Chapter 1
INTRODUCTION

1.1 Objectives of the Present Work
The principal objectives of this work have been formulated as:

(i) To prepare adsorbents from common clay minerals such as kaolinite and montmorillonite by calcination under controlled conditions,

(ii) To prepare other adsorbents from kaolinite and montmorillonite by intercalating with polyoxo and quaternary ammonium cations, and also by acid treatment,

(iii) To characterize the adsorbents with XRD and FTIR, and to determine such properties as specific surface area, cation exchange capacity (CEC), etc.,

(iv) To use the adsorbents in batch process for removing toxic metal cations from water by using synthetic effluents, and to evaluate the effects of various experimental conditions such as pH, concentration of metal ions, amount of adsorbent, etc. on adsorption capacity,

(v) To make a thorough study of the kinetics of adsorbate-adsorbent interactions in order to understand the mechanism of the interactions,

(vi) To test the validity and applicability of different adsorption isotherms to the adsorption equilibrium and hence to find out adsorption affinity and adsorption capacity of the natural and modified clays for the metal adsorbates, and

(vii) To determine the relevant thermodynamic parameters, $\Delta H$, $\Delta S$, $\Delta G$, for all the clay-metal interaction processes in order to examine spontaneity and other relevant characteristics that determine the suitability or otherwise of the adsorbents.

1.2 Clays and Clay Minerals: General and Structural Features
1.2.1 General features
The term clay is used to refer to the finest-grain natural, earthy argillaceous particles in a sediment, soil or rock. It is an aggregate of minerals and colloidal substances (Grim, 1962). According to Wentworth scale or $\phi$-scale (phi-scale) (Wentworth, 1922), geologists define clay minerals as hydrated alumino phyllosilicates smaller than 4$\mu$. However, the general definition of these hydrous alumino-silicate minerals includes
those minerals that dominantly make up the colloid fraction (< 2μ) of soils, sediments, rocks and water (Pinnavaia, 1983). The term clay is used in reference to material that becomes plastic when mixed with a small amount of water (Klein and Hurlbut, 1985). The particles of clay minerals may be crystalline or amorphous, platy or fibrous and may vary from colloid dimensions to those above the limit of resolution of an ordinary microscope (Deer et al., 1985a). Krishnaswamy (1972) has recognized seven different types of clay depending on the basis of physical and refractory properties. They are:

1. Pottery clay: It is the most common form used in making pottery.
2. China clay or Kaolin: This type of clay is known to produce a high degree of colloidal suspension in water, which is produced by the decomposition of feldspars in granites.
3. Fire clay: This is used for making furnaces, etc.
4. Lithomarge: This type of clay is a residual part formed in a tropical climate, having poor suspension ability in water.
5. Ball clay: This type of clay shows a high degree of plasticity with refractory characteristics up to 1100°C.
6. Fuller's Earth: This is natural bleaching clay, generally used as a remover of grease.
7. Bentonite: This is essentially made up of the particular clay mineral, 'montmorillonite' having a volcanic origin. The light greenish gray or buff coloured plastic clay is used in petroleum industry for drilling mud.

1.2.2 Origin, occurrence and formation
Clays, together with organic matter, water, and air, are the main components of soil. Accordingly, clays can be broadly classified into three types:

1. Neoformed clays: These can form directly in a soil by precipitation from solution. Neoformed clays that have undergone instance leaching are composed of least soluble elements such as Fe³⁺, Al³⁺ and Si⁴⁺. These soils contain clays such as gibbsite, kaolinite, goethite and amorphous oxides and hydroxides of aluminum and iron. Clays formed in soils that are poorly drained can contain more soluble
elements such as Na	extsuperscript{+}, K	extsuperscript{+}, Ca	extsuperscript{2+} and Mg	extsuperscript{2+} in addition to the least soluble elements. These soils contain clays such as smectite, chlorite and illite.

2. *Transformed clays*: These can form from the partial alteration of clays already present in the soil. The examples of this type of clay includes soil chlorite and soil vermiculite, the first type is formed by the precipitation of aluminum hydroxide in smectite interlayers and the second one is formed by the leaching of interlayer potassium from illite.

3. *Inherited clays*: These types of clays are inherited from the underlying bedrock or from sediments transported into the soil by wind, water or ice. Examples of inherited clays in a soil are illite and chlorite – containing soils formed on shale composed of these minerals.

In the genesis of clay minerals in soils, there are three important factors to be considered:

(i) Chemical composition of the parent rock and its porosity.
(ii) The drainage of the area in which a weathering rock is situated.
(iii) The climate.

1.2.3 Soil mineralogy

The minerals in soils can be classified into (a) Primary minerals, which are formed at elevated temperatures and inherited from the igneous and metamorphic rocks, and (b) Secondary minerals, those formed by low temperature reactions and inherited by soils from sedimentary rocks or formed in soils by weathering (Brewer, 1964; Dixon and Weed, 1977). Primary minerals make up the main part of sand (particles ranging from 0.05 – 1.00 mm in diameter) and silt (particles ranging from 0.002 – 0.05 mm in diameter) fractions of most soils. Primary minerals occur in the clay fraction (particles less than 0.002 mm in diameter) of little weathered soils, e.g., those derived from fine-grained rock floor derived by glacial grinding of rocks. Layer silicates of soils, play a prominent role in most soils in determining the physical properties such as plasticity,
structure and chemical properties such as cation exchange, ion release, and ion fixation (Stelly and Dinauer, 1968). The deposition of significant amounts of mica, vermiculite, and other layer silicates as well as quartz and carbonates occurs as aerosolic dusts. These are common in the arid regions of both hemispheres, transported by circumglobal westerly winds and deposited in rainfall on land and ocean bottom (Jackson et al., 1973). Micas occur almost universally in soil clays, primarily originating by inheritance from the parent rock from which the soil was formed.

Vermiculite, which is a product of weathering of micas and possibly also of chlorites, occurs extensively in soils. Potassium in micas has been replaced predominantly by exchangeable calcium, aluminum, and magnesium and the interlayer space is expanded to yield a unit cell c-spacing of 14 Å or more so as to accommodate exchangeable interlayer cations and water (Ramon and Jackson, 1964). The minerals of the montmorillonite or smectite isomorphous series are freely expansible layer silicates responsible for soil plasticity. An environment abundant in the exchangeable cations, calcium and magnesium, silica rich, moist, and not excessively leached, favours the formation of montmorillonite. Kaolinite occurs commonly in well-weathered soils.

### 1.2.4 Structural features

The clay minerals have well defined crystal structure composed of two basic units:

(i) A tetrahedral sheet composed of silicon-oxygen tetrahedra linked to neighboring tetrahedra by sharing three corners to form a hexagonal network, and,

(ii) An octahedral sheet usually composed of six oxygen atoms or hydroxyl groups arranged in an approximately regular octahedron around aluminum or some other cations with the adjacent octahedra being shared. Fig. 1.1 represents the tetrahedral and the octahedral units.
Fig. 1.1: The tetrahedral and the octahedral units of clay structure (a) silica tetrahedron, (b) Al, Mg octahedron
Two types of clay minerals are recognized from the point of view of structure. They are:

(a) **Clay mineral with two-layer sheet**: Some clay minerals consist of repeating layers of two-layer sheet. A two-layer sheet is a combination of a tetrahedral layer (T) and an octahedral layer (O) as the repeating unit. The sheets are about 7.2 Å thick. The repeating layers are held together by hydrogen bonding and secondary valence force e.g. kaolinite.

(b) **Clay mineral with three-layer sheet**: The most common clay minerals with three-layer sheet are illite and montmorillonite. A three-layer sheet consists of an octahedral sheet (O) in the middle with tetrahedral sheet (T) at the top and one at the bottom. Repeated layers of these sheets form the clay minerals.

The stacking pattern of the two types of clay minerals can be represented as:

Two-layer sheet: – (TO) – (TO) – (TO) –
Three-layer sheet: – (TOT) – (TOT) – (TOT) –

These two patterns were first outlined by Pauling (1930a). A number of workers (Newnham and Brindly, 1956; Brindly, 1961; Radoslovich and Norrish, 1962, Grim, 1968a) reported that considerable distortion of the clay units must be considered in order to fit them into determined unit cell dimensions of the minerals. The interlayer space in clay minerals is the space between two layers. Each layer may be electrically neutral or may not be. In the first case, there need not contain any chemical species in the interlayer space; but in the later case, some additional ions may be present in the interlayer space to neutralize the charge of the layer. The cations like K\textsuperscript{+}, Na\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, etc., are sometimes present to neutralize the excess negative charge in the interlayer space and make the clay mineral neutral as a whole.

**1.2.5 Classification**

Clay minerals are classified by their arrangement of tetrahedral and octahedral sheets. Thus, 1:1 clay minerals contain one tetrahedral and one octahedral sheet per clay layer; 2:1 clay mineral contains two tetrahedral sheets with an octahedral sheet between them. Similarly, 2:1:1 clay mineral contains an octahedral sheet that is adjacent to a 2:1 layer.
These are classified further according to whether the octahedral sheet is dioctahedral or trioctahedral. In dioctahedral clays, two out of three cation positions in the octahedral sheet are filled, every third position being vacant. In trioctahedral clay minerals, all three octahedral positions are occupied. The main groups of the clay minerals that occur commonly in nature are (Bailey, 1988; Baruah, 1998):

1. The **kaolinite group** includes kaolinite, dickite, and halloysite. Halloysite contains a monomolecular layer of water in the interlayer position, increasing the basal spacing from 7 to 10.1 Å. Halloysite occurs as curled plates or tubes and dehydrates irreversibly to metahalloysite upon drying. The basal spacing of metahalloysite is 7.2 Å, so halloysite is seldom recognized in samples that have been allowed to dry between collection and analysis.

2. The **mica group** includes muscovite, illite, and glauconite. The common polymorphs of muscovite, 1M and 2M, differ in the stacking arrangement of their layers. Only the 2M polymorph is thermodynamically stable, but the 1M and 1Md (1M with deformation as in illite) forms are nevertheless common in nature. Biotite is a trioctahedral mica, but its basal spacing is similar to that of the other micas, about 10 Å.

3. The **smectite group** includes montmorillonite and vermiculite. Both minerals have interlayer water, but montmorillonite is commonly dioctahedral whereas vermiculite is trioctahedral.

4. The **chlorite group** includes penninite, clinochlore, ripidolite and chamosite, among other named varieties. All are similar in structure, differing mainly in cation composition. It is relatively easy to distinguish low-Fe from high-Fe chlorites on the basis of their basal spacing. Chlorites have a brucite layer in the interlayer position.

Apart from this classification, some mixed layer clay minerals are also found which consist of a regular or random stacking of layers composed of members of one or more groups of clay minerals (Weaver, 1956). These are also called interstratified clay minerals. e.g. Rectorite (Reynolds, 1980).
1.2.6 Structure of kaolinite

The structure of kaolinite was first suggested by Pauling (1930b). The detailed structure was given by Gurner (1932); Brindley and Robinson (1946); Brindley (1951); Brindley and Nakahira (1958); Zvyagin (1960); Newnham (1961); Brindley (1961); Bailey (1963); Bish (1993).

Kaolinite is a 1:1 layer silicate where the basic structure consists of a tetrahedral SiO$_4$ sheet and an octahedral sheet where Al$^{3+}$ is present as the octahedral cation. Both the sheets combine in such a way that the tips of the silica tetrahedra point towards the octahedral sheet forming a common layer. The tetrahedral layer is inverted over the octahedral layer and the apical ‘O’ atoms of the tetrahedral sheet (Fig.1.2) are shared by the octahedral sheet. In the common layer of O-atoms between the octahedral and tetrahedral sheets, two-thirds of the O-atoms are shared by silicon and aluminum atoms. The remaining one-third of the groups in this layer consists of hydroxyl groups, coordinated to the Al-atoms alone. Only two-thirds of the possible positions in the octahedral sheets are filled with Al, the remaining one-third is vacant. The Al-atoms are placed in such a manner that any two Al-atoms are separated by two hydroxyl groups—one above and one below; making a hexagonal distribution in a single plane in the center of the octahedral sheet. The hydroxyl groups are placed directly against the centers of oxygen-hexagons of the basal plane of the tetrahedral layer (Theng, 1979). Diagrammatic representation of kaolinite is given in Fig. 1.3.

In kaolinite, the successive layers are superimposed so that O-atoms, which lie at the base of one layer, are paired by OH- groups at the top of its neighboring layer. The O-atoms and OH-groups between the layers are paired with hydrogen bonding. This arrangement gives rise to a single layered triclinic structure.

Kaolinite, (Si$_4$)$_3$V(Al$_4$)$_3$O$_{10}$(OH)$_8$, has the theoretical composition of SiO$_2$ 46.54 %, Al$_2$O$_3$ 39.50 %, H$_2$O 13.96 % expressed in terms of the oxides. The formula indicates that there is no substitution of Si$^{4+}$ with Al$^{3+}$ in the tetrahedral layer and no substitution of Al$^{3+}$ with Mg$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Ca$^{2+}$, Na$^+$ or K$^+$ in the octahedral layer. Thus, the net layer charge of kaolinite is: [4 (+ 4)] + [4 (+ 3)] + [10 (- 2)] + [8 (- 1)] = 0, but in nature,
Fig. 1.2: Structure of kaolinite

Fig. 1.3: Diagrammatic representation of kaolinite
kaolinite has a small net negative charge arising from broken edges on the clay crystals. This negative charge, although small, is responsible for the surface not being completely inert. Some workers have also reported substitution of octahedral Al\textsuperscript{3+} with Fe\textsuperscript{2+} and/or Ti\textsuperscript{4+} in kaolinite (Grim, 1968a). The crystallographic dimensions of kaolinite was given as a: 5.15 Å, b: 8.95 Å, c: 7.39 Å, α: 91.8°, β: 104.5°, γ: 90°. These values were also supported by electron diffraction studies as made by Zvyagin (1960). The author reported that relative to the position which corresponds to closest packing of anions, the lower and upper bases of the octahedrons are rotated through 3 and 5° angles and the bases of the tetrahedrons, on an average, through 20°. The common edges of the octahedrons are shortened, and the octahedrons are to some extent flattened. The aluminum atoms are displaced toward the lower OH bases and the silicon atoms toward the bases of the tetrahedrons. Thus the atoms of the bases of the polyhedrons do not lie in one plane and are of several different z coordinates. Single-crystal analysis of kaolinite reveals that the tetrahedra are rotated in a manner where the bases of tetrahedra form a ditrigonal pattern with the average angle of rotation equal to 21°. The same types of ditrigonal array are also found in octahedra, but the angles are being 6.5° and 4° for top and bottom ends respectively (Drits and Kashaev, 1960). There are some other clay minerals, which possess identical structure with kaolinite, e.g. Dickite, Nacrite and Halloysite. These minerals show different stacking patterns of the layers from that of kaolinite, although they are chemically identical (Deer et al., 1985b). Dickite is 2-layered, nacrite is 6-layered and halloysite has a water molecule between the layers, which can increase the interlayer distance (Hendricks, 1938). These are all rare minerals (Sudo and Simoda, 1978).

1.2.7 Structure of montmorillonite

The structure of montmorillonite was first elucidated by Hofmann et al. (1933), and was later modified by Marshall (1935); Maegdefrau and Hofmann (1937); and Hendricks (1942). Montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedron of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms in this layer, which are common to both sheets, are all oxygens instead of hydroxyl. It is thus referred to as
three-layered clay minerals with T-O-T layers making up the structural unit (Fig. 1.4). The diagrammatic representation of montmorillonite is shown in Fig. 1.5.

These silica-alumina-silica units are continuous in the ‘a’ and ‘b’ crystallographic directions and are stacked one above the other in the ‘c’ directions. In the stacking of these units, oxygen layers of each unit are adjacent to oxygen of the neighboring units. This causes a very weak bond and an excellent cleavage between the units. The outstanding feature of this clay structure is that water and other polar molecules can enter between the layers causing the lattice to expand in the ‘c’ directions. The montmorillonite does not possess a fixed ‘c’-axis direction, but can vary from 9.6 Å; the variations depend on the absence or presence of interlayer molecules. The ‘c’-axis spacing also varies with the nature of the interlayer cation present between the silicate layers.

The thickness of the water layers between the silicate units also depends on the nature of the exchangeable cations at a given water vapour pressure. Under ordinary conditions, one molecular water-layer and a ‘c’-axis spacing of about 12.5 Å occur in montmorillonite having Na as the exchangeable ion; with Ca, there are frequently two-molecular water layers and a ‘c’-axis spacing of about 15.5 Å. The expansion capacities are reversible unless the structure completely collapses by the removal of all the interlayer polar molecules. Experiments by Mering (1946), and Bradley and Grim (1948), with montmorillonite in the presence of large quantities of water suggest that with certain adsorbed cations, e.g., Na⁺, the unit layers completely separate but that with other cations, for e.g., Ca²⁺ and H⁺, the separation is not complete. The formula for montmorillonite is, \( (Si_{7.8}Al_{0.2})^{IV}(Al_{3.4}Mg_{0.8})^{VI}O_{26}(OH)_4 \) and the theoretical composition without the interlayer material is SiO₂, 66.7%, Al₂O₃, 28.3%, H₂O, 5%. The above formula indicates that there is substitution for Si⁴⁺ by Al³⁺ in the tetrahedral layer and for Al³⁺ by Mg²⁺ in octahedral layer. Thus net layer charge of montmorillonite is: 

\[
[7.8 (+4)] + [0.2 (+3)] + [3.4 (+3)] + [0.6 (+2)] + [20 (-2)] + [4 (-1)] = -0.8 \text{ charge/unit cell.}
\]

The resulting positive net charge deficiency is balanced by exchangeable cation adsorbed between the unit layers and around their edges.
Fig. 1.4: Structure of montmorillonite

Fig. 1.5: Diagrammatic representation of montmorillonite
Montmorillonite generally occurs in equidimensional, extremely thin flake-shaped units; whereas elongates and needle-shaped units are also common. The probable cause of these elongated structures may be due to the directional strain of the lattice, which occurs due to substitutions within the lattice of ions of a size, which do not fit into octahedral positions (Grim, 1962). In montmorillonite, the symmetry of the layers is \( C_2 \) rather than \( C_{2/m} \) (Mering and Glaeser, 1953). The detailed X-ray diffraction bands may best be explained by supposing that there are regions of local ordering with random displacements of multiples of \( b/3 \) (Nakahira, 1952).

1.3 Properties of Clay Minerals

1.3.1 Composition

Grim (1968b) has pointed out some factors, which control the properties of clay minerals. These are classified as follows:

1. **Clay mineral composition**: This includes the identity and relative abundance of all the clay minerals present. The physical properties of the clay materials may be tremendously influenced even by the very small amounts of certain clay mineral constituents. The perfection of the crystallinity is important to determine the individual properties of clay minerals. Moreover, somewhat different properties are observed if the several clay minerals in a clay material are a mixture of discrete particles or an intimate interlayer mixture.

2. **Non-clay mineral composition**: This refers to the identity of the non-clay minerals, their shape and relative abundance, and the particle size distribution of each constituent. They generally tend to be concentrated in particles coarser than 2 \( \mu \), but fine-grained materials may also be present. It was reported that an appreciable amount of cristobalite was present having less than 1 \( \mu \) in diameter intimately mixed with smectite clays (Gurner, 1940). Some trace elements are also important in determining the condition of deposition and the surface area of clay minerals.

3. **Organic material**: Clay materials may contain different types of organic substances; which may be present as discrete particles of wood, leaf matters, etc. or
adsorbed organic molecules on the surface of clay minerals; or may be intercalated between the silicate layers of clay minerals. The organic constituents are an important determining factor of the properties of clay materials.

4. **Exchangeable ions and soluble salts**: The physical properties of clay minerals depend to some extent on the adsorbed exchangeable ions as well as water-soluble salts carried by the clay mineral component. For e.g., the presence of sodium ion and calcium ion show different extent of plasticity in the clay minerals.

5. **Texture**: This factor refers to the particle-size distribution of the constituent particles, the shape of the particles, the orientation of the particles in space and with respect to each other, and the forces tending to bind the particles together.

1.3.2 **Specific surface area**
The specific surface of clay mineral is the surface area of clay particles per unit mass, e.g. the lateral dimensions of kaolinite platelets are about 1000 to 20,000 Å with thickness of 100 to 1000 Å. Similarly, montmorillonite particles have lateral 1000 to 5000 Å with thickness of 10 to 50 Å. The clay minerals that have smallest particle size show highest surface area. So, the specific surface area of kaolinite will be small compared to that of montmorillonite.

1.3.3 **Ion exchange capacity**
Depending on deficiency in the positive or negative charge balance (locally or overall) of mineral structures, clay minerals are able to adsorb cations and anions and retain them around the outside of the structural unit in an exchangeable state, generally without affecting the basic silicate structures. The common exchangeable cations are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+ and Na^+; whereas SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^- are the common exchangeable anions. These ions influence substantially the physical characteristics of clay minerals. The exchange reaction differs from simple adsorption because it has a quantitative relationship between reacting ions. Exchange capacities of clays vary with particle size, perfection of crystallinity and nature of the adsorbed ions; hence, a range of values exits for a given mineral rather than a single specific capacity.
The cation exchange capacity (CEC) of clay minerals can be explained as:

(a) The clay minerals having broken bonds along the edges can give rise to unbalanced negative charges, on which cations can be adsorbed. According to Grim (1968c), these broken bonds are mainly responsible for the exchange property of kaolinite. It follows that the smaller the particle size, the more is the broken bonds and higher is the ion-exchange capacity.

(b) In some clay minerals, an unbalanced negative charge can occur, due to the substitution of Si$^{4+}$ by Al$^{3+}$ (in the tetrahedral layer) or by substitution of Al$^{3+}$ by bivalent cations (e.g. Mg$^{2+}$ in the octahedral layer). These unbalanced charges lead to adsorption of cations. The large CEC of montmorillonite is thought to be due to this substitution.

(c) Sometimes a cation can replace H from exposed OH-groups, which can be freely exchanged with others. Such exposed OH-groups occur around the broken edges of clay minerals.

Some workers (Mukherjee and Mitra, 1946; Marshall, 1949) have shown that a single cation may be adsorbed by a clay mineral with a wide range of bonding energies and that this is fundamentally related to the position on the silica-alumina packet at which the cation is adsorbed.

The possible causes for the anion-exchange reactions on clays are:

(a) The broken bonds, around the edges of the clay minerals, would provide negative as well as positive positions around the edges of the clay minerals so that anion-exchange capacity due to this would equal the cation-exchange capacity.

(b) Dickman and Bray (1941) have reported that OH groups on the surface of clay minerals apparently can enter into exchange reactions. Similar reason has been given by McAuliffe et al. (1947).

(c) The geometry of the anion in relation to the geometry of the clay mineral structural unit is another important factor of anion-exchange capacity (Grim, 1968d). Anions, which have about the same size and geometry as the silica tetrahedra, may be adsorbed by the silica tetrahedral sheets, by fitting on to the edges and growing as
extensions of these sheets. The examples of such anions are phosphate, borate, etc.,
the anions whose geometry do not fit that of the silica tetrahedral sheets, e.g. sulfate,
chlorite, etc., cannot be so adsorbed.

Schoen (1953) reported that an average ratio for cation-exchange to anion-exchange
 capacities is about 0.5 for kaolinite and 6.7 for montmorillonite. The adsorption of
anions is not comparable to the adsorption of cations because of greater dependence on
the nature of the anion than cation and on pH. It is to be noted that having a lower CEC
value than most clay minerals, kaolinite shows higher anion exchange capacity which
may be due to the presence of replaceable OH ions on the outside of the structural
sheets (Deer et al., 1985b).

1.3.4 Clay-water retention and effect of heat
Clay minerals contain water in several forms. The water may be held in pores, on the
surfaces along the interlayer planes, and around the edges. These may be removed by
drying under ambient conditions (at 373 - 423 K for some time). The clay minerals also
have structural water due to the –OH groups. On slow heating at above 673K, the clay
minerals give off the water. The clay structure is completely destroyed on heating above
1173 K (Grim, 1962).

Though the water content in the clay minerals can be reduced by heating at different
temperature, some other interesting changes take place during the heating process. On
heating between 673 K and 923 K, the kaolinite clay is converted to metakaolin, which
is an endothermic process. On further heating between 923 K to 1253 K, metakaolin is
converted to silicon spinal which is an exothermic phase change system. The repeated
heating at about 1673 K, the silicon spinal can produce ceramics, mullite and
cristobalites (Briendly and Nakahira, 1959; Worrall, 1986). The montmorillonite clay
minerals lose their hydroxyl water in the range of 673 to 973 K. Bradley and Grim
(1951), have shown that a considerable variety of high-temperature crystalline phases
may be formed when montmorillonite is heated above 1173 K and they may persist to at
least 1573 K. Some of the high-temperature phases formed include spinal, α-quartz,
cristobalite, cordierite, and mullite. The high-temperature phases developed are not the same for all clay minerals.

1.3.5 Acidity in clays

Both Brönsted (proton donor) and Lewis (electron acceptor) type of acidities have been reported in clays (Tanabe, 1981), with the Brönsted sites mainly associated with the interlamellar region and the Lewis sites with edge sites (Yahiaoui et al., 2003). The presences of these acid sites were established by acidity measurement techniques like, Hammett indicator, pyridine adsorption/desorption (Vijaya et al., 1998), and IR and NMR spectroscopic studies. When H⁺ ions occupy the exchange sites on the clay surface or H⁺ ions occur at the clay surface due to dissociation of water molecules of hydrated exchangeable metal cations – the Brönsted acid sites are found in the clay. Moreover, if Al³⁺ is substituted for Si⁴⁺ in tetrahedral layer, this gives rise to a delocalized negative charge, balanced by H₃O⁺ cations leading to Brönsted sites. The Lewis acidity arises when an exposed Al³⁺ cation is in the crystallite edges. Lewis sites can also occur when an Al³⁺ arises from a Si-O-Al bond rupture or dehydroxylation of some Brönsted sites takes place (Jasra et al., 1999). The acidity function of natural kaolinite and natural montmorillonite has been reported as −3.0 to −5.6 and +1.5 to −3.0 (Narayanan and Despande, 1999).

1.3.6 Swelling capacity and clay-water retention

Some clay minerals expand when they are placed in polar solvents, like H₂O. Due to this expansion (often known as swelling), molecules can be placed inside the expanded interlayer. The thickness of the adsorbed water (both surface and interlayer) depends on the exchangeable cation. Barshed (1955) has described inter-layer water adsorption and expansion in montmorillonite, as taking place in five stages. In samples saturated with cations of equal charges but varying in size, the larger the ionic radius the higher the relative humidity at which expansion occurs. Expansion beyond a unimolecular water layer does not take place in montmorillonite saturated with K⁺, Rb⁺ or Cs⁺ ions. The large surface area of clay minerals is important in water adsorption.
1.3.7 Pillaring

Barrer and MacLeod (1955) first introduced the concept of transforming a lamellar solid into a porous structure by inserting laterally spaced molecular props between the layers of a smectite clay mineral. Pillaring is the process by which a layered compound is transformed into a thermally stable micro- and / or mesoporous material with retention of the layer structure. The material obtained is a pillared compound or a pillared layered solid. A pillared derivative is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest molecules. In fact, the intercalated clays undergo calcination at a moderately high temperature (such as 773 K) in order to transform the polyoxocations to metal oxidic particles cross-linked to the clay lamellae, thus preventing the collapse of the interlayer space and generating a stable porous structure (Gil et al., 2000). In pillared clays, the interlayers of two-dimensional silicate layers of clay with a thickness of about 1 nm are kept apart by ceramic oxides with a dimension of nano- to subnano-metre sizes (Zhu and Yamanaka, 1997).

Though the study of pillared clays has been dominated mostly by smectite-type clay, nowadays, the range of materials that can be pillared has expanded beyond smectite-type clay minerals and pillaring agents also include inorganic as well as organic compounds (Sehoonheydt et al., 1999). Usually a pillared compound has the following characteristics:

(i) the layers are propped apart vertically and do not collapse upon removal of the solvent;
(ii) the minimum increase in basal spacing is the diameter of the N\textsubscript{2} molecule, commonly used to measure surface areas and pore volumes: 0.315-0.353 nm;
(iii) the pillaring agent has molecular dimensions and is laterally spaced in the interlamellar space on a molecular length scale;
(iii) the interlamellar space is porous and at least accessible to molecules as large as N\textsubscript{2}; there is no upper limit to the size of the pores.

Montmorillonite is a clay mineral with substantial isomorphic substitution having a 2:1 layered structure consisting of one octahedral sheet and two tetrahedral sheets.
Exchangeable cations between the 2:1 units balance the negative charges generated by isomorphic substitution within the montmorillonite structure (Dahn et al., 2002). In the montmorillonite structure, an interlayer swelling occurs when it is exposed to water. The swelling procedure depends on valences and atomic radii of the exchangeable cations. Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites (Hennig et al., 2002). In montmorillonite, adsorption can occur both at the edge sites, which leads to inner-sphere metal complexes, and at the planar (internal) sites of the clay mineral, which results in outer-sphere metal complexes (Elzinga and Sparks, 1999).

Kaolinite, which is a layered aluminosilicate with almost perfect 1:1 layer structure (Young and Hewat, 1988), is often classified as non-expandable clays (Frost et al., 1999). Although the reactivity of kaolinite for interaction is very low due to the inherent H-bonding between the layers (Kuroda et al., 1999), Wada (1961) introduced a new type of compounds by expanding kaolinite with potassium acetate and other organic salts. The kaolinite interlayer region undergoes intercalation, where the intercalating agents decrease the electrostatic attraction between the lamellae by increasing the dielectric constant when the compounds penetrate between the layers (Van Olphen, 1977a; Kelleher and O’Dwyer, 2002).

Intercalation of clays cross-linked with inorganic or organic clusters (pillared interlayered clays, PILC or cross-linked clays, CLC), has received wide attention recently as shape-selective catalysts, separating agents, supports, adsorbents, etc. These materials have a two-dimensional pore size larger than conventional zeolites and exhibit specific properties depending on the nature of the pillar (Ohtsuka et al., 1993). In particular clays pillared with metal oxides are of great importance because of their high thermal stability, high surface area, and intrinsic catalytic activity. These materials are usually prepared by ion-exchanging cations in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear complex ions bearing inorganic ligands (hydroxo ligand, chloro ligand), large metal complex ions bearing organic ligands, etc. The intercalated species are capable of preventing the collapse of the interlayer spaces,
propping open the layers as pillars, and forming interlayer space. On heating, the intercalated inorganic species are converted to metal oxide clusters, generating a stable microporous structure with a high surface area.

Burch and Warburton (1986a) introduced Zr-tetramers from fresh zirconyl chloride solution into montmorillonite. Ohtsuka et al. (1993) have shown that the zirconium species exist in a number of polynuclear ionic species in zirconium oxychloride solution and pillaring can give three kinds of microporous clays with 7-, 12-, and 14-Å interlayer spacings. The major species in zirconium oxychloride solutions at room temperature has been shown as the zirconium tetramer, \([\text{Zr}_4(\text{OH})_{8+x}(\text{H}_2\text{O})_{16-x}]^{(8-x)+}\), giving the intercalation compound with a 7-Å interlayer spacing. Upon hydrolytic polymerization of the zirconium tetramer in solution, the more highly polymerized zirconium species are generated that can provide the intercalation compounds with 12- or 14-Å interlayer spacings. The two polymeric species forming the intercalates with 12- and 14-Å interlayer spacings are composed of three-dimensionally polymerized clusters based upon the tetramer. Pereira et al. (1998) prepared pillared Zr-montmorillonite in a similar way. Other than Zr\(^{4+}\), the polycations, namely, Al\(^{3+}\), Si\(^{4+}\), Ti\(^{4+}\), Fe\(^{3+}\), Cr\(^{3+}\), or Ga\(^{3+}\) etc have also been used as inorganic pillar (Karmanis et al., 1997; Zhu and Yamanaka, 1997; Gil et al., 2000; Vicente and Lambert, 2001; Valverde et al., 2005). Preparation of pillared montmorillonite with quaternary ammonium cations (QACs) of the form \([(\text{CH}_3)_3\text{NR}]^+\) or \([(\text{CH}_3)_3\text{NR}_2]^+\), namely TMA (tetramethylammonium), TMP (tetramethylphosphonium) and TMPA (trimethyl-phenylammonium) cations has also been reported (Stevens and Anderson, 1996; Lawrence et al., 1998). Preparation of N, N'-didodecyl -N, N'- tetramethylethanediammonium (DEDMA) montmorillonite had been reported recently (Akcay et al., 2006).

1.3.8 Acid activation

Treatments of clay minerals with inorganic acids of rather high concentration and usually at high temperature are known as acid activation. Acid treatments of clay minerals are an important control over mineral weathering and genesis (Jackson and Sherman, 1952; Eberl et al., 1993). Such treatments can often replace exchangeable cations with H ions and Al and other cations escape out of both tetrahedral and
octahedral sites, but leaving the SiO$_4$ groups largely intact (Theocharis et al., 1988). This process generally increases the surface area and acidity of the clay minerals (Ravichandran and Sivasankar, 1997), along with the elimination of several mineral impurities and partial dissolution of the external layers. The change of surface areas and porous structure of clays depend on the clay minerals, other clay minerals and non-clay minerals present as well as the chemical composition, the type of cations between the layers, the type of the acid, the process temperature and the process period, etc. (Onal et al., 2002).

The depopulation of the octahedral layer of montmorillonite may lead to different levels of structural decomposition depending on individual resistance to acid attack of the initial clay minerals (Breen et al., 1995). On acid attack, the crystalline structure of kaolinite is transformed thermally to amorphous metakaolin and the octahedral Al ions are preferentially released from the clay structure leading to formation of additional Al-OH and Si-OH bonds, without troubling the original mineral structure (Suraj et al., 1998). It has been reported that acid activation followed by thermal treatment increases the adsorption capacity to a good extent (Rodrigues, 2003). Due to complex changes of clay minerals in acid environments, their surface properties are also modified (Jozefaciuk and Bowanko, 2002). Christidis et al. (1997) reported that HCl treatment of bentonites leads to a 5 times increases of surface area of the raw clays. The increase of the surface area under acid treatment may be caused by production of finely dispersed silicon oxides from destruction of mineral structures, removal of amorphous Al or silica components plugging surface pores or interlamellar spaces, formation of cracks and voids in the surfaces (Jozefaciuk and Bowanko, 2002). After acid attack, the number of weakly acidic surface functional groups increased while the number of groups of stronger acidic character decreased (Jozefaciuk, 2002).

1.4 Utilization of Clay Materials

Most of the clays when mixed with varying proportion of water show plasticity, which is a property of a material to undergo permanent deformation in any direction without rupture under a stress beyond that of elastic yielding. This quality of clays is used for preparing bricks, tiles, ceramic goods, various refractory materials and porcelain
insulators. Petroleum industry is an important field where clay is one of the very important ingredients. Clays are often used for drilling mud in petroleum exploration (Prasad et al., 1991). For this purpose, the Wyoming clays, mainly montmorillonite, are used having sodium as the major exchangeable cation.

The use of clays as catalyst for different types of chemical reactions is well known. Originally the clays were used in the purification of vegetable oils as a catalyst. Clays are also used as catalysts for numerous reactions like electrophilic substitution, addition and elimination reaction, dehydrogenation, hydrogenation, condensation reaction, thermal and hydrolytic decomposition, etc. (Balogh and Laszlo, 1993). The modified clays are often much more effective catalysts in the case of alkylation using alcohol as the reagent (Pinnavaia, 1993). Halligudi et al. (1995) reported that modified clays (e.g., Ru-montmorillonite) can selectively catalyse hydrogenation of benzene to cyclohexane in presence of higher aromatic homologous namely xylene. Burch and Warburton (1986b) studied the catalytic activity of Zr containing pillared interlayer clays for the conversion of methanol into hydrocarbons.

Some other important areas of clay utilizations are:

- The low inertness, low abrasiveness, good adsorption and flow properties of clays (mainly kaolin) make them effective carrying agents in dust and spray forms.
- Clays are used in paper industry. The clay-coating makes possible for sharp photographic illustrations and brilliant colour printing.
- In the manufacture of both natural and synthetic rubber, kaolinite and bentonite clays are used as functional filler.
- In manufacturing paint and ink, clays are used as extenders because of their chemical inertness, smooth flow properties, ease of dispersion and high pigment volume concentrations.
- The adsorption properties of clays are used for the disposal of radioactive wastes by adsorbing the same, followed by calcination above 1273 K, which transforms the adsorbed material to an incapable, cemented form.
- White kaolinite clay is one of the important ingredients in cement industry, namely Portland cement.
• Clays can remove the colloidal impurities from wine, beer etc.
• The water retention capacity, strength and plasticity of mortars can be improved by using clays.
• Very fine size kaolinite clay (2 to 5μ) is used for cotton and linen finishing in textile industries.
• Clays are used in manufacturing greases of superior quality – with resistance to water and heat.
• The dispersion and adsorptive properties of clay minerals make it possible to use them as the low cost purifiers of water for removing colloidal matter from water.
• Clays are often used in the manufacture of pesticides, plastics and resins as well as leather and cosmetic industry.

1.5 Clays and the Environment

1.5.1 General role of clays in the environment

The role of clays in the environment is well known. Even in biological evolution and generation of pre-biotic components – the participation of clays has been mentioned (van Olphan, 1977b). This role can be explained in the following ways:

1. The porous structure of clays makes it a potential adsorber. The edges and the faces of clays can adsorb different types of cations, anions as well as non-ionic and polar organic contaminants from water. The strength of such interaction is determined by the particular structural and other features of the clay minerals.
2. The interactions between clays and the adsorbed pollutants have some stereo specificity as the clay surface imposes certain steric constraints on the adsorbed molecules due to their positions in the interlayer space.
3. It is reported that the crystal imperfections in clay minerals affect the adsorption and reaction processes on their surfaces (Crains-Smith and Hartman, 1986).
4. The van der Waals interactions, hydrophobic bonding effects and even H-bonding sometimes play an important role through which the pollutant can be held on to clay surfaces.
All these binding forces probably are at work, in a particular clay mineral. van Olphan (1963) pointed out the probable difference and importance of the bonds found at the edges of clay mineral particles as compared with those on the large flake surfaces.

The chemical reactions that occurred between the clay surfaces and the pollutants, are generally of three types – oxidation-reduction, acid-base and catalytic. van Olphan (1977c) has cited the following types of active sites in clays:

(a) **Brønsted acid sites or proton donor sites**: The interactions of cations with adsorbed or interlayer water molecules are responsible for these active sites. Type of cations, its positions on the clay surfaces and the water content of the clay determine the strength of this acidity.

(b) **Lewis acid sites or electron acceptor sites**: These occur in absence of adsorbed water molecules.

(c) **Oxidizing sites**: The presence of some cations (e.g. Fe$^{3+}$) in octahedral positions or due to adsorbed oxygen on surfaces, clay mineral acts as an oxidizing agent.

(d) **Reducing sites**: Clay mineral can behave as a reducing agent due to the presence of some cations (e.g. Fe$^{2+}$).

(e) **Surface hydroxyl group**: These are mostly found in the edges, which are bound to Si, Al or other octahedral ions.

The adsorptive properties of clay minerals are supposed to be due to its large surface area and other properties, like cation exchange capacity. Both Brønsted and Lewis type of acidity in clays (Tanabe, 1981) boosted the adsorption capacity of clay minerals to a great extent. It has been reported that if the uptake of pollutant is below CEC of the clays, the mechanism of adsorption is dominated by ion exchange, but the cause of adsorption becomes hydrophobic bonding if the uptake is more than CEC values (Jamirah and Dental, 1993). In general, the adsorption capacity depends on some primary factors, namely pH and temperature of the medium, nature of the clay minerals (adsorbent), presence of organic matter, nature of the adsorbates, etc. (Sheng and Boyd, 2000). It was also reported that polarity and hydrophobic character of the surface of some bentonite clays enhance retention of organic pollutants (Mortland et al., 1986).
1.5.2 Clays as versatile scavengers of metals

Tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. Hazardous and toxic metal cations reach surface and groundwater following the natural geochemical route as well as the industrial pathway. These are also harmful to the environment as a whole because of their non-biodegradable and persistent nature even at low concentration. The metals accumulate in living tissues and get biomagnified through the food chain (An et al., 2001). The metals of major concern are aluminium, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel and zinc. Concentration of heavy metals over permissible level, in water, may cause severe public health problems. Heavy metal contamination of fresh water bodies and aquatic lives is becoming a serious concern from human point of view.

Clay minerals have been found as good adsorbent for various metal ions, which probe themselves as priority pollutants in the environment (Ramahashay, 1987). The adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) from a landfill leachates onto kaolinite was studied by Majone et al. (1993, 1998). The removal of Pb(II), Cu(II), Cd(II), Zn(II), Ni(II) and Co(II) was done by using local kaolinite clays of Assam and Meghalaya, India, which followed the Freundlich isotherm vary closely (Phukan, 1994). The study reported that, the adsorption capacity of the clays for the metal ions followed the order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II) > Co(II). In a similar work, Yavuz et al. (2003) used raw kaolin for removing Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution where the adsorption affinity was in the order of Cu(II) > Ni(II) > Co(II) > Mn(II) and the monolayer adsorption capacity was 10.78, 1.67, 0.92 and 0.45 mg/g respectively at 298 K. These endothermic interactions were driven by entropy increase. The influence of temperature (between 283 to 343 K) on adsorption of Cd(II) and Co(II) on kaolinite was investigated by Angove et al. (1998). The adsorption isotherms fit closely a simple Langmuir model at all temperatures (pH 5.5) for both the cations. From the values of thermodynamic parameters, the processes were concluded as endothermic in nature.
Mellah and Chegrouche (1997) used natural bentonite for uptake of zinc from aqueous solution and reported the maximum Langmuir monolayer capacity as 52.91 mg/g (for an initial Zn(II) concentration of 300 mg/L) at 293 K. The bentonite-Zn(II) interactions were exothermic and favoured by high values of initial Zn(II) concentration and decreased particle size of clay adsorbent. The removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solution on bentonite was shown to be endothermic (Gozen et al., 1997). The adsorption followed the order Zn(II)> Cu(II)> Cd(II)>Pb (II). The removal of Cr(III), Cr(VI) and Ag(I) by bentonite was reported by Khan et al. (1995a). The adsorption of Cr(III) and Ag(I) on bentonite was found to be exothermic while the Cr(VI)-bentonite interactions were endothermic. Bentonite has a Langmuir monolayer capacity of 16.3 meq/1000g at 298 K for Sr(II) (Khan et al., 1995b) with as much as 99% adsorption at pH 8.5. Thermodynamically the adsorption process was shown to be spontaneous supported by increase in entropy (\(\Delta S = 0.139 \text{ kJ/K mol at 298 K}\)) and decrease in Gibbs energy (\(\Delta G = -10.69 \text{ kJ/mol at 298 K}\)), despite being endothermic (\(\Delta H = 30.62 \text{ kJ/mol at 298 K}\)).

Amount of bentonite necessary to remove Pb(II) from solution has been shown to be \(~0.5\) g for 10 mg of Pb(II) at a pH 3.4 in 100 cm\(^3\) solution and the Pb(II)-bentonite interactions were endothermic in nature followed by a decrease in free energy (Naseem and Tahir, 2001). Alvarez-Ayuso and Garcia-Sanchez (2003) used natural and Na-exchanged bentonites for the removal of Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from aqueous solution. The authors reported that Langmuir model was most suitable in explaining the results and the maximum adsorption capacity was 49.8, 24.2, 23.1, 30.0 and 26.2 mg/g respectively for Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II). The process, favoured by increasing pH, was shown to be very rapid with >95% uptake in 30 min.

Strawn et al. (2004) reported the adsorption of Cu(II) by smectites (montmorillonite and bedellite) as a function of varying ionic strength and pH. The X-ray adsorption fine structure (XAFS) and electron paramagnetic resonance (EPR) spectroscopic experiments on Cu(II) adsorbed on clays revealed that Cu-Cu linkages in the multinuclear complexes were 2.65 Å apart having a coordination number near one. The adsorption of Ni on pyrophyllite, montmorillonite and a 1:1 pyrophyllite—
montmorillonite mixture was studied at pH 7.5 and a reaction time of 40 min. by using X-ray absorption fine structure spectroscopy (XAFS) to estimate the distribution of Ni over the mixture components (Elzinga and Sparks, 1999). The results suggest that the pyrophyllite component is more competitive for Ni uptake than the montmorillonite component. Both adsorption and surface precipitation were important mechanisms in the overall Ni uptake in the clay mixture.

Hennig et al. (2002) used extended X-ray absorption fine structure (EXAFS) spectroscopy for determining the structural environment of aqueous uranyl adsorbed onto montmorillonite. The study has revealed that uranyl uptake at pH ~ 5.0 to ~ 7.0 and at an initial uranyl concentration of 5 ×10⁻⁵ M takes place at amphoteric surface hydroxyl sites as inner-sphere complex. The measured bond distances between uranium and the equatorial oxygen atoms are in the range of 2.34 Å and 2.37 Å indicating inner-sphere coordination. At ~ 3.4 Å the presence of a U–Al backscattering pair was determined. This backscattering pair indicates that the binding of the uranyl unit to amphoteric surface hydroxyl sites occurs preferably as a bidentate inner-sphere complex on aluminol groups. EXAFS spectroscopy has also been used for studying the adsorption of thorium on montmorillonite by Dahn et al. (2002). The study showed that, Th(IV) loading varied between 1.0–157.0 μmol g⁻¹ at pH 3.0 and 14.0 –166.0 μmol g⁻¹ at pH 5.0 and equaled 41.0 μmol g⁻¹ at pH 2.0. At pH 5.0 and high surface loading the EXAFS spectrum resembled that of amorphous Th(OH)₄, suggesting the precipitation of Th hydrous hydroxide. Th(IV) was shown to bond the montmorillonite surface by sharing double corners with Si tetrahedra.

Sepiolite has been used as an adsorbent for Cd(II), Cu(II) and Zn(II) (Sanchez et al., 1999). Kara et al. (2003) used sepiolite as an adsorbent for Co(II) with the results indicating spontaneous, physical and entropically driven interactions. Another clay mineral, illite was used as an adsorbent for Cd(II) (Echeverria et al., 2002) and the process was found to be dependent on ionic strength, initial concentration of Cd(II) and pH. Cd(II) adsorption increased with pH reaching 100 % at pH 8.0. The interactions were endothermic in nature.
The adsorption capacity and the effect of pH were investigated for Cd(II), Pb(II) and Zn(II) removal on Lithuanian gluconite, a natural three-layer sheet aluminosilicate occurring mainly in marine sediments (Smith et al., 1996). The results revealed that the comparative adsorption capacity at a given initial pH increased for increasing atomic weight of the metals, showing the order of adsorption as Pb(II) > Cd(II) > Zn(II). Atanassova (1999) evaluated the effect of competing Cu(II), Zn(II), Cd(II) and Ni(II) ions in 0.01M Ca(NO₃)₂ on adsorption and desorption by soil clay fractions (Vertisol, Gleyic Acrisol and Planosol). The total adsorption of Zn(II) and Cd(II) decreased in the order: Vertisol > Acrisol > Planosol clay. Cu(II) was predominantly specifically adsorbed, and the specific adsorption of Zn(II) was depressed by competition with Cu(II) in the three clays. Abraham and Anirudhan (1999) studied the influence of humic acid on Cd(II) adsorption by montmorillonite at different pH levels. In this study, the maximum adsorption of Cd(II) was observed at pH 6.5; but in presence of humic acid, the removal was significantly reduced at lower pH.

Along with the pure clay minerals, many modified clay minerals have also been tested for their effectiveness as adsorbents. Lin and Juang (2002) tried to modify the adsorptive properties of montmorillonite by introducing sodium dodecylsulfate before adsorbing Cu(II) and Zn(II). The modified clay had higher affinity towards the metal ions and the equilibrium was attained within 120 min. The interactions were endothermic, which followed pseudo-first order kinetics yielding a rate constant of 6.64 x 10⁻⁴ and 3.14 x 10⁻³ min⁻¹ at 298 K for Zn(II) and Cu(II) respectively. Adsorption of Cu(II) ions onto a 1:10 phenanthroline-grafted Brazilian bentonite was reported by De Leon et al. (2003). The modified clay showed a maximum uptake of Cu(II) at ~ 110 mg/g, which was almost 10 times more compared to the untreated bentonite. The desorption of Cu(II) from the modified clay revealed high uptake irreversibility and physical stability of the clay adsorbent in both strongly acidic and basic solutions. Aluminum pillared montmorillonite clay was used to successfully remove Sr(II) and Cs(II) from aqueous solution (Karamanis et al., 1997).
1.5.3 Clays as scavengers of organic and non-metallic inorganic pollutants

The aqueous environment has been threatened by various other hazardous substances. Organic pollutants like phenol and substituted phenol, benzene, toluene, different pesticides and herbicides, dyes and paints, etc., are adding to the water system anthropogenically. The clays and modified clays possess good scavenging capacity for all these pollutants from water. A few references highlighting the use of clays during the last few years for removal of typical organic and non-metallic inorganic pollutants from water are presented in Table 1.1.

1.6. Conclusion

It is evident from literature search that natural as well as modified forms of clay minerals have been used worldwide as scavengers of pollutants from aqueous medium. Though different types of clays have been used for removal of pollutants, it is observed that natural and modified montmorillonites have been the most extensively used clays. Kaolinite and modified kaolinite do find use in this process, but their use is rather limited. In many cases, the literature describes only the possible use without going into the details of kinetics, thermodynamics and other important considerations which can establish this group of materials as viable adsorbents in the fast-growing pollutant-treatment technology. The present work aims to fill up some of the gaps in the existing knowledge base.
Table 1.1: A selection of recently published works on removal of inorganic non-metallic and organic pollutants using clays and modified clays

<table>
<thead>
<tr>
<th>Clay adsorbent</th>
<th>Pollutants</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite and montmorillonite</td>
<td>Diquat and paraquat</td>
<td>Oberoi, 1990</td>
</tr>
<tr>
<td>Dimethyl distearylammonium-, and dimethyl benzylammonium- hectorite</td>
<td>Atrazine</td>
<td>Bottero et al., 1994</td>
</tr>
<tr>
<td>Na- or Ca-montmorillonite, dimethyldistearylammonium-montmorillonite (DDA-M), and DDA-M re-exchanged with Ca$^{2+}$</td>
<td>Tannic acid, phenol, and 2,4,5-trichlorophenol,</td>
<td>Dental et al. 1995</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2, 4-dichlorophenol</td>
<td>Islam et al., 1997</td>
</tr>
<tr>
<td>Al- and Ca-smectites</td>
<td>Atrazine</td>
<td>Sawhney and Singh, 1997</td>
</tr>
<tr>
<td>Alumina-pillared montmorillonite</td>
<td>2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol</td>
<td>Danis et al., 1998</td>
</tr>
<tr>
<td>Tetramethylammonium-, hexadecyltrimethylammonium-, hexadecylbenzyldimethylammonium- and dioctodecyldimethylammonium-montmorillonite</td>
<td>Tannic acid and 1,2,4-trichlorobenzene</td>
<td>Dental et al. 1998</td>
</tr>
<tr>
<td>Tetramethylammonium- and tetramethylphosphonium-montmorillonite</td>
<td>Phenol and chlorinated phenol</td>
<td>Lawrence et al., 1998</td>
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<tr>
<td>Bentonite</td>
<td>Phenol</td>
<td>Viraraghavan and Alfaro, 1998</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium- and didodecyldimethylammonium-smectite</td>
<td>Trichloroethylene</td>
<td>Zhao and Vance, 1998</td>
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<tr>
<td>Trimethylphenylammonium-, methylphenylpyridinium- and trimethylammonium indane- hectorite</td>
<td>Mixture of benzene, toluene, xylene, and ethylbenxene</td>
<td>Jaynes and Vance, 1999</td>
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<tr>
<td>Montmorillonite coated by hydroxyl aluminum species</td>
<td>Simazine</td>
<td>Sannino et al., 1999</td>
</tr>
<tr>
<td>Clay adsorbent</td>
<td>Pollutants</td>
<td>Reference</td>
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<tr>
<td>Palygorskite and sepiolite</td>
<td>Methylene blue and crystal violet</td>
<td>Shariatmadari et al., 1999</td>
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<tr>
<td>Al- and Fe-Al-pillared smectite</td>
<td>Atrazine, propazine, prometryne, propanil propachlor, and molinate</td>
<td>Konstantinou et al., 2000</td>
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<td>Natural, alkaline-modified and acid-modified bentonite</td>
<td>Ammonical nitrogen</td>
<td>Rozic et al., 2000</td>
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<td>Trimethylphenylammonium-, trimethylammoniumadamantine- and hexadecyltrimethylammonium-montmorillonite</td>
<td>Benzene, toluene, ethylbenzene, o-, m-, p-xylene</td>
<td>Sharmasarkar et al., 2000</td>
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<td>Calcined bentonites</td>
<td>Metolachlor</td>
<td>Bojemueller et al., 2001</td>
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<td>Activated clay</td>
<td>Basic red 18 and acid blue 9</td>
<td>Ho et al., 2001</td>
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<td>Hexadecyltrimethylammonium-kaolinite</td>
<td>Nitrate, arsenate and chromate</td>
<td>Li and Bowman, 2001</td>
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<td>Perlite</td>
<td>Victoria blue</td>
<td>Demirbas et al., 2002</td>
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<tr>
<td>Kaolinite</td>
<td>Methylene blue</td>
<td>Ghosh and Bhattacharyya, 2002</td>
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<td>Bentonite and perlite</td>
<td>p-chlorophenol</td>
<td>Koumanova and Peeva-Antova, 2002</td>
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<td>Calcined alunite</td>
<td>Acid blue 40 and acid yellow 17</td>
<td>Ozacar and Sengil, 2002</td>
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<td>Natural kaolinite</td>
<td>Phosphate</td>
<td>Sei et al., 2002</td>
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<tr>
<td>Smectite (SWy-2 and SAz-1)</td>
<td>Dinitrophenol herbicides</td>
<td>Sheng et al., 2002</td>
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<tr>
<td>Clay adsorbent</td>
<td>Pollutants</td>
<td>Reference</td>
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<tr>
<td>Tetraalkylammonium- smectite</td>
<td>Benzene and trichloroethylene</td>
<td>Chun et al., 2003</td>
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<tr>
<td>Perlite</td>
<td>Methyl violet</td>
<td>Dogan and Alkan, 2003</td>
</tr>
<tr>
<td>Natural and acid activated bentonite and sepiolite</td>
<td>Acid yellow 194, acid blue 349 and acid red 423</td>
<td>Espantaleon et al., 2003</td>
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<tr>
<td>Pyrophyllite and montmorillonite</td>
<td>Anionic polyacrylamide polymer</td>
<td>Heller and Keren, 2003</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>AuCl&lt;sup&gt;4&lt;/sup&gt;</td>
<td>Hong et al., 2003</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium-, dodecyltrimethylammonium-palygorskite and sepiolite</td>
<td>Chromate and nitrate</td>
<td>Li et al., 2003</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;-, Al&lt;sup&gt;3+&lt;/sup&gt;-, Cu&lt;sup&gt;2+&lt;/sup&gt;-, Ca&lt;sup&gt;2+&lt;/sup&gt;-, K&lt;sup&gt;+&lt;/sup&gt;-, Na&lt;sup&gt;+&lt;/sup&gt;- exchanged montmorillonite</td>
<td>Quinolinecarboxylic acid herbicides</td>
<td>Pusino et al., 2003</td>
</tr>
<tr>
<td>Calcined alunite</td>
<td>Reactive blue 114, reactive yellow 64 and reactive red 124</td>
<td>Ozacar and Sengil, 2003</td>
</tr>
<tr>
<td>Diatomite</td>
<td>Methylene blue</td>
<td>Shawabkeh and Tutunji, 2003</td>
</tr>
<tr>
<td>Zr-montmorillonite</td>
<td>Humic acid and tannic acid</td>
<td>Vinod et al. 2003</td>
</tr>
<tr>
<td>Humic acid immobilized montmorillonite</td>
<td>Methylene blue, crystal violet and rhodamine B</td>
<td>Vinod and Anirudhan, 2003</td>
</tr>
<tr>
<td>Tetraethylammonium- bentonite</td>
<td>p-chlorophenol</td>
<td>Akcay, 2004</td>
</tr>
<tr>
<td>Pure clay (Arizona smectite, Wyoming smectite, hectorite) and organic (octadecylammonium- and dioctadecyldimethylammonium-) clays</td>
<td>Metsulfuron methyl and nicosulfuron herbicides</td>
<td>Carrizosa et al., 2004</td>
</tr>
<tr>
<td>Clay adsorbent</td>
<td>Pollutants</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------------------------------------------------------------------</td>
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<tr>
<td>Synthetic montmorillonite, beidellite, saponite, and fluor-tetrasilic</td>
<td>Phosphate</td>
<td>Kasama et al., 2004</td>
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<tr>
<td>expandable mica pillared with cationic, Keggin ion</td>
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<tr>
<td>Montmorillonite</td>
<td>Phenol</td>
<td>Yapar and Yilmaz, 2004</td>
</tr>
<tr>
<td>Tetradecyl trimethylammonium - and hexadecyl trimethylammonium-bentonites</td>
<td>Phenol</td>
<td>Yilmaz and Yapar, 2004</td>
</tr>
<tr>
<td>Ca-montmorillonite (Ca-Mont) exchanged with titanium cations</td>
<td>Basic green 5 and basic violet 10</td>
<td>Wang et al., 2004</td>
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<td>Dodecyllammonium- sepiolite</td>
<td>2,4-dichlorophenoxyacetic acid</td>
<td>Akcay et al., 2005</td>
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<tr>
<td>Bentonite and sepiolite</td>
<td>Methylene blue</td>
<td>Bilgic, 2005</td>
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<td>Surfactant-modified sepiolite</td>
<td>Acid red 57</td>
<td>Ozcan and Ozcan, 2005</td>
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<td>Raw and heat-activated sepiolite</td>
<td>Phenolic and lignin compounds</td>
<td>Ugurlu et al., 2005</td>
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<td>Hexadecyl trimethyl ammonium-bentonite</td>
<td>Phenol</td>
<td>Yapar et al., 2005</td>
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<td>Tetrabutylammonium- montmorillonite</td>
<td>p-chlorophenol</td>
<td>Akcay, 2006</td>
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<td>( N,N)-didodecyl-( N,N)-tetramethylethanediammonium-montmorillonite</td>
<td>2,4-dichlorophenoxyacetic acid, 2,4-</td>
<td>Akcay et al., 2006</td>
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<td>dichlorophenoxybutyric acid, 4-chloro-2-</td>
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<td>methylphenoxyacetic acid, and 2,4, 5-</td>
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<td>trichlorophenoxyacetic acid</td>
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<tr>
<td>Sepiolite</td>
<td>Acid blue 193</td>
<td>Ozcan et al., 2006</td>
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