the clay and synthesis of the metal complexes were also done as described previously. Here, the Na-Mnt was partially exchanged with a metal complex like [Ni(phen)$_3$]$^{2+}$ or [Ni(bpy)$_3$]$^{2+}$ and partially with an active metal like Cu$^{2+}$ or Cd$^{2+}$. 

2.1.13.1 Synthesis of Cu-[Ni(phen)_3]- and Cu-[Ni(bpy)_3]-Mnt

(a) 0.5 gm of -2 μm Na-Mnt was dispersed in 200 ml of distilled water under constant stirring followed by ultrasonication. To it, an aqueous solution containing 0.2 CEC-Eqv of [Ni(phen)_3]^{2+} or [Ni(bpy)_3]^{2+} was added and stirred for 30 min. The slurry was centrifuged at 12,000 rpm for 15 min, and after washing, the residue was redispersed in 200 ml of water. To this suspension 0.038 gm of CuCl_2 (0.8 CEC-Eqv) in water was added and stirred for 24 hrs. The suspension was centrifuged and residue was washed. Exchange of Cu^{2+} was repeated to ensure required loading.

Finally, the residue was washed and dried at around 50 ± 5°C in air oven for 8 hrs. The light blue product was kept in airtight bottles.

(b) 0.5 gm of Na-Mnt was dispersed in 200 ml of distilled water and 0.5 CEC-Eqv. of [Ni(phen)_3]^{2+} or [Ni(bpy)_3]^{2+} was added to it and stirred for 30 min. The slurry was centrifuged at 12,000 rpm for 15 min and the residue was washed with distilled water and redispersed in 200 ml water. 0.5 CEC-Eqv of CuCl_2 (0.024 gm) in water was added to the slurry and stirred for 24 hrs. The suspension was centrifuged as before. The residue was washed with distilled water and dried at around 50 ± 5°C in air oven for 8 hrs. The light blue product was kept in dry bottles.
2.1.13.2 Synthesis of Cd-[Ni(phen)$_3$]- and Cd-[Ni(bpy)$_3$] -Mnt

(a) The metal complex Mnt composite was prepared by dispersing 0.5 gm Na-Mnt in water and treating the clay with 0.2 CEC-Eqv of [Ni(phen)$_3$]$^{2+}$ or [Ni(bpy)$_3$]$^{2+}$. The slurry was centrifuged and washed. The composite was redispersed in 200 ml of distilled water and 0.8 CEC-Eqv of CdCl$_2$ (0.052 gm) in water was added to the suspension. The reaction was completed as in 2.1.13.1. The composite obtained was pale gray.

(b) Similarly, another metal complex–Mnt composite was prepared by treating 0.5 CEC-Eqv of [Ni(phen)$_3$]$^{2+}$ or [Ni(bpy)$_3$]$^{2+}$ and 0.5 gm of dispersed Na-Mnt. After centrifuging and washing the mass, it was again dispersed in 200 ml of distilled water and 0.5 CEC-Eqv of CdCl$_2$ (0.032 gm) was added to it. The reaction was completed as in 2.1.13.1. The composite was pale gray.

2.1.13.3 Adsorption of H$_2$S and NH$_3$ gas by the Cu/Cd-metal complex-Mnt composites

The metal-metal complex-clay composites were dried at around 50 ± 5°C for 8 hrs. The composites containing Cu$^{2+}$ ions were exposed to H$_2$S and NH$_3$ gas when the colour became black and blue respectively. When the composites containing Cd$^{2+}$ ions were exposed to H$_2$S gas, the pale gray colour of the mass turned yellow.
2.2 Instruments

The instrumental details are given in this section under the following headings.

2.2.1 Infrared spectrophotometer

Infrared spectrophotometer was used frequently in identifying the Mnt and metal complex-Mnt composites. The instrument used was Perkin-Elmer Infrared Spectrophotometer, Model 580B.

The FT-IR spectra were taken in KBr (analytical grade and dried at 110°C) pressed disc of about 12 mm diameter and 1 mm thickness, prepared by applying about 1 ton pressure for about 10 min on finely ground particles containing about 3 mg material and 97 mg KBr in the range 400-4000 cm⁻¹.

2.2.2 X-ray diffractometer

The X-ray diffraction patterns were taken in the range 2θ = 2-60° at a rate of 6°/min using CuKα radiation. The instrument used was X-Ray Diffractometer Jeol JDX-1lp3A, Japan.

2.2.3 Thermal Analyzers

The thermogravimetric (TG), Differential thermogravimetric (DTG) and Differential thermal analysis (DTA) were carried out with thermal analyzers at a
heating rate at 20°C/min in air atmosphere. The instruments were Shimadzu Model 30-H, Kyota, Japan and TA instruments Model SDT 2960, Simultaneous DTA-DTG. Some analyses were done with the help of instrument of Model Universal V2.3C TA instruments.

2.2.4 UV-VIS Spectrophotometer

The measurements by UV-VIS spectrophotometer were done in the wavelength range of 400-1000 nm. The instrument used was Shimadzu, UV-160 A, Japan.

2.2.5 C, H, N - Analyzer

The elemental analysis was carried out by a C, H, N -Analyzer from Perkin-Elmer, Model 2400.

2.1.7 Surface area measurement

The BET surface area was measured with the help of an instrument of Model Coulter SA.

2.1.8 Gas Chromatogram

The gas chromatogram used was of the Model Chemito 8510 FIDGC.

2.1.9 Autoclave

For autoclaving Roller Oven used was of the Model Chromalox, OFI, Testing Equipment USA, Part No. 17300, Serial No. 87-38.

Another instrument used was from Heidolph, Germany Type MR 3001K8.
2.1.10 Ultrasonicator

Ultrasonic bath used were (i) Julabo type USR 1/2 905, HF frequency 35KHz. (ii) Julabo type USR 3/3, HF frequency 35 KHz.

The ultrasonic horn used was Virsonic Cell Disrupter, Model 16-850.

2.1.11 Microwave oven

The microwave oven used was from LG Multiwave, Model MF 283MC.

2.1.12 Ultracentrifuge

The ultracentrifuge used was Sorval Plus, Dupont, USA.

2.1.13 SEM-EDX

SEM-EDX experiments were carried out in an instrument of Model SEM (LEO S4301), UK coupled with link ISIS detector for Energy Dispersive X-Ray analysis (EDX).